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 $E_{1/2}(ox) = +0.33$ 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, $\Delta E_p = 110$ 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 $E_{1/2}(ox)$ 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*[‡]

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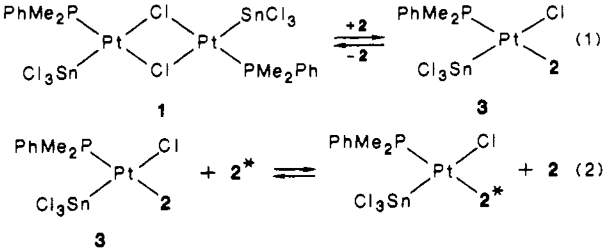
The chemistry of trichlorostannate coordination compounds is complicated by a number of possible dynamic processes.[1] In the chemistry of platinum both the complexes and their exchange phenomena are of interest in that molecules such as $PtCl(SnCl_3)(PPh_3)_2$ and $Pt(SnCl_3)_5^{3-}$ are hydroformylation[2] 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.

[†] Spectrospin AG.
[‡] ETHZ.

(1) Anderson, G.; Clark, H. C.; Davies, J. A. *Organometallics* **1982**, *1*, 64; Albinati, A.; Pregosin, P. S.; Rüegger, H. *Inorg. Chem.* **1984**, *23*, 3223.
(2) Schwager, K.; Knifton, J. F. *J. Catal.* **1976**, *45*, 256. Knifton, J. F. *J. Org. Chem.* **1976**, *41*, 793.
(3) Bailar, J. C. In *Inorganic Compounds with Unusual Properties*; King, R. B., Ed.; Advances in Chemistry 173; American Chemical Society: Washington, D.C., 1979; p 1.
(4) Sandström, J. *Dynamic NMR Spectroscopy*; Academic: London, 1982. *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic: New York, 1975.
(5) Bax, A. *Two-Dimensional Nuclear Magnetic Resonance in Liquids*; Delft University Press: Dordrecht, Holland, 1982.
(6) Anderson, G. K.; Clark, H. C.; Davies, J. A. *Inorg. Chem.* **1983**, *22*, 427, 434.
(7) Pregosin, P. S.; Rüegger, H. *Inorg. Chim. Acta* **1984**, *86*, 55. Arz, C.; Herbert, I. R.; Pregosin, P. S. *J. Organomet. Chem.* **1986**, *308*, 373.
(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.
(9) Albinati, A.; Moriyama, H.; Rüegger, H.; Pregosin, P. S. *Inorg. Chem.* **1985**, *24*, 4430.

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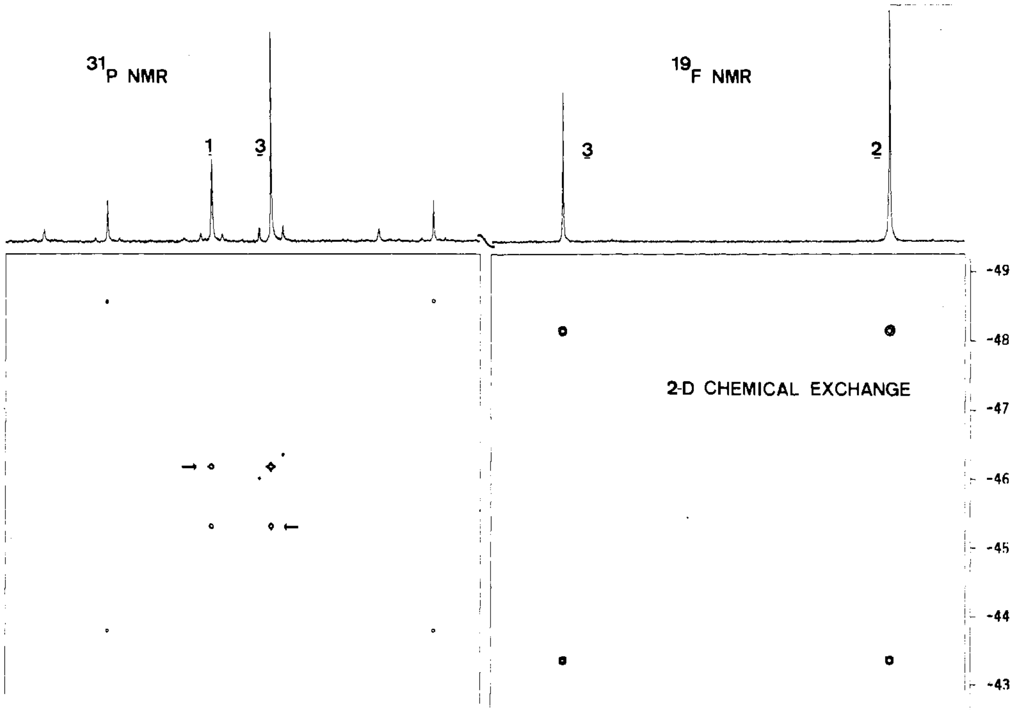
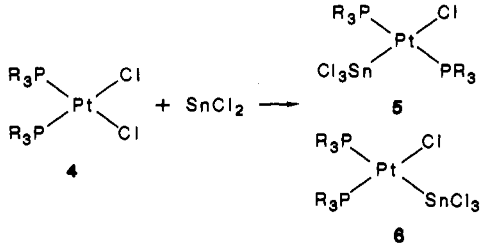


Figure 1. Two-dimensional exchange spectra for the reaction of **1** with **2**: (left) ^{31}P; (right) ^{19}F. The arrows (left) indicate the cross peaks. The high-field ^{19}F signal arises from uncoordinated nitrile. The chemical shift scale in the figure is defined relative to trifluorotoluene; the shifts relative to $CFCl_3$ are given in the Experimental Section.

Addition of excess **2** shifts the equilibrium between **1** and **3** so as to favor the mononuclear complex but does *not* depress the nitrile exchange (see Figure 2), so that **3** retains a measure of lability. The phosphorus side of this exchange chemistry is the same for benzonitrile in that the 2-D ^{31}P spectra reveal the same exchange processes; however, we can only assume that PhCN behaves as p-FC_6H_4CN in terms of nitrile exchange. Clearly multinuclear 2-D exchange NMR spectroscopy is illustrative and allows us to readily distinguish several simultaneous processes.

2. Equilibria Involving Tin(II) Chloride. In the previous example we demonstrated exchange processes not related to the tin ligand. We now consider some chemistry, shown in eq 3 and 4, where the $SnCl_2$ is active.



(3)

a, R = p-$CH_3C_6H_4$ = Tol; **b**, R = Et

$$\mathbf{5a} + SnCl_2 \rightleftharpoons \underset{\mathbf{7}}{trans\text{-}Pt(SnCl_3)_2(PTol_3)_2} \quad (4)$$

$\delta(^{31}P) = 6.1$
$^1J(^{195}Pt,^{31}P) = 2165$ Hz
$^2J(^{117,119}Sn,^{31}P) = 237$ Hz

Reaction of *cis*-$PtCl_2(PTol_3)_2$ (**4a**) with ca. 0.8 equiv of $SnCl_2$ at 20 °C affords a mixture of the trans and cis isomers of $PtCl(SnCl_3)(PTol_3)_2$,[10,11] (**5a** and **6a**, respectively) plus some unreacted **4a**. Analysis of the 2-D ^{31}P data (see Figure 3) based on the ideas described above yields the following: (a) The ^{31}P resonance of **4a** exchanges with both resonances of **6a**, but not at all with **5a**. (b) There is no exchange of ^{31}P spin between isotopomers of platinum. Taken together, these data exclude loss of $PTol_3$ as the source of the exchange between **4a** and **6a** and suggest that the exchange is best described as

$$\mathbf{4a} + SnCl_2 \rightleftharpoons \mathbf{6a} \quad (5)$$

and this is supported by a follow-up experiment in which additional $SnCl_2$ is added to give ca. 1.2 equiv of $SnCl_2$/platinum. This results in the disappearance of **4a** and the appearance of **7**, *trans*-$Pt(SnCl_3)_2(PTol_3)_2$, as a mixture with **5a** and **6a**. The ^{31}P 2-D exchange spectrum (Figure 4) of this solution shows that (c) **6a** is still undergoing an exchange that equilibrates the two nonequivalent phosphorus spins and (d) **5a** exchanges with **7**. It is worth noting that the signals in Figures 3 and 4 appear relatively sharp.

Since there is exchange of the ^{31}P environments of **6a** at roughly the same rate[12] in both experiments and since **4a** exchanges with

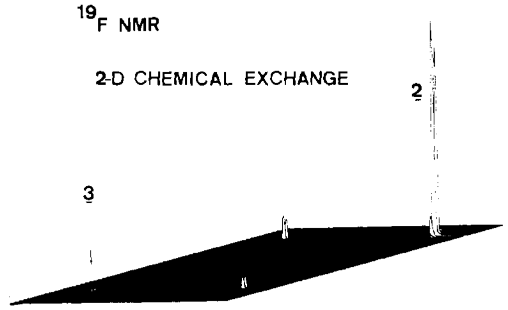


Figure 2. 2-D ^{19}F exchange spectrum for the reaction of **1** with excess p-fluorobenzonitrile. The arrow indicates the signal arising from the complex.

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[10] Complexes **5** and **6** have been prepared by previously described methods and studied by using ^{31}P, ^{119}Sn, and ^{195}Pt NMR spectroscopy.[11] For new complexes we give ^{31}P data in the text.

[11] (a) Pregosin, P. S.; Sze, S. N. *Helv. Chim. Acta* **1978**, *61*, 1848. (b) Ostoja Starzewski, K. H. A.; Pregosin, P. S.; Rüegger, H. *Helv. Chim. Acta* **1982**, *65*, 785. See also ref 9.

[12] The intensities of the cross preaks are *very* qualitative indications of the exchange rate.

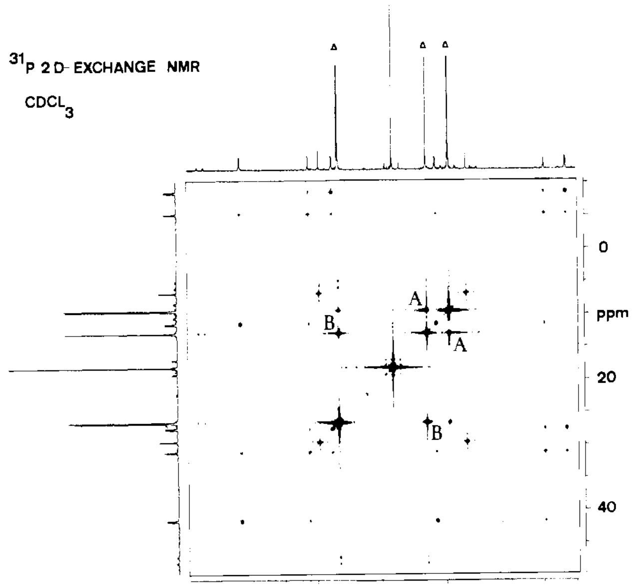


Figure 3. ^{31}P 2D exchange spectrum for the reaction of **4a** with ca. 0.8 equiv of $SnCl_2$. The letters A and B are positioned next to the cross peaks for exchange between **4a** and ^{31}P trans to Cl (A) and **4a** and ^{31}P cis to Cl (B). There are also cross peaks for the exchange between the two different resonances in **6a** (above and to the right of both B's). The Δ's indicate the exchanging species.

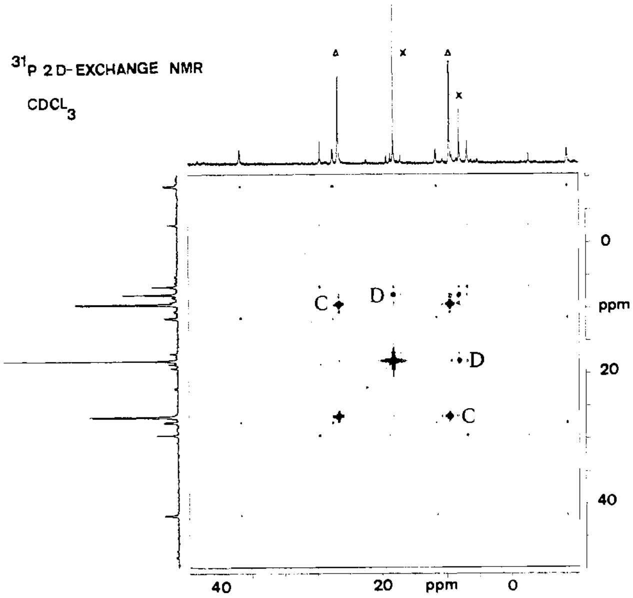
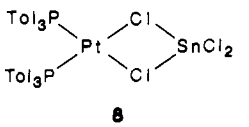


Figure 4. ^{31}P 2-D exchange spectrum for the reaction of **4a** with 1.2 equiv of $SnCl_2$. The letters C are positioned close to the cross peaks showing exchange between the two different resonances in **6a**, whereas the D's indicate the cross peaks for the exchange between **5a** and **7**. The Δ's indicate exchanging resonances in **6a**, whereas the ×'s indicate **5a** (low field) and **7** (high field).

6a, we can imagine that $SnCl_2$ is moving from one molecule of **4a** to another. Consequently, the isomerization cannot proceed solely via an intramolecular mechanism, e.g., via the five-coordinate $PtCl_2(SnCl_2)(PTol_3)_2$ or a symmetrical intermediate such as **8**. The exchange between **5a** and **7** is consistent with chemistry



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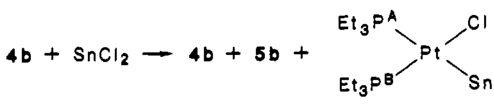
analogous to that in eq 5, i.e., $SnCl_2$ moving in and out of a Pt–Cl bond. We shall return to the cis–trans isomerization **4a**–**5a** shortly.

Table I. Temperature Dependence of the Cis–Trans Isomer Distribution for $PtCl_2(PEt_3)_2 + SnCl_2$ (CH_2Cl_2–$CDCl_3$, 1:1)

		% composition		
time, min	*T*, °C	**4**	**5**	**6**
5	−70	89	2	9
25	−70	83	3	14
45[a]	−50	79	5	16
65[b]	−20	72	22	6

[a] Temperature raised to −50 °C and maintained for 20 min. [b] Temperature raised to −20 °C and maintained for 20 min.

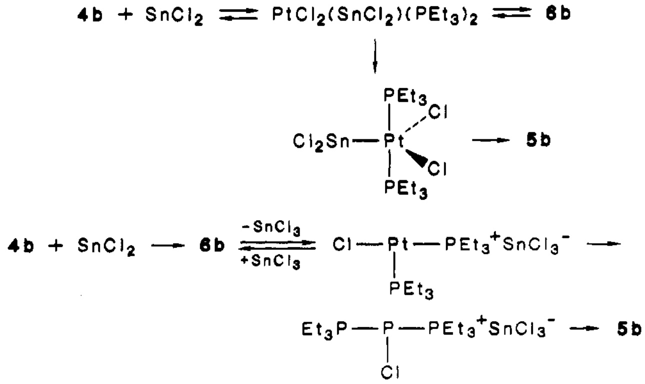
Changing the phosphine from $PTol_3$ to PEt_3, i.e., **4a** to **4b**, significantly affects the dynamics. At room temperature **4b** reacts rapidly and quantitatively in either $CHCl_3$ or CH_2Cl_2 to give the trans isomer **5b**.[11] Use of ca. 0.5 equiv of $SnCl_2$ affords 0.5 equiv of **5b** and *cis*- and *trans*-$PtCl_2(PEt_3)_2$ in about a 4:1 ratio. ^{31}P 2-D exchange data for this solution show *no* exchange between any of the three components at this temperature. If solutions of 1 equiv each of $SnCl_2$ and **4b** are mixed at −70 °C (CH_2Cl_2/$CDCl_3$, 1:1) and the course of the reaction monitored by $^{31}P\{^1H\}$ NMR, one observes the formation of *cis*-$PtCl(SnCl_3)(PEt_3)_2$ in modest quantities. Raising the temperature promotes the isomerization with details shown in Table I.



6b

$\delta(^{31}P^A) = 21.2$, $\delta(^{31}P^B) = 9.3$
$^1J(^{195}Pt,^{31}P) = 2952$ Hz (P^A), 3414 Hz (P^B)
$^2J(^{117,119}Sn,^{31}P) = 4020$ Hz (P^A), 250 Hz (P^B)

It would seem that **6b** is a kinetically formed complex that relatively rapidly isomerizes to **5b**. Although not directly pertinent, mixing solutions of analytically pure *trans*-$PtCl(SnCl_3)(PEt_3)_2$ (**5b**) and *trans*-$PtCl(SnCl_3)(AsEt_3)_2$ does not afford any of the mixed-ligand complex $PtCl(SnCl_3)(AsEt_3)(PEt_3)$,[11b] in keeping with the lack of exchange found for **5b**. We cannot ignore the fact that, for both phosphines, we begin with cis-dichloro isomers and end with some trans products. Given the different time scales for the reactions of the two phosphines (−20 °C for PEt_3, +20 °C for $PTol_3$), it seems unlikely that the smaller, better σ-donor PEt_3 dissociates at low temperature, whereas the larger, weaker σ-donor $PTol_3$ requires a higher temperature. For the PEt_3 case we can conceive of isomerization via the two possibilities



The first makes use of the known[13] tendency of strong σ-donors to occupy axial positions in a trigonal bipyramid, whereas the second involves a "T-shaped" three-coordinate species, for which there may be a barrier to isomerization.[14] We have no evidence in favor of either of these.

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(13) Shapley, J. R.; Osborn, J. A. *Acc. Chem. Res.* **1973**, *6*, 305. Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.

(14) Tatsumi, K.; Hoffman, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857.

For the PTol$_3$ case, we cannot completely exclude phosphine dissociation and note only that if this does occur, it is much slower than the exchange induced due to SnCl$_2$ moving in and out of a Pt–Cl bond and lies outside the range of our magnetization "mixing" time (see Experimental Section). In contrast to the case for the PEt$_3$ complexes, mixing solutions of analytically pure **6a** and *cis*-PtCl(SnCl$_3$)(AsTol$_3$)$_2$ *does* produce the mixed arsine–phosphine complex slowly at room temperature.[11b]

Part of our interest in the dynamics of these *cis*-PtCl$_n$(SnCl$_3$)$_{2-n}$(PR$_3$)$_2$ complexes stems from our previous study on their reactivity. With dihydrogen the tolyl complexes react in CDCl$_3$ at room temperature with 1 atm of H$_2$ within a period of minutes to give almost quantitative yields[15] of *trans*-PtHX(PTol$_3$)$_2$ (X = Cl, SnCl$_3$), whereas the Et analogue are *unreactive*[16] under the same conditions. Clearly, the relative kinetics and dynamics of these trichlorostannate complexes remain of interest and we consider that 2-D exchange spectroscopy will prove valuable in evaluating the latter.

Experimental Section

Complexes and Solutions. The complexes studied were synthesized as described previously,[9,11] and the solutions for NMR study were prepared as follows:

Mixtures of [Pt(SnCl$_3$)(μ-Cl)(PMe$_2$Ph)]$_2$, [Pt(SnCl$_3$)(Cl)(PMe$_2$Ph)(4-FC$_6$H$_4$CN)], and 4-FC$_6$H$_4$CN. (a) To a solution of [Pt(SnCl$_3$)(μ-Cl)(PMe$_2$Ph)]$_2$ (18.0 mg, 15.0 μmol) in CDCl$_3$ (0.5 mL) was added *p*-fluorobenzonitrile (4.0 mg, 33.0 μmol), resulting in the following concentrations of compounds: **1**, 7.5 mM; **2**, 45.0 mM; **3**, 22.5 mM. This gives an equilibrium constant for reaction 1 of $K = 66$ M^{-1}.

NMR data for [Pt(SnCl$_3$)(μ-Cl)(PMe$_2$Ph)]$_2$ (**1**): $\delta(^{31}\text{P}) = -8.7$, $^1J(\text{Pt,P}) = 3626$ Hz, $^2J(\text{Sn,P}) = 233$ Hz, $^1J(\text{Pt,Pt}) = 457$ Hz. NMR data for [Pt(SnCl$_3$)(Cl)(PMe$_2$Ph)(4-FC$_6$H$_4$CN)] (**3**): $\delta(^{31}\text{P}) = -14.9$, $^1J(\text{Pt,P}) = 3540$ Hz, $^2J(\text{Sn,P}) = 261$ Hz; $\delta(^{19}\text{F}) = -107.2$; $\delta(^{119}\text{Sn}) = -251$, $^1J(\text{Pt,Sn}) = 28\,750$ Hz. NMR data for 4-FC$_6$H$_4$CN (**2**): $\delta(^{19}\text{F}) = -112.0$.

(b) More *p*-fluorobenzonitrile (30.0 mg, 250 μmol) was added to the solution in (a), resulting in the disappearance of signals due to complex **1** in the ^{31}P NMR spectrum.

Solution Containing [Pt(SnCl$_3$)(Cl)(PMe$_2$Ph)(C$_6$H$_5$CN)]. To a solution of [Pt(SnCl$_3$)(μ-Cl)(PMe$_2$Ph)]$_2$ (24 mg, 20 μmol) in CDCl$_3$ (0.5 mL) was added benzonitrile (ca. 50 mg).

NMR data for [Pt(SnCl$_3$)(Cl)(PMe$_2$Ph)(C$_6$H$_5$CN)]: $\delta(^{31}\text{P}) = -15.0$, $^1J(\text{Pt,P}) = 3524$ Hz, $^2J(\text{Sn,P}) = 256$ Hz; $\delta(^{119}\text{Sn}) = -255$, $^1J(\text{Pt,Sn}) = 28\,883$ Hz.

Solutions Containing [Pt(Cl)$_n$(SnCl$_3$)$_{2-n}$(PR$_3$)$_2$]. These solutions were prepared in analogy to previously reported methods.[9,11]

NMR Measurements. The NMR spectra were obtained as CDCl$_3$ solutions with Bruker WM-250 and AC-250 instruments operating at 235 MHz for ^{19}F, 101 MHz for ^{31}P, and 93 MHz for ^{119}Sn, respectively. The chemical shifts are recorded relative to CFCl$_3$ (^{19}F), H$_3$PO$_4$ (^{31}P), and SnMe$_4$ (^{119}Sn), with positive shifts to lower field.

One-Dimensional NMR Spectra. ^{19}F NMR spectra were measured with a sweep width of 9400 Hz and acquisition of 64K complex data points in a time of 3.5 s, resulting in a digital resolution of 0.29 Hz/point.

^{31}P NMR spectra were recorded with a sweep width of 8000 Hz and acquisition 32K complex data points in a time of 2 s. The digital resolution in the final spectrum was 0.5 Hz/point.

^{119}Sn NMR spectra were measured with a spectral width of 50 000 Hz and acquisition of 8K complex data points with an acquisition time of 82 ms. Transformation was done by zero filling to 16K data points, and an exponential multiplication with a line-broadening factor of 30 Hz was applied. The digital resolution in the final spectrum was 6 Hz/point.

Two-Dimensional NMR Spectra. The two-dimensional chemical exchange correlated NMR spectra were carried out by using the NOESY sequence $90°x$–t_1–$90°x$–T–$90°x$–acquisition.[17] The time T, which allows for chemical exchange, was chosen to be 0.8 s for the [Pt(Cl)$_n$(SnCl$_3$)$_{2-n}$(PR$_3$)$_2$] chemistry. The mixing time T was 0.6 s in the case of the reaction of the dimer with *p*-fluorobenzonitrile and 0.5 s in the case of benzonitrile itself. The mixing times are important to note in that very slow exchange will not be detected.

For phosphorus exchange experiments the following parameters and procedures were commonly employed: 512 FID's of 2048 data points covering a sweep width of 4800 Hz were measured with an acquisition time of 0.2 s and 32 transients each. Transformation was carried out with no zero filling in F2 by using shifted sine-bell apodization. In F1 zero filling to 1028 data points was applied and the same apodization function as for F2 was used. The resulting matrix was displayed in the magnitude mode and symmetrized with respect to the diagonal. The final digital resolution was typically 4.6 Hz/point.

For the fluorine exchange experiments the parameters were as follows: 128 FID's of 512 data points covering a range of 1600 Hz were measured with an acquisition time of 0.16 s. sixteen transients were recorded to give a sufficient signal/noise ratio. Zero filling was applied in the F1 domain but not in F2, and the data were transformed by using pseudo echo apodization in both frequency domains. The resulting matrix was displayed in the magnitude mode and symmetrized with respect to the diagonal. The final digital resolution was 6.4 Hz/point.

Acknowledgment. P.S.P. thanks the Swiss National Science Foundation and the ETH Zürich for support, as well as the Johnson-Matthey Research Centre for the loan of K$_2$PtCl$_4$.

Registry No. **1**, 109124-64-3; **2**, 1194-02-1; **3**, 109124-65-4; **4a**, 31173-67-8; **4b**, 15692-07-6; **5a**, 83199-43-3; **5b**, 67619-49-2; **6a**, 67656-58-0; **6b**, 109124-66-5; **7**, 109124-67-6; [Pt(SnCl$_3$)(Cl)(PMe$_2$Ph)(C$_6$H$_5$CN)], 109124-68-7; benzonitrile, 100-47-0.

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[15] Pregosin, P. S.; Rüegger, H. *Inorg. Chim. Acta* **1981**, *54*, 159.

[16] Rüegger, H. Ph.D. Thesis, ETH Zürich, 1983.

[17] Benn, R.; Günther, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 350.

Contribution from the Department of Chemistry,
University of South Alabama, Mobile, Alabama 36688

Anion Affinity of Carbonylbis(triphenylphosphine)rhodium(I) in CH$_2$Cl$_2$: Fluoride vs. Its Halide Analogues

Daniel M. Branan, Norris W. Hoffman,* E. Andrew McElroy, Nathan C. Miller, David L. Ramage, Anne F. Schott, and Sidney H. Young

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Forster[1] earlier reported that halide preference in aprotic media for the d^8 complexes *trans*-M(PPh$_3$)$_2$(CO)X and *cis*-M(CO)$_2$X$_2^-$ (M = Rh, Ir) followed the order X = Cl > Br > I and suggested that "in rigorously aprotic solvents, fluoro derivatives may frequently be found to be the most stable halocarbonyl species". We report herein the first quantitative results to substantiate that speculation.

Experimental Section

trans-Rh(PPh$_3$)$_2$(CO)X (called RhX hereafter; X = Cl, Br, I) were prepared as in the literature.[2-4] The fluoro analogue (RhF) was synthesized according to Vaska's method.[5] All were dried at reduced pressure and checked for purity by using thin-layer chromatography (silica gel) and IR and visible spectroscopy. Dichloromethane (Fisher ACS reagent) was dried over freshly activated Mol Sieve 4A or via distillation under nitrogen from CaH$_2$ (indistinguishable results). The bis(triphenylphosphine)nitrogen(1+) salts, PPNX (X = Cl, Br, I),[6,7] were used as purchased from Strem after drying at reduced pressure. PPNF·CH$_2$Cl$_2$ was prepared as described by Ruff.[8] Solution preparations (in standard volumetric glassware) and manipulations were performed by using standard techniques in a Vacuum Atmospheres recirculating glovebox.

IR spectra were recorded in 5.0-mm CaF$_2$ cells on a Perkin-Elmer 1430 spectrophotometer equipped with a 3600 Data Station. The cells

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(1) Forster, D. *Inorg. Chem.* **1972**, *11*, 1686.

(2) Evans, D.; Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1968**, *11*, 99.

(3) Chatt, J.; Shaw, B. L. *J. Chem. Soc. A* **1966**, 1437.

(4) Vaska, L.; Peone, J., Jr. *J. Chem. Soc., Chem. Commun.* **1971**, 418.

(5) Vaska, L.; Peone, J., Jr. *Inorg. Synth.* **1974**, *15*, 65.

(6) The PPNX salts were selected as halide sources due to ready availability, nonhygroscopic nature, reasonable solubility, and low molar absorptivity: Martinsen, A.; Songstad, J. *Acta Chem. Scand., Ser. A* **1977**, *A31*, 645.

(7) Bekkevoll, S.; Svorstoel, I.; Hoeiland, H.; Songstad, J. *Acta Chem. Scand., Ser. B* **1983**, *B37*, 935. Songstad's group has reported that some PPN salts displace Cl in dichloromethane at moderately rapid rates; however, the halides were not included in that group. We did not observe complications attributable to such reactions.

(8) Douglas, W.; Ruff, J. K. *J. Organomet. Chem.* **1974**, *65*, 65. We have found that the substance so synthesized functions as an adequate source of F$^-$ in preparative reactions but contains sufficient methanol to preclude its use in equilibrium studies.

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