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Cationic and Neutral Chloride Complexes of Palladium(II) with the Nonaqueous Solvent Donors Acetonitrile, Dimethyl Sulfoxide, and a Series of Amides. Mixed Sulfur and Oxygen Coordination Sites in a Dimethyl Sulfoxide Complex

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Nitrosyl tetrafluoroborate dissolved in acetonitrile reacts with metallic palladium to form $[Pd(CH_3CN)_4](BF_4)_2$, which functions as a convenient precursor to other cationic palladium(II) complexes. Cationic Pd(II) complexes of the type $[PdL_4]X_2$ along with neutral $[PdL_2Cl_2]$ complexes, where L is CH_3CN, DMSO, DMF, DMA, NMF, or NMA and X is the noncoordinating perchlorate or tetrafluoroborate, have been prepared and partially characterized. All complexes were found to be diamagnetic with the metal ion contributing a small paramagnetism. Infrared spectra (4000–270 cm^{-1}) were recorded and assignments for the main absorption bands were used to determine the ligand donor sites and to comment on the relative acceptor ability of palladium(II). The complex $Pd(DMSO)_4^{2+}$ has the novel feature of containing both sulfur- and oxygen-bonded dimethyl sulfoxide. The ir spectra are most consistent with two sulfur and two oxygen coordination sites in a *cis* configuration. The solid sulfur-bonded complex *trans*-$Pd(DMSO)_2Cl_2$ is found to convert to the *cis* complex in acetonitrile solution.

Introduction

Several characteristics of palladium(II) chemistry which have promoted recent interest are (1) formation of square-planar complexes and (2) bonding properties intermediate between the first transistion series and the heavy metals. Palladium(II) complexes have played an important role in recent experimental and theoretical attempts to characterize the electronic structure of square-planar complexes.[3,4] Also, investigations of ligand isomerization and related phenomena have centered around Pd(II) owing to its intermediate bonding properties.[5,6] For example, several palladium(II) thiocyanate complexes contain one sulfur- and one nitrogen-bonded thiocyanate.[7,8]

Previous studies of Pd(II) complexes have been largely restricted to anionic and neutral complexes owing to the absence of convenient methods for obtaining the cationic complexes. This paper in part reports on the preparation and partial characterization of cationic Pd(II) complexes with some common monodentate donors. The complex $Pd(DMSO)_4^{2+}$ is particularly interesting, for it is the first example of a complex containing both sulfur- and oxygen-coordinated dimethyl sulfoxide.

Experimental Section

Materials.—Palladium chloride was obtained from Englehard Industries, Inc., while sponge palladium and nitrosyl tetrafluoroborate (vacuum sublimed before use) were purchased from K & K Laboratories. N,N-Dimethylacetamide (DMA), N,N-dimethylformamide (DMF), N-methylacetamide (NMA), N-methylformamide (NMF), dimethyl sulfoxide (DMSO), and acetonitrile (CH_3CN) were all obtained from Fisher Scientific Co. They were used without further purification in the preparation of the complexes. All weighings and transfers of materials were carried out in an inert-atmosphere box.

Analyses.—C, H, N, and O analyses were performed by Galbraith Laboratories, Inc. Palladium was determined gravimetrically with dimethylglyoxime.[9]

Magnetic Data.—Magnetic susceptibilities were measured at 24 ± 1° by the Gouy method,[10] using solid $Hg[Co(NCS)_4]$ as the calibrant. The estimated error in χ_m is ±15 cgs units.

Preparation of Palladium Complexes. $[Pd(CH_3CN)_4](BF_4)_2$.—Sponge palladium (0.4518 g) was added to a solution of nitrosyl tetrafluoroborate (1.0620 g) in acetonitrile (50 ml).[11] The resulting mixture was immediately evacuated to remove air oxygen. Periodically, vacuum was applied to remove nitric oxide given off during the reaction. After 9 hr, the mixture was filtered, yielding a yellow solution from which a yellow complex was obtained by slow addition of anhydrous ether. The complex was dried *in vacuo* for 5 hr.

$[PdL_4](BF_4)_2$.—Cationic palladium(II) tetrafluoroborate complexes with DMSO, DMSO-d_6, NMF, and NMA were prepared by dissolving $[Pd(CH_3CN)]_4(BF_4)_2$ in the respective ligand, precipitating the complex with ether, and then recrystallizing from the ligand three times. The complexes were dried *in vacuo* for 5 hr. The absence of acetonitrile in these complexes was demonstrated by the ir spectra.

$[PdL_4](ClO_4)_2$.—Cationic palladium(II) perchlorate complexes with DMSO, DMF, and DMA were prepared by dissolving $PdCl_2$ in the respective ligand and adding stoichiometric amounts of anhydrous silver perchlorate to the resultant solution. Silver chloride was filtered and the DMF and DMA complexes were precipitated by the addition of anhydrous ether, while the DMSO complex was precipitated by chloroform. The complexes were dried *in vacuo* for 5 hr. Attempts to prepare the NMF and CH_3CN complexes by this procedure resulted in decomposition to metallic palladium.

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PdL$_2$Cl$_2$.—The neutral complexes PdL$_2$Cl$_2$ were all prepared by dissolving PdCl$_2$ in the respective ligand, filtering off any undissolved PdCl$_2$, and then adding ether to precipitate the complexes. The complexes were dried *in vacuo* for 5 hr.

Infrared Spectra.—Infrared spectra for the range 4000–600 cm^{-1} were recorded as Nujol mulls between NaCl plates unless otherwise specified. Far-ir spectra (620–270 cm^{-1}) were recorded as Nujol mulls between polyethylene disks. All spectra (cm^{-1}) were recorded on the Perkin-Elmer 421. The 350-cm^{-1} region was calibrated by use of water vapor.[12]

[Pd(CH$_3$CN)$_4$](BF$_4$)$_2$.—CH$_3$CN peaks: 3323 (vw), 3010 (sh), 2347 (ms), 2318 (w), 1360 (w, sh), 1024 (ms), 960 (mw); BF$_4^-$ peaks: 1281 (mw), 1055 (vs), 760 (vw), 517 (ms); others: 442 (m), 420 (m), 365 (w), 350 (sh). Fluorolube: 3015 (m), 2949 (ms), 1416 (mw), 1360 (mw).

Pd(CH$_3$CN)$_2$Cl$_2$.—CH$_3$CN peaks: 3291 (w), 2332 (m), 2303 (mw), 1406 (w), 1353 (mw), 1021 (m), 951 (w); others: 443 (mw), 407 (w), 359 (ms), 327 (sh). Fluorolube: 2985 (mw), 2923 (m), 1403 (w), 1353 (mw).

[Pd(DMSO)$_4$](ClO$_4$)$_2$.—DMSO peaks: 3023 (sh), 3013 (m), 1434 (sh), 1413 (w), 1404 (sh), 1319 (mw), 1302 (vw), 1150 (ms), 1140 (ms, sh) 1030 (m), 1021 (sh), 981 (ms), 948 (w), 920 (s), 905 (s), 732 (mw), 682 (mw), 376 (sh), 363 (ms), 352 (sh), 333 (w); ClO$_4^-$ peaks: 2018 (w), 1091 (vs), 621 (ms), 450 (sh); others: 2723 (vw), 757 (sh), 705 (vw) 493 (ms), 437 (ms), 419 (ms), 395 (sh).

[Pd(DMSO)$_4$](BF$_4$)$_2$.—The spectrum is very similar to that of the perchlorate complex except for the anion frequencies; BF$_4^-$ peaks: 1284 (w), 1090 (sh), 1055 (vs), 765 (w), 517 (m).

[Pd(DMSO-d_6)$_4$](BF$_4$)$_2$.—DMSO-d_6 peaks: 2276 (sh), 2268 (m), 2261 (m), 2254 (sh), 2129 (mw), 2124 (sh), 1146 (vs), 1141 (sh), 1036 (sh), 1024 (s), 1004 (s), 935 (sh), 916 (s, sh), 904 (s), 841 (ms), 835 (sh), 825 (ms), 781 (m), $\sim$720 (w), 647 (w), 631 (mw), 345 (ms), $\sim$337 (sh), 305 (mw), 302 (sh), 287 (sh), 277 (vw); BF$_4^-$ peaks: 1283 (mw), 1096 (sh), 1062 (vs), 766 (vw), 518 (ms); others: 468 (s), 403 (sh), 394 (ms).

[Pd(DMF)$_4$](ClO$_4$)$_2$.—DMF peaks: 3063 (sh), $\sim$2005 (w), 1646 (s), 1487 (w), $\sim$1448 (sh), 1432 (sh), 1422 (sh), 1406 (sh), 1385 (sh), 1360 (ms), 1345 (ms), 1244 (m), 1125 (sh), 1003 (sh), 859 (vw), $\sim$720 (ms), 664 (mw), 419 (sh), 415 (sh), $\sim$356 (sh); ClO$_4^-$ peaks: 1086 (s), 931 (sh), 621 (ms); others: 2722 (vw), 463 (ms), 400 (s), 394 (sh). Fluorolube: 1358 (ms), 1344 (ms).

Pd(DMF)$_2$Cl$_2$.—DMF peaks: 3010 (sh), 2026 (vw), 1629 (vs), 1487 (w), 1434 (s), 1420 (sh), 1400 (sh), 1239 (m), 1149 (vw), 1113 (ms), 1015 (mw), 1051 (mw), 856 (vw), 700 (s), 422 (sh), 342 (sh), 325 (sh); others: 2728 (vw), 429 (ms), 385 (ms), 374 (sh), 347 (ms), 297 (sh). Fluorolube: 1371 (sh), 1361 (s).

[Pd(DMA)$_4$](ClO$_4$)$_2$.—DMA peaks: 1599 (s), 1486 (mw), 1418 (w), 1400 (m), 1256 (m), 1196 (vw), 1141 (sh), 1024 (w), 966 (mw), 750 (m), 665 (w), 587 (mw), 500 (m); ClO$_4^-$ peaks: $\sim$2014 (w), 1089 (s), 925 (vw), 620 (ms); others: 2723 (vw), 458 (m), 391 (w).

Pd(DMA)$_2$Cl$_2$.—DMA peaks: 1588 (s), 1499 (sh) 1488 (mw), 1429 (mw), 1398 (m), 1256 (mw), 1194 (vw), 1052 (sh), 1024 (mw), 968 (w), 751 (mw), 666 (w), 588 (w), 498 (m); others: 450 (m), 350 (ms), 334 (w, sh).

[Pd(NMF)$_4$](BF$_4$)$_2$.—NMF peaks: 3380 (vs, br), 3060 (sh), 3033 (sh), 1629 (vs, br), 1540 (sh), 1530 (m), 1520 (sh), 1416 (m), 1350 (s), 1260 (mw), 1248 (mw), 1156 (m), 955 (w), 812 (m), 803 (sh), $\sim$718 (m), 671 (sh), 389 (ms), 375 (sh), 335 (vw), 298 (vw); BF$_4^-$ peaks: 1287 (w), 1058 (vs, vbr), 763 (w), 519 (m); others: 479 (m), 466 (ms).

[Pd(NMA)$_4$](BF$_4$)$_2$.—NMA peaks: 3370 (s, br), 3262 (sh), 3119 (mw), 2977 (sh), 2941 (mw), 2889 (sh), 2815 (sh), $\sim$1605 (s, br), $\sim$1547 (s), 1428 (m), 1399 (m), 1374 (m), 1347 (sh), 1318 (w), 1155 (m), 1018 (s), 904 (w), 860 (w), 709 (sh), 661 (m), 622 (vw), 587 (m), 438 (w), 404 (m); BF$_4^-$ peaks: 1282 (w), $\sim$1065 (s, br), 762 (w), 515 (m); others: 476 (m), $\sim$378 (sh), 354 (vw). (Complex was run as a smear.)

Pd(NMA)$_2$Cl$_2$.—The infrared spectrum (4000–600 cm^{-1}) is in reasonable agreement with that reported by Pivcova and Schneider.[13] Far-ir spectrum (cm^{-1}): 576 (s), 481(m), 400 (m), 346 (s), 330 (sh).

Results

The complexes [PdL$_4$]X$_2$ and PdL$_2$Cl$_2$, where L is DMSO, CH$_3$CN, DMF, NMF, DMA, or NMA and X is perchlorate or tetrafluoroborate, have been prepared. Ionic perchlorate or tetrafluoroborate anions are assigned for all of the cationic complexes on the basis of ir spectra (see Experimental Section), which contain only single bands for the asymmetric stretch (ν_3, T$_2$) and deformation mode (ν_4, T$_2$) along with a weak symmetric stretching vibration (ν_1, A$_1$).[14]

All of the Pd(II) complexes measured were found to be diamagnetic (Table I) and thus consistent with a roughly planar array of donor atoms about Pd(II).

Only one Pd–Cl stretching frequency was resolved in the PdL$_2$Cl$_2$ complexes, suggesting a *trans* structure for the solid chloride complexes[15] (Table II). Infrared spectral frequencies which have been utilized in defining the coordination sites and in comparing the acceptor properties of Pd(II) with those of other divalent metal ions are found in Tables III–V.

Discussion

Dimethyl Sulfoxide Complexes.—Infrared spectral studies of DMSO complexes have proven useful in distinguishing between coordination through the oxygen or sulfur donor site.[16,17] The X-ray structure determination of *trans*-Pd(DMSO)$_2$Cl$_2$[18] and *cis*-Pd(DMSO)$_2$(NO$_3$)$_2$[19] have demonstrated that DMSO coordinates through the sulfur atom. The bands at 1116 cm^{-1} in the chloride complex and at 1157 and 1136 cm^{-1} in the nitrate complex were assigned to ν_{SO} (sulfur bonded).[17,19] Examination of the ir spectra for the Pd(DMSO)$_4^{2+}$ complexes[20] (Table I) reveals strong bands at 1150 and 1140 cm^{-1} which are only slightly shifted by deuteration that can be attributed to ν_{SO} and demonstrate the presence of sulfur-coordinated DMSO (Figure 1, Table III).

Coordination of DMSO through the sulfoxide oxygen is characterized by a shift of ν_{SO} to lower energy (Table III) (*e.g.*, for [Fe(DMSO)$_4$Cl$_2$][FeCl$_4$],[21] ν_{SO} (oxygen bonded = 933 cm^{-1}).[17] Inspection of the Pd(DMSO)$_4^{2+}$ spectra in the 900–1000-cm^{-1} region reveals several bands that might correspond to ν_{SO} for oxygen-bonded DMSO; however, the assignment of ν_{SO} in this spectral region is complicated by the presence of methyl rocking

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(20) B. B. Wayland and R. F. Schramm, *ibid.*, **23**, 1465 (1968).

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TABLE I
ANALYTICAL DATA AND MAGNETIC SUSCEPTIBILITIES FOR PALLADIUM(II) COMPLEXES

	Analyses, %										
	Theory				Found				$10^{-6}\chi$, cgs units[a]		
Complex	C	H	N	Pd	C	H	N	Pd	χ_m	χ_d	χ_p
$[Pd(CH_3CN)_4](BF_4)_2$	21.64	2.73	12.62	23.96	21.51	2.82	12.54	. . .	−94	−187	+93
$Pd(CH_3CN)_2Cl_2$	18.52	2.33	. . .	41.02	18.74	2.15	. . .	40.95	−18	−119	+101
$[Pd(DMSO)_4](ClO_4)_2$	15.55	3.91	. . .	17.22	15.28	3.75	. . .	17.43	−170	−271	+101
$[Pd(DMSO)_4](BF_4)_2$	16.22	4.08	. . .	. . .	16.40	4.01	. . .	. . .	. . .	. . .	. . .
$Pd(DMSO)_2Cl_2$	. . .	. . .	. . .	31.96	. . .	. . .	. . .	31.70	−86	−166	+80
$[Pd(DMF)_4](ClO_4)_2$[b]	24.11	4.72	9.37	17.77	24.03	4.91	9.26	17.51	−132	−249	+117
$Pd(DMF)_2Cl_2$	22.28	4.36	. . .	. . .	22.40	4.21	. . .	. . .	−85	−155	+70
$[Pd(DMA)_4](ClO_4)_2$	29.39	5.55	. . .	16.27	29.15	5.55	. . .	15.92	−93	−296	+203
$Pd(DMA)_2Cl_2$	27.33	5.16	. . .	30.27	27.29	4.97	. . .	30.00	−40	−179	+139
$Pd(NMA)_2Cl_2$	22.28	4.36	8.66	. . .	22.01	4.29	8.44	. . .	. . .	. . .	. . .
$[Pd(NMF)_4](BF_4)_2$	18.61	3.90	10.85	. . .	18.93	3.79	10.90	. . .	. . .	. . .	. . .
$[Pd(NMA)_4](BF_4)_2$	. . .	. . .	. . .	18.59	. . .	. . .	. . .	18.21	. . .	. . .	. . .

[a] χ_d, χ_p, and χ_m are, respectively, the diamagnetic, paramagnetic, and total molar susceptibilities. [b] Calcd: O, 32.12. Found: O, 32.03.

TABLE II
PALLADIUM–CHLORINE STRETCHING VIBRATION IN *trans*-PdL_2Cl_2 COMPLEXES

Complex	ν_{Pd-Cl}, cm^{-1}
$Pd(CH_3CN)_2Cl_2$[a]	359
$Pd(DMSO)_2Cl_2$[b]	353
$Pd(DMF)_2Cl_2$[c]	347
$Pd(DMA)_2Cl_2$	350
$Pd(NMA)_2Cl_2$	346

[a] R. A. Walton, *Spectrochim. Acta*, **21**, 1795 (1965). [b] R. A. Walton and B. F. G. Johnson, *ibid.*, **22**, 1853 (1966). [c] The assignment of this vibration is complicated by the presence of bands at 360 and 322 cm^{-1} in free DMF.

TABLE III
REPRESENTATIVE SULFUR- AND OXYGEN-BONDED DMSO COMPLEXES

Complex	Donor atom	ν_{SO}	ν_{M-L}
DMSO(l)[c]	. . .	1055	. . .
DMSO-d_6(l)[c]	. . .	1064	. . .
$Pd(DMSO)_2Cl_2$[c]	S	1116	415[a,d]
$Pd(DMSO\text{-}d_6)_2Cl_2$[c]	S	1113	. . .
$Pd(DMSO)_2(NO_3)_2$[e]	S	1157, 1136	430[a]
$[Pd(DMSO)_4]X_2$	S	1150, 1140	437, 420[a]
$[Pd(DMSO\text{-}d_6)_4](BF_4)_2$	S	1146, 1141	403, 394[a]
$SnCl_4 \cdot 2DMSO$[c]	O	915	482, 477[b,f]
$SnCl_4 \cdot 2DMSO\text{-}d_6$[c]	O	929, 914	. . .
$[Cr(DMSO)_6](ClO_4)_3$[c]	O	928	529[b,g]
$[Ni(DMSO)_6](ClO_4)_2$[c]	O	955	444[b,g]
$[Pd(DMSO)_4]X_2$	O	920, 905	493[b]
$[Pd(DMSO\text{-}d_6)](BF_4)_2$	O	916, 904	468[b]

[a] Palladium–sulfur stretch. [b] Metal–oxygen stretch. [c] F. A. Cotton, R. Francis, and W. D. Horrocks, Jr., *J. Phys. Chem.*, **64**, 1534 (1960). [d] R. A. Walton and B. F. G. Johnson, *Spectrochim. Acta*, **22**, 1853 (1966). [e] D. A. Langs, C. R. Hare, and R. G. Little, *Chem. Commun.*, **21**, 1080 (1967). [f] T. Tanaka, *Inorg. Chim. Acta*, **1**, 217 (1967). [g] C. V. Berney and J. H. Weber, *Inorg. Chem.*, **7**, 283 (1968).

TABLE IV
RELEVANT VIBRATIONAL FREQUENCIES AND ASSIGNMENTS FOR METAL ION–ACETONITRILE COMPLEXES (CM^{-1})

	ν_{CN}	$\Delta\nu_{CN}$	$\delta_s(CH_3)(\nu_3)$	$\nu_{C-C}(\nu_4)$	$\Delta\nu_4$	$\nu_3 + \nu_4$
$CH_3CN_{(g)}$[a]	2266	. . .	1371	920	. . .	2293(l)[b]
$[Pd(CH_3CN)_4](BF_4)_2$	2347	+81	1360	960	+40	2318
$Pd(CH_3CN)_2Cl_2$[c]	2332	+66	1353	951	+31	2303
$Zn(CH_3CN)_4^{+2}$[a]	2306	+40	1368	939	+19	. . .

[a] K. F. Purcell and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 919 (1966). [b] P. Venkateswarlu, *J. Chem. Phys.*, **19**, 293 (1951). [c] The assignment given above for ν_{CN} in $Pd(CH_3CN)_2Cl_2$ is different from that reported by R. A. Walton, *Spectrochim. Acta*, **21**, 1795 (1965). Our assignment is based upon the position of the combination band $\nu_3 + \nu_4$.

bands. In order to examine for the possible presence of oxygen-bonded DMSO, the deuterated complex Pd-$(DMSO\text{-}d_6)_4^{2+}$ was prepared and its ir spectrum was recorded (Figure 1). The methyl rocking bands shift ~200 cm^{-1} in the deuterated complex thus clearing the ν_{SO}(oxygen bonded) region for inspection. The strong bands at 920 and 905 cm^{-1} in $Pd(DMSO)_4^{2+}$ undergo only very slight shifts to 916 and 904 cm^{-1} in the deuterated complex and are thus assigned to ν_{SO} for oxygen-bonded DMSO.

Further evidence for the presence of mixed sulfur and oxygen coordination sites is supplied by the presence of more ir bands than would be expected for four equivalent DMSO ligands. In particular, the spectral regions for δ_s(CSO) and δ_a(CSO) each contain two or more bands. In the far-ir there are at least three bands (493, 437, 420 cm^{-1}) that can be associated with Pd–ligand stretching frequencies, while only one would be expected for an idealized D_{4h} symmetry. The splitting of ν_{SO} in both the sulfur-bonded and oxygen-bonded regions along with at least three ir-active Pd–ligand stretches is most consistent with a *cis* arrangement of S- and O-bonded DMSO ligands. More detailed structural consideration for $Pd(DMSO)_4^{2+}$ must await the results of the X-ray structure determination now in progress.

It is also interesting to note that the frequency shift $\Delta\nu_{SO}$(oxygen bonded) is much larger than any previously reported for a divalent metal ion complex with DMSO.[17] This is consistent with the relatively strong metal–ligand bonding generally associated with square-planar complexes.

In sulfur-bonded bis-DMSO complexes, the DMSO

Table V

Important Ir Frequencies and Assignments in Palladium(II) Amide Complexes

Compound	ν_{CO}	$\Delta\nu_{CO}$	ν_{CN}	$\Delta\nu_{CN}$	δ_{CH}	δ_{OCN}	$\Delta\delta_{OCN}$	Pd–O
DMF(g)[a]	1714[b]	. . .	1496[b]	. . .	1382[b]	660[c]	. . .	. . .
$[Pd(DMF)_4](ClO_4)_2$	1646	−68	1487	−9	1344	720	+60	463
$Pd(DMF)_2Cl_2$	1629	−85	1487	−9	1361	700	+40	∾429[d]
NMF(g)[e]	1727[b]	. . .	1490[f]	. . .	1385[c]	771[c]	. . .	. . .
$[Pd(NMF)_4](BF_4)_2$	1629	−98	1530	+40	1350	812	+41	479, 466
NMA(g)[e]	1718	. . .	1487[f]	. . .	1413[c,g]	627[c]	. . .	. . .
$[Pd(NMA)_4](BF_4)_2$	∾1605	−(∾113)	∾1547	+(∾60)	1399	661	+34	476
$Pd(NMA)_2Cl_2$	1605	−113	1555	+68	1393	651	+24	481
DMA(g)[a]	1695	. . .	1492	. . .	1400[g]	730[c,h]	. . .	. . .
$[Pd(DMA)_4](ClO_4)_2$	1599	−96	1486	−6	1400	750	+20	458
$Pd(DMA)_2Cl_2$	1588	−107	1488	−4	1398	751	+21	450

[a] R. L. Jones, *J. Mol. Spectry.*, **11**, 411 (1963). [b] The ν_{CO}, ν_{CN}, and δ_{CH} (in-plane deformation) are mutually coupled. [c] Liquid spectrum. [d] Assignment of this vibration is complicated by the presence of ligand vibrations in that region. [e] T. Miyazawa, T. Shimanouchi, and S. Mizushima, *J. Chem. Phys.*, **24**, 408 (1956). [f] Both ν_{CO} and ν_{CN} are coupled with δ_{NH}. [g] In-plane CH_3–N bending frequency. [h] Since normal-coordinate analysis has not been done, this is our suggested assignment.

ligands are commonly found in the *cis* configuration.[19,22] The Pd–S bond distances in the *cis*-nitrate complex are significantly shorter than those in the *trans*-chloride complex, which is considered to be the result of more favorable dπ–dπ Pd–S bonding in the *cis* configuration. Assuming that the observed *cis* structures are the thermodynamically most stable form and do not simply result from kinetic stability, then the presence of the *trans* structure for $Pd(DMSO)_2Cl_2$ is surprising. The *trans* configuration of $Pd(DMSO)_2Cl_2$ may not be the most stable molecular form but is obtained in the solid state because it leads to a more stable crystal form. A study of $Pd(DMSO)_2Cl_2$ in solution was undertaken to aid in understanding this problem. The ir spectrum for solid *trans*-$Pd(DSMO)_2Cl_2$ has a single S–O stretch at 1116 cm^{-1} and single Pd–S and Pd–Cl stretches at 415 and 353 cm^{-1}, respectively.[23] A single S–O stretching frequency at 1125 cm^{-1} in DMSO solution indicates retention of the *trans* structure in DMSO solvent. However upon dissolution in acetonitrile, two bands appear in the S–O stretching region at 1154 and 1134 cm^{-1} and ν_{Pd-S} shifts to 429 cm^{-1}. These values are very close to the ν_{SO} frequencies of 1157 and 1136 cm^{-1} and ν_{Pd-S} of 430 cm^{-1} observed for *cis*-$Pd(DMSO)(NO_3)_2$ (Table III). This increase in ν_{SO} and the splitting are good evidence for the presence of the *cis* sulfur-bonded complex in acetonitrile solution. Similar studies in CH_2Cl_2 and $CHCl_3$ were hampered by solvent absorptions in the ν_{SO} region and the limited solubility of the complex in these solvents. Isolation of the crystalline complex from every solvent studied yielded only *trans*-$Pd(DMSO)_2Cl_2$. The limited solubility of the complex in nonbasic solvents precludes a decision as to whether the *cis* or *trans* isomer is the most stable molecular form. This work does, however, leave open the possibility that the isolation of only the *trans* complex as a solid may be caused by crystal packing.

Acetonitrile Complexes.—Coordination of acetonitrile through nitrogen is characterized in the ir spectra by increase in both the C–N and C–C stretching frequencies. Purcell and Drago[24] have shown that acetonitrile coordination strengthens the C–N and C–C σ bonding which results in increased force constants. On palladium complex formation, the C–N stretching frequency for acetonitrile ($\nu_{CN(g)}$ 2266 cm^{-1}) increases to 2347 cm^{-1} in $Pd(CH_3CN)_4^{2+}$ and to 2332 cm^{-1} for $Pd(CH_3CN)_2Cl_2$, while ν_{C-C} increases from 920 cm^{-1} for the free ligand to 960 and 951 cm^{-1} for the two palladium complexes, respectively (Table IV). The magnitudes for $\Delta\nu_{CN}$ and $\Delta\nu_{C-C}$ are among the largest for metal ion complexes[24] which is again suggestive of relatively strong Pd-ligand bonding in square-planar complexes. The frequency shift data also suggest that the palladium–acetonitrile bonding is slightly stronger in the cationic complex $Pd(CH_3CN)_4^{2+}$ than in the neutral complex *trans*-$Pd(CH_3CN)_2Cl_2$.

Amide Complexes.—The carbonyl oxygen is assigned as the principal donor site in all of the amide complexes, in part on the basis of the shift to lower frequency of the band primarily associated with the carbonyl stretching frequency as well as frequency shifts of other relevant bands such as the increase in frequency of the O–C–N bending mode.[25,26] A list of characteristic amide vibrations and the "palladium–oxygen" stretching frequency for the amide complexes can be found in Table V. Although $\Delta\nu_{CO}$ for the amide complexes is among the largest reported for divalent metal ions, the relative acceptor ability of Pd(II) with amide oxygen donors compared to other metal ions cannot be determined by the use of $\Delta\nu_{CO}$, for the ν_{CO} vibration is coupled with ν_{CN} and other modes.[27–29] The DMF

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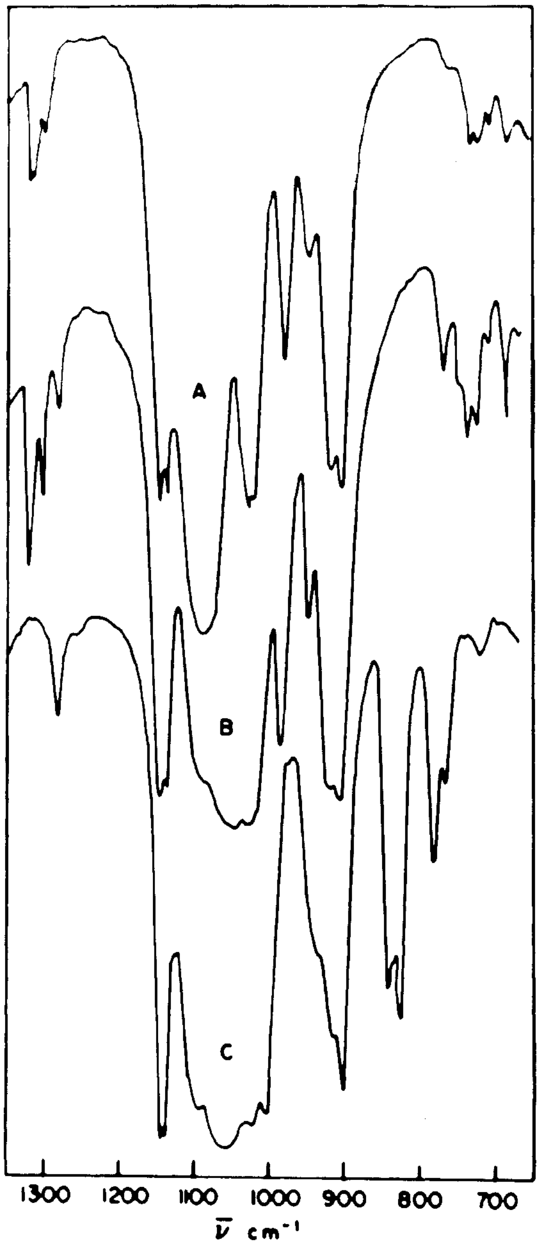

Figure 1.—Infrared spectra of cationic palladium(II) dimethyl sulfoxide complexes: (A) $[Pd(DMSO)_4](ClO_4)_2$; (B) $[Pd(DMSO)_4](BF_4)_2$; (C) $[Pd(DMSO\text{-}d_6)_4](BF_4)_2$.

complexes will be used to illustrate this point, since a normal-coordinate analysis for DMF is available.[27]

Normal-coordinate analysis for DMF indicates that ν_{CO}, ν_{CN}, and δ_{CH} are mutually coupled to a significant extent. Valence bond considerations predict that oxygen coordination will result in a decrease in ν_{CO} and an increase in ν_{CN}. This expectation is not experimentally obtained for the palladium–DMF complexes presumably owing to the complications caused by coupling. Furthermore, $\Delta\nu_{CO}$ suggests that the Pd–DMF bonding is stronger in the neutral chloride complex than in the cationic complex, while $\Delta\delta_{CH}$ indicates the reverse order and $\Delta\nu_{CN}$ suggests that the interaction is very similar. The use of these three mutually coupled vibrations for frequency shift comparisons is clearly complicated by coupling and the changes in coupling on complex formation.

The O–C–N bending mode found at 660 cm^{-1} in DMF is not coupled and is thus a better choice for frequency shift comparisons. The O–C–N bending occurs at 720 cm^{-1} in $Pd(DMF)_4^{2+}$. This shift of $\sim$60 cm^{-1} is larger than for any other divalent metal ion–DMF complex and is comparable to trivalent complexes (*e.g.*, for $Al(DMF)_6^{3+}$ $\Delta\delta_{OCN} = 60$ cm^{-1}).[26] These data again suggest relatively strong palladium(II)–ligand bonding. Also the smaller frequency shift ($\Delta\delta_{OCN} = 40$ cm^{-1}) for the neutral chloride complex $Pd(DMF)_2Cl_2$ suggests that the palladium–ligand bonding is more effective in the cationic complex $Pd(DMF)_4^{2+}$. This is further substantiated by the Pd–O stretching frequencies of 463 and 429 cm^{-1} in $Pd(DMF)_4^{2+}$ and $Pd(DMF)_2Cl_2$, respectively.

Since normal-coordinate analysis has demonstrated that δ_{OCN} is strongly coupled in the other three amides,[28,29] frequency shifts cannot be used to compare the palladium–ligand bonding of the cationic with the neutral chloride complex or to comment on the relative acceptor ability of Pd(II) with these amides.

Conclusions

The presence of anions with very small coordinating ability is essential for the general preparation of the complexes $[PdL_4]X_2$ where Pd(II) is bound directly to only neutral monodentate ligands (L). The anions perchlorate or tetrafluoroborate were found to satisfy this requirement. Two methods were used to introduce the "noncoordinating" anion into the complex: (1) titration of a solution of palladium chloride in the donor solvent with silver perchlorate or silver tetrafluoroborate and (2) reaction of metallic palladium with NO^+,BF_4^- in acetonitrile to yield $[Pd(CH_3CN)_4](BF_4)_2$. This acetonitrile complex is a useful precursor to other cationic Pd(II) complexes, and owing to the facile replacement of acetonitrile, this complex should prove generally useful in Pd(II) chemistry.

All Pd(II) complexes prepared were found to be four-coordinate and diamagnetic and thus consistent with square-planar geometry. Infrared spectra indicate that perchlorate and tetrafluoroborate anions are essentially ionic and that both sulfur and oxygen donor sites occur in the dimethyl sulfoxide complex while nitrogen and oxygen donation are, respectively, found in the acetonitrile and amide complexes. The ir frequency shifts for modes involving the donor atom are among the largest reported for divalent metal ion complexes suggesting that relatively strong palladium–ligand bonding occurs in these square-planar complexes. Frequency shift data also suggest that the cationic complexes PdL_4^{2+} involve slightly stronger metal–ligand bonding than the neutral complexes PdL_2Cl_2.

The complex $Pd(DMSO)_4^{2+}$ is the first example of DMSO exhibiting both sulfur and oxygen coordination sites in a complex; in fact, it is the first case to our knowledge where a neutral ligand exhibits well-defined mixed donor sites. Far-ir spectra suggest a *cis* arrangement of oxygen- and sulfur-bonded DMSO ligands. The complex $Pd(DMSO)_2Cl_2$ which exists as the *trans* isomer in the solid is found to convert to the *cis* isomer in acetonitrile solution.

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Amine Complexes of Beryllium Hydride[1]

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Several tertiary amine complexes of beryllium hydride have been synthesized by three different preparative routes. In the first, trimethylamine is allowed to react with the liquid adduct diethylberyllium–diethylaluminum hydride to produce the crystalline beryllium hydride–trimethylamine complex. The other two procedures involve direct reaction between the amine and polymeric beryllium hydride either by (1) heating the mixture in a sealed system or (2) ball-milling the reactants together. The complexes were characterized by chemical analysis, infrared and nmr spectra, and X-ray powder diffraction measurements. These data, along with molecular weight determinations, indicate that the fundamental unit in every case is the hydrogen-bridged BeH_2 dimer.

Introduction

Unlike the case of the group IIIa hydrides borane,[2] alane,[3] and gallane,[4] there have been no tertiary amine complexes reported for the simple hydrides of the group IIa metals. Because of its "electron-deficient" character, beryllium hydride is the one member of its group most likely to give stable complexes with donor molecules. Holley and Lemons[5] presented some evidence for the formation of beryllium hydride etherate, although the simple 1 : 1 adduct was not isolated. The existence of the trimethylamine complex was predicted by these authors, but a successful synthesis was never reported. The nearest approach was that of Bell and Coates[6] by their preparation of the trimethylamine complex of methylberyllium hydride, and since the hydrogen bridges in methylberyllium hydride were not cleaved by treatment with excess trimethylamine, one might conclude that it would be difficult to prepare the beryllium hydride adduct by direct combination of the amine with polymeric beryllium hydride.

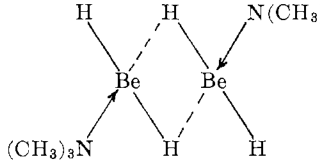
In this paper we report the synthesis and properties of a number of tertiary amine complexes of beryllium hydride. Three different methods of preparation are described, two of which involve a convenient, direct synthesis.

Results and Discussion

The trimethylamine complex of beryllium hydride (I) can be prepared by reaction of the diethylberyllium–diethylaluminum hydride adduct (II) with liquid trimethylamine

$$\underset{\text{II}}{(C_2H_5)_2Be\cdot 2(C_2H_5)_2AlH} + 3(CH_3)_3N \longrightarrow \underset{\text{I}}{(CH_3)_3N\cdot BeH_2} + 2(C_2H_5)_3Al\cdot N(CH_3)_3$$

When the excess trimethylamine is allowed to evaporate, I slowly precipitates from the liquid residue. It is recovered as colorless, needlelike crystals, which are sensitive to air and moisture. The complex is moderately soluble in trimethylamine and aromatic hydrocarbons. In diethyl ether it initially dissolves and then precipitates as an amine-deficient species by partial dissociation. Cryoscopic molecular weight measurements indicate that I is dimeric in benzene solution. The hydrogen-bridged structure



is proposed for the dimer. This structure is closely

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