2910 *Inorg. Chem.* **1987**, *26*, 2910–2912

Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

Reactions of $ReH_7(PPh_3)_2$ with Bidentate Aromatic Heterocycles

Gregory A. Moehring and Richard A. Walton*

Received February 3, 1987

The chemistry of mononuclear hydrido(phosphine)rhenium complexes that contain up to seven hydride ligands has been the focus of our recent studies aimed at exploring the reactions of polyhydride complexes with electrophiles and nucleophiles.[1-3] At present there is a dearth of information concerning the chemistry of rhenium polyhydrides that contain nitrogen donors, with the notable exception of those with nitrile ligands.[1-5] Previous investigations have explored the reactions of the heptahydride complex $ReH_7(PPh_3)_2$ with amine ligands and have shown that the compounds $ReH_5(PPh_3)_2L$ (L = pyridine, piperidine, cyclohexylamine, or *tert*-butylamine)[2,6] are readily formed. Protonation of these latter complexes in nitrile solvents (RCN) affords the monohydrido cations $[ReH(NCR)_3(PPh_3)_2L]^{2+}$.[2,3] In the present report we examine the behavior of $ReH_7(PPh_3)_2$ toward the bidentate nitrogen donors 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), and 1,4-pyrazine (pyz). These systems reveal some interesting differences from the complexes that contain monodentate amines.

Experimental Section

Starting Materials. The complex $ReH_7(PPh_3)_2$ was prepared by the standard literature method.[6] All other reagents and solvents were obtained from commercial sources. Solvents were deoxygenated and/or distilled prior to use. All reactions were carried out under an atmosphere of nitrogen.

A. $ReH_5(PPh_3)_2(pyz)$. The reaction between $ReH_7(PPh_3)_2$ (0.357 g, 0.497 mmol) and 1.2 g of melted pyrazine (15 mmol) for 10 min yielded a dark orange solid upon cooling the mixture. This was washed thoroughly with ethanol to afford orange microcrystals of $ReH_5(PPh_3)_2(pyz)$; yield 0.335 g (85%). Anal. Calcd for $C_{40}H_{39}N_2P_2Re$: C, 60.36; H, 4.94. Found: C, 59.53; H, 4.97.

B. $[ReH_5(PPh_3)_2]_2(\mu\text{-pyz})$. A solution of $ReH_7(PPh_3)_2$ (0.153 g, 0.213 mmol) and $ReH_5(PPh_3)_2(pyz)$ (0.154 g, 0.194 mmol) in 10 mL of refluxing THF was stirred for 10 min. The solvent was evaporated off under vacuum and the dry residue dissolved in CH_2Cl_2 and loaded onto a silica gel column. The dark violet band was eluted from the column with CH_2Cl_2 and this solution added to 100 mL of *n*-pentane. The dark purple microcrystals that formed were filtered off and dried under vacuum; yield 0.080 g (27%). The complex was isolated as the $^1/_2CH_2Cl_2$ solvate; the presence of CH_2Cl_2 was confirmed by ^1H NMR spectroscopy (δ +5.35 in C_6D_6). Anal. Calcd for $C_{76.5}H_{75}ClN_2P_4Re_2$: C, 59.09; H, 5.34. Found: C, 58.72; H, 4.88.

C. (i) $ReH_3(PPh_3)_2(phen)$. A melt reaction between $ReH_7(PPh_3)_2$ (0.243 g, 0.338 mmol) and an excess of 1,10-phenanthroline (2.6 g, 14 mmol) was carried out at 120 °C for 15 min. The mixture was cooled to room temperature and the violet solid washed thoroughly with ethanol and then dried. This solid (0.247 g) was then suspended in 5 mL of acetonitrile and the mixture acidified with $HBF_4{\cdot}Et_2O$ (0.30 mL, 0.45 mmol) and stirred for 5 min. An excess of NEt_3 (0.50 mL) was then added,[7] and after an additional 30 min, the dark blue powder was filtered off and dried in vacuum; yield 0.191 g (63%). Anal. Calcd for $C_{46}H_{41}N_2P_2Re$: C, 64.48; H, 4.62. Found: C, 63.44; H, 4.43.

(ii) $ReH_3(PPh_3)_2(bpy)$. This complex was prepared in a manner similar to preparation C(i) from 0.278 g (0.387 mmol) of $ReH_7(PPh_3)_2$ and 2.7 g (17 mmol) of 2,2′-bipyridine. The temperature for the melt reaction was 90 °C; yield 0.134 g (40%). Anal. Calcd for $C_{44}H_{41}N_2P_2Re$: C, 63.50; H, 4.67; N, 3.13. Found: C, 62.93; H, 4.67; N, 2.84.

D. (i) $[ReH_4(PPh_3)_2(phen)]BF_4$. A suspension of $ReH_3(PPh_3)_2(phen)$ (0.158 g, 0.177 mmol) in 5 mL of acetonitrile was treated with $HBF_4{\cdot}Et_2O$ (0.20 mL, 0.30 mmol). The solution was stirred for 5 min and then added to a mixture of diethyl ether, 50 mL, and *n*-pentane, 50 mL. The dark pink precipitate was filtered off and dried in vacuum; yield 0.162 g (92%). The compound was isolated as a monohydrate; the presence of water was confirmed by ^1H NMR spectroscopy (δ +1.60 in CD_2Cl_2). Anal. Calcd for $C_{46}H_{44}BF_4N_2OP_2Re$: C, 57.66; H, 4.23. Found: C, 57.17; H, 4.18.

(ii) $[ReH_4(PPh_3)_2(bpy)]BF_4$. This complex was prepared in the same manner as preparation D(i), starting from 0.097 g (0.11 mmol) of $ReH_3(PPh_3)_2(bpy)$; yield 0.083 g (78%). Anal. Calcd for $C_{46}H_{42}BF_4N_2P_2Re$: C, 57.69; H, 4.42; N, 2.92. Found: C, 57.22; H, 4.79; N, 2.49.

E. (i) $[ReH_2(PPh_3)_2(phen)(NCMe)]PF_6$. Acetonitrile, 5 mL, was added to a flask that contained $ReH_3(PPh_3)_2(phen)$ (0.174 g, 0.195 mmol) and $(C_7H_7)PF_6$ (0.048 g, 0.20 mmol). The mixture was stirred for 10 min, and precipitation was induced by the addition of 50 mL of diethyl ether and 50 mL of *n*-pentane. The dark pink precipitate was filtered off and dried in vacuum; yield 0.126 g (60%). Anal. Calcd for $C_{50}H_{43}F_6N_3P_3Re$: C, 55.65; H, 4.02; N, 3.89. Found: C, 55.64; H, 4.37; N, 3.09.

(ii) $[ReH_2(PPh_3)_2(bpy)(NCMe)]PF_6$. This complex was prepared in the same manner as preparation E(i), starting from 0.240 g (0.276 mmol) of $ReH_3(PPh_3)_2(bpy)$; yield 0.128 g (44%). Anal. Calcd for $C_{48}H_{43}F_6N_3P_3Re$: C, 54.64; H, 4.11. Found: C, 54.04; H, 4.53.

Physical Measurements. Infrared spectra were recorded as Nujol mulls between KBr plates on an IBM Instruments IR 32 Fourier Transform (4800–400 cm^{-1}) spectrometer. Cyclic voltammetric experiments were performed by using a Bioanalytical Systems Inc. Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B X-Y recorder. Measurements were carried out on CH_2Cl_2 solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. A Pt-bead working electrode was used. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature and are uncorrected for junction potentials.[8] $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-200 spectrometer operated at 80.98 MHz using an internal deuterium lock and 85% H_3PO_4 as an external standard. Positive chemical shifts were measured downfield from H_3PO_4. ^1H NMR spectra were recorded at 90 MHz on a Perkin-Elmer R-32 spectrometer. Resonances were referenced internally to residual protons in the deuterated solvent (CD_2Cl_2, δ +5.35; C_6D_6 δ +7.27).

Microanalyses were performed by Dr. H. D. Lee of the Purdue University microanalytical laboratory.

Results and Discussion

(a) Reactions with 1,4-Pyrazine. The complex $ReH_5(PPh_3)_2(pyz)$ (pyz = 1,4-pyrazine) can be isolated from the reaction of $ReH_7(PPh_3)_2$ with an excess of molten pyrazine. This complex thus joins a class of $ReH_5(PPh_3)_2L$ (L = py, $C_6H_{11}NH_2$, piperidine, *t*-$BuNH_2$) compounds that have been prepared previously.[2,6] These $ReH_5(PPh_3)_2L$ complexes are yellow,[2,6] while the pyrazine complex is bright orange due to a metal-to-ligand charge-transfer band at 494 nm ($\epsilon \sim 18\,000$ in CH_2Cl_2) in its electronic absorption spectrum. While other $ReH_5(PPh_3)_2L$ complexes exhibit a binomial triplet ($J_{P-H} \simeq 18$ Hz) in their room-temperature ^1H NMR spectra for the hydride resonances,[2,6] the hydride resonance for $ReH_5(PPh_3)_2(pyz)$ appears as a broad singlet (δ −3.65) at 35 °C in C_6D_6. We attribute the lack of P–H coupling to a slow exchange of hydride ligands on the NMR time scale. As the temperature is raised to 55 °C, this resonance sharpens into the expected binomial triplet centered at δ −3.61 (J_{P-H} = 17.4 Hz). When a CD_2Cl_2 solution of this complex is cooled to −75 °C, the hydride resonance splits into four signals at δ −0.98 (t, J_{P-H} = 28 Hz), −2.53 (d, J_{P-H} = 30 Hz), −7.59 (t, J_{P-H} = 24 Hz), and −8.75 (s), which have an intensity ratio of 1:2:1:1, respectively.[9] Thus, in this low-temperature limit, the

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Table I. IR and NMR Spectroscopic Properties of Bpy and Phen Complexes of Rhenium Polyhydrides

	chem shift, δ			IR,[c] cm^{-1}	
	^{1}H NMR[a]				
complex	Re–H[b]	MeCN	^{31}P{^{1}H} NMR[a]	ν(Re—H)	ν(C≡N)
$ReH_3(PPh_3)_2(bpy)$	$\sim$−3.1 (m)[d] $\sim$−4.2 (m)[d]		+31.2 (s)[e]	1946 m, br	
$ReH_3(PPh_3)_2(phen)$	−2.71 (t, 19.8)[f] −3.74 (t, 15.9)[f]		+32.2 (s)[e]	2034 vw, 1956 m, 1919 m	
$[ReH_4(PPh_3)_2(bpy)]BF_4$	−4.1 (t, 19.6)[g]		+30.5 (s)[g]	2048 w, 1994 w	
$[ReH_4(PPh_3)_2(phen)]BF_4$	−3.95 (t, 18.4)[g]		+29.9 (s)	2002 w	
$[ReH_2(PPh_3)_2(bpy)(NCMe)]PF_6$	−1.12 (m)	2.05 (s)	+23.6 (s)[g]	2064 w, 1983 w	2259 w
$[ReH_2(PPh_3)_2(phen)(NCMe)]PF_6$	−0.60 (t, 13.1)	2.17 (s)	+23.0 (s)	2071 w, 1998 w	2255 w

[a] Spectra recorded in CD_2Cl_2 unless otherwise stated. Abbreviations are as follows: s = singlet, t = triplet, m = multiplet. [b] Numbers in parentheses are J(P–H) in Hz. [c] Nujol mull spectra. [d] Spectrum recorded at 35 °C. When the solution was cooled to −40 °C, these two resonances sharpened and appear as triplets in an intensity ratio of 1:2 for δ −3.1 [J(P–H) $\simeq$ 18 Hz] and −4.2 [J(P–H) $\simeq$ 14 Hz]. [e] Recorded in C_6D_6. [f] The resonances at δ −2.71 and −3.74 have an intensity ratio of 1:2. A similar spectrum was observed in C_6D_6 ($\delta \simeq -1.6$ and $\simeq -2.9$) at 35 °C; when this solution is warmed to 75 °C, these two resonances broadened and collapsed to give a broad signal at $\delta \simeq -2.5$. [g] Recorded in $(CD_3)_2CO$.

spectrum resembles that reported for $ReH_5(AsEtPh_2)_3$ (and its phosphine analogue) in 2:1 CF_2Cl_2–$CHFCl_2$ at −135 °C.[10] These spectra are consistent with those expected based upon the known structure for $ReH_5(PMePh_2)_3$.[11] The complex is further characterized by a singlet at δ +43.25 in its ^{31}P{^{1}H} NMR spectrum (recorded in CD_2Cl_2), and ν(Re–H) modes as sharp features at 2030 vw, 1998 w, 1933 w, and 1877 w cm^{-1} in the Nujol mull IR spectrum.

The pyrazine-containing complex $ReH_5(PPh_3)_2(pyz)$ reacts with 1 equiv of $ReH_7(PPh_3)_2$ to form the first pyrazine-bridged polyhydride complex $[ReH_5(PPh_3)_2]_2(\mu\text{-pyz})$. This dark blue complex is spectroscopically quite similar to mononuclear $ReH_5(PPh_3)_2(pyz)$. The blue color arises from a metal-to-ligand charge-transfer band at 616 nm ($\epsilon \sim 18\,000$ in CH_2Cl_2). As with $ReH_5(PPh_3)_2(pyz)$, the hydride resonance in the ^{1}H NMR spectrum is again a broad singlet at 35 °C (δ −3.31 in C_6D_6). When the solution is warmed to 55 °C this resonance resolves into a binomial triplet at δ −3.19 (J_{P-H} = 19.8 Hz). The IR spectrum (Nujol mull) of this complex shows broad, weak ν(Re–H) modes at 1988 and 1848 cm^{-1}. The ^{31}P{^{1}H} NMR spectrum in CD_2Cl_2 shows a singlet at δ +40.1. This solution decomposes slowly on standing to form $ReH_5(PPh_3)_2(pyz)$ (δ +43.25) as the main phosphine-containing product. This observation is confirmed by monitoring the electronic absorption spectrum (in CH_2Cl_2) with time; the 616-nm band decreases in intensity as that at 494 nm increases. The other rhenium-containing species that are formed in this dissociation are derived from the putative species $[ReH_5(PPh_3)_2]$; these include $Re_2(\mu\text{-H})_4H_4(PPh_3)_4$ and $ReH_7(PPh_3)_2$[12-14] together with minor amounts of other products.

The electrochemical properties of these pyrazine complexes generally resemble those reported previously for other complexes of the type $ReH_5(PPh_3)_2L$.[15] The cyclic voltammogram (CV) of $ReH_5(PPh_3)_2(pyz)$ in 0.1 M TBAH–CH_2Cl_2 consists of an irreversible oxidation at $E_{p,a}$ = +0.40 V ($i_{p,a}/i_{p,c} \gg 1$) with additional prominent oxidations at $E_{p,a}$ = +0.71, +1.54, and +1.63 V and much weaker waves at $E_{p,a}$ = +1.02 and +1.25 V vs. Ag/AgCl. Most of these processes probably correspond to the formation of chemical products following oxidation to the unstable cation $[ReH_5(PPh_3)_2(pyz)]^+$. The CV of $[ReH_5(PPh_3)_2]_2(\mu\text{-pyz})$ is similar, with an irreversible oxidation at $E_{p,a}$ = +0.20 V followed by additional oxidations at +0.50, +0.65, and +1.50 V vs. Ag/AgCl.

(b) Reactions with 2,2′-Bipyridine and 1,10-Phenanthroline. The reaction of $ReH_7(PPh_3)_2$ with either 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen) produces a mixture of $Re_2(\mu\text{-H})_4H_4(PPh_3)_4$[6,16] and $ReH_3(PPh_3)_2$(L-L) (L-L = bpy or phen) that can easily be separated. The two complexes $ReH_3(PPh_3)_2$(L-L) are members of a relatively scarce group of neutral seven-coordinate rhenium trihydride compounds.[1,17-19] The color of these compounds is one of their most distinguishing features. While other members of this class are yellow, the bpy and phen complexes are green and purple, respectively. The more important spectral properties of these two complexes are listed in Table I.[20] Note that the ^{1}H NMR spectra at 35 °C show two sets of triplets for the Re–H resonances. This is in accord with a rigid seven-coordinate geometry at or near room temperature.

The CV's of these complexes are very characteristic of this class of trihydridorhenium compounds as a comparison with literature data[1] for $ReH_3(PPh_3)_3(NCMe)$, $ReH_3(PPh_3)_3$(CN-t-Bu), and $ReH_3(dppe)_2$ attests. The CV's of solutions of $ReH_3(PPh_3)_2(bpy)$ and $ReH_3(PPh_3)_2(phen)$ in 0.1 M TBAH–CH_2Cl_2 display a couple (corresponding to a one-electron oxidation of the bulk complex) at $E_{1/2}$ = −0.30 and −0.25 V vs. Ag/AgCl, respectively. These couples are characterized by a peak separation ($\Delta E_p = E_{p,a} - E_{p,c}$) of 100 mV at v = 200 mV/s and current ratios $i_{p,a}/i_{p,c}$ very close to unity when switching potentials of −0.1 and −1.0 V are used. Single-scan CV's show that following the oxidation step, several oxidation waves are encountered if the sweeps are carried out to +1.4 V. The most prominent of these processes are at $E_{p,a}$ = +0.1, +0.65, and +0.90 V (the latter has a coupled reduction wave at $E_{p,c} \simeq$ +0.80 V) in the case of the bpy complex, and at $E_{p,a}$ = +0.05, +0.65, and +0.90 V (with $E_{p,c}$ = +0.79 V) for $ReH_3(PPh_3)_2(phen)$.

Reactions that appear to be characteristic of neutral trihydridorhenium complexes are reversible protonation and hydride abstraction followed by coordination of a neutral donor ligand.[1] The complexes $ReH_3(PPh_3)_2$(L-L) (L-L = bpy or phen) undergo both these reactions. Protonation with $HBF_4\cdot Et_2O$ in acetonitrile gives dark pink $[ReH_4(PPh_3)_2(L\text{-}L)]BF_4$, whereas their treatment with $(C_7H_7)PF_6$ in acetonitrile affords the dihydrides $[ReH_2(PPh_3)_2(L\text{-}L)(NCMe)]PF_6$. The key spectroscopic properties of

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(9) Very similar behavior is observed for the pyridine analogue $ReH_5(PPh_3)_2(py)$. At −90 °C in CD_2Cl_2 four well-resolved resonances are apparent at δ −0.76 (t, J_{P-H} = 28 Hz), −2.49 (d, J_{P-H} = 25 Hz), −8.16 (t, J_{P-H} = 24 Hz), and −9.40 (s) in an intensity ratio 1:2:1:1.

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(20) Electronic absorption spectra of CH_2Cl_2 solutions of the complexes $ReH_3(PPh_3)_2$(L-L) and $[ReH_4(PPh_3)_2(L\text{-}L)]BF_4$ are as follows (λ_{max} in nm, ϵ values given in parentheses): for $ReH_3(PPh_3)_2(bpy)$, 630 (3000), $\sim$440 sh, 380 (9600), 300 (17 000); for $ReH_3(PPh_3)_2(phen)$: 600 sh, 570 (7900), 370 (12 000), 270 (22 000); for $[ReH_4(PPh_3)_2(bpy)]BF_4$, 540 (4600), 384 (4800), 310 (21 000); for $[ReH_4(PPh_3)_2(phen)]BF_4$, 522 (5800), $\sim$330 sh, 276 (23 000).

these complexes are summarized in Table I.[20] The bpy complexes $[ReH_4(PPh_3)_2(bpy)]BF_4$ and $[ReH_2(PPh_3)_2(bpy)(NCMe)]PF_6$ dissolve in acetonitrile to give solutions (ca. 1×10^{-3} M) that have conductivities (Λ_m = 142 and 156, respectively) that are characteristic of 1:1 electrolytes.

On the basis of a comparison of the electrochemical properties of these tetrahydrido- and dihydridorhenium complexes with data for related species that do not contain amine ligands (e.g. $[ReH_4(PPh_3)_3(NCMe)]PF_6$ and $[ReH_2(PPh_3)_3(NCMe)_2]PF_6$),[1] it appears that close electronic relationships exist. Thus the CV of $[ReH_4(PPh_3)_2(bpy)]BF_4$ in 0.1 M TBAH–CH_2Cl_2 shows an irreversible oxidation at $E_{p,a}$ = +0.89 V and an irreversible reduction at $E_{p,c}$ = −1.58 V, in addition to product waves at $E_{p,a}$ = +1.15 V (weak) and +1.38 and +1.48 V vs. Ag/AgCl. The phen complex has a very similar CV to this with $E_{p,a}$ = +0.97 V and $E_{p,c}$ = −1.55 V, as well as product waves at $E_{p,a}$ = +1.10 and +1.45 V vs. Ag/AgCl. For $[ReH_4(PPh_3)_3(NCMe)]PF_6$,[1] the first oxidation occurs at $E_{p,a}$ = +1.20 V and a product wave at $E_{p,a}$ = +1.4 V vs. Ag/AgCl, but there is no readily accessible reduction. This implies that $E_{p,c} \simeq -1.6$ V in the case of the bpy and phen complexes is most likely associated with a ligand (L-L) based reduction.

The CV's of solutions of the dihydridorhenium complexes in 0.1 M TBAH–CH_2Cl_2 are very similar. For $[ReH_2(PPh_3)_2(bpy)(NCMe)]PF_6$ there is a reversible oxidation at $E_{1/2}$ = +0.28 V and an irreversible reduction (probably bpy based) at $E_{p,c}$ = −1.80 V, as well as a prominent product wave at $E_{p,a}$ = +1.20 V vs. Ag/AgCl. The phen analogue has processes at $E_{1/2}(\text{ox})$ = +0.33 V, $E_{p,c}$ = −1.78 V, and $E_{p,a} \simeq +1.25$ V vs. Ag/AgCl. For the oxidation at $E_{1/2} \simeq +0.3$ V, ΔE_p = 110 mV and $i_{p,a}/i_{p,c}$ = 1.0 (±0.1). In the case of the analogous complex $[ReH_2(PPh_3)_3(NCMe)_2]PF_6$,[1] the comparable $E_{1/2}(\text{ox})$ value is +0.43 V. Again there is no accessible reduction down to −2.0 V in the absence of the bpy and phen ligands.

(c) Concluding Remarks. The present study has established that penta-, tetra-, tri- and dihydridorhenium species can be stabilized in the presence of mixed phosphine/heterocyclic tertiary amine ligand sets. These complexes are quite stable and show resemblances to related rhenium hydrides that are stabilized by phosphines only or by a mixture of phosphine and nitrile (or isocyanide) donors.[1,2,6]

Acknowledgment. We thank the National Science Foundation for support of this research (Grant No. CHE85-06702 to R.A.W.) and the National Institutes of Health (Grant No. RR-01077 from the Division of Research Resources) for funds for the purchase of the Varian XL-200 spectrometer.

Registry No. $ReH_5(PPh_3)_2(pyz)$, 109391-54-0; $[ReH_5(PPh_3)_2]_2(\mu\text{-}pyz)$, 109391-55-1; $ReH_3(PPh_3)_2(phen)$, 109391-56-2; $ReH_3(PPh_3)_2(bpy)$, 109391-57-3; $[ReH_4(PPh_3)_2(phen)]BF_4$, 109432-11-3; $[ReH_4(PPh_3)_2(bpy)]BF_4$, 109391-59-5; $[ReH_2(PPh_3)_2(phen)(NCMe)]PF_6$, 109391-61-9; $[ReH_2(PPh_3)_2(bpy)(NCMe)]PF_6$, 109432-27-1; $ReH_7(PPh_3)_2$, 12103-40-1.

Contribution from Spectrospin AG,
CH-8117 Fällanden, Switzerland, and Laboratorium für
Anorganische Chemie,
ETHZ, CH-8092 Zürich, Switzerland

Trichlorostannate Complexes of Platinum(II). Monitoring Exchange via 2-D ^{31}P NMR Spectroscopy

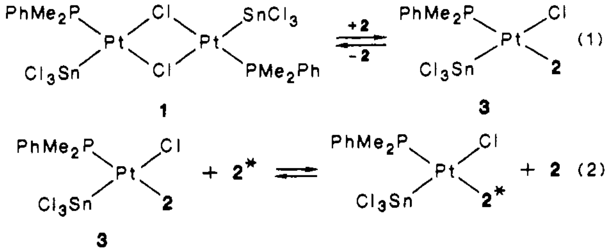
Heinz Rüegger† and Paul S. Pregosin*‡

Received January 14, 1987

The chemistry of trichlorostannate coordination compounds is complicated by a number of possible dynamic processes.[1] In the chemistry of platinum both the complexes and their exchange phenomena are of interest in that molecules such as $PtCl(SnCl_3)(PPh_3)_2$ and $Pt(SnCl_3)_5^{3-}$ are hydroformylation[2] and hydrogenation[3] catalyst precursors, respectively. Since catalysts for these reactions are often coordinatively unsaturated, it would be useful to characterize the tendency for the precursors to either dissociate or add ligands. Moreover, in view of the extensive use of NMR spectroscopy to characterize such processes,[4] one would like to know which ligand is dynamic and when and if "sharp" resonances indicate a static situation. We report here ^{31}P NMR spectroscopic results involving two-dimensional (2-D) exchange experiments[5] for some trichlorostannate complexes of Pt(II) and define which processes are relatively facile.

Results and Discussion

1. Dimer–Monomer and Nitrile Exchange Reactions. One important characteristic of platinum–trichlorostannate chemistry is the lability of the complexes. Anderson et al.[6] have shown that mono(phosphine), mono(trichlorostannate) complexes are useful hydroformylation catalysts, and as we have been interested in **1** and its analogues,[7] we have considered the reaction and dynamics of **1** with *p*-fluorobenzonitrile (**2**), a relatively modest nitrogen donor, in the hopes of creating a labile coordination sphere. Our analytical approach involves 1- and 2-D ^{31}P NMR spectroscopy.



The ^{31}P 2-D exchange spectrum[8] of a $CDCl_3$ solution containing **1** and ca. 2 equiv of **2** is shown in Figure 1. The conventional spectrum shows unreacted **1** and a new component whose structure we assign as **3**, on the basis of solution and solid-state results for similar reactions with anilines.[9] The strong cross peaks demonstrate that **1** and **3** are exchanging *despite* relatively sharp resonances and the presence of $^{117,119}Sn$ satellites indicative of coupling of the tin ligand atom to ^{31}P. If the phosphine were to dissociate and then recombine with a different platinum, there would be exchange between the ^{195}Pt ($I = {}^1/_2$, 33.7%) satellites and the main band; however, this is *not* observed in this reaction and in all of the subsequent experiments. Consequently, we have an exchange between monomer and dimer that involves nitrile addition and subsequent removal. The selection of the *p*-fluorobenzonitrile is not fortuitous and allows us to use 2-D ^{19}F exchange spectroscopy to confirm that uncoordinated **2** and **3** are also exchanging (see Figure 1) so that we may summarize the two simultaneous processes as shown in eq 1 and 2, where the **2*** notation implies only a different molecule of *p*-fluorobenzonitrile.

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† Spectrospin AG.
‡ ETHZ.

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(8) The diagonal containing the 1-D spectrum runs from lower left to upper right. Exchange is indicated by two cross peaks whose line makes a perpendicular to the diagonal. ^{195}Pt satellites exchange with each other due to fast ^{195}Pt relaxation.

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