be due to the incursion of the spontaneous thermal reduction of hydronium by Cr(II). A dark reaction was noted in some Eu(II) solutions at 5–6 M $HClO_4$ in this study which would have given spuriously high quantum yields. For the data reported here, up to 3.7 M $HClO_4$, *no* dark reaction of Eu(II) was noted under the experimental conditions. Raphael and Malati[17] have determined an isotope effect on $CrCl_2$ photolysis in D_2O. By use of the data in ref 4 for the light system, the ratio Φ_{H_2}/Φ_{D_2} was found to be 1.4 at pH 1. They have proposed that the acid dependence is due to the reaction

$$D + Cr^{2+} + D_2O \rightarrow Cr^{3+} + DO^- + D_2 \qquad (24)$$

This reaction, we feel, is very unlikely to account for the acidity data.

A third form of acid dependence of Φ_{H_2} appears in the photolysis of $V(ClO_4)_2$.[18] V(II) photolyzes similarly to Cr(II) and is half-order in $[H^+]$ at lower acidities; however Φ_{H_2} reaches a maximum at 2 M $HClO_4$ and decreases slightly in more concentrated perchloric acid solutions.

A common feature of the photooxidation of Fe(II), Eu(II), Cr(II), and V(II) aquo ions is the half-order dependence from the pH range up to approximately 2 M solutions of strong acids. At this point bulk solution phenomena such as ion-pair formation as for Fe(II), spontaneous thermal reductions of solvent (standard reduction potential for both Cr(III) and Eu(III) is −0.4 V), or possible dehydration–polymerization reactions become important in determining Φ_{H_2}.

We are continuing the investigation of the effect of neutral scavengers such as 2-propanol on the efficiency of hydrogen formation, as well as the investigation of anionic metal complexes.

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Registry No. Eu^{2+}, 16910-54-6; H^+, 12408-02-5.

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Electronic Spectra of Some Transition Metal and Lanthanide Ions in Anhydrous Hydrogen Fluoride

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Electronic spectra have been recorded in solution in anhydrous hydrogen fluoride of the cations nickel(II), cobalt(II), praseodymium(III), and neodymium(III). The fluorides of these cations are not sufficiently soluble for spectra to be observed by conventional procedures. Solutions of sufficient concentration have been prepared by treatment of suspensions of the fluorides with boron trifluoride. The spectra so obtained show a general resemblance to the corresponding spectra in aqueous solution, although the detailed numerical values are almost exactly equal to those for coordinated fluoride anions. This suggests that under these conditions the metals are present in solution as simple solvated cations with coordination similar to that in water in each case.

Introduction

Techniques based on the use of cells with Kel-F bodies and sapphire windows have been available for investigation of solutions in anhydrous hydrogen fluoride (AHF) in the ultraviolet and visible spectral regions for over 20 years. However very little work has been done and, for the most part, organic systems have been studied. The present situation is little different from that given in a review[1] by Kilpatrick and Jones in 1967.

To date almost no spectroscopy has been possible for metal ions dissolved in AHF because of the lack of availability of suitably soluble species. The fluorides of the metals of group 1 and of thallium(I) have quite high solubilities.[2] As the charges on the cation increase, the solubilities of the ionic fluorides decrease markedly[2] so that even the fluorides of group 2 with the exception of SrF_2 and BaF_2 have limited solubilities. However as the oxidation state of the metal in a fluoride becomes high and the molecular nature of the fluoride becomes predominant, solubility again becomes relatively high as has been shown for the highest fluorides of metals such as vanadium,[3] molybdenum, tungsten, uranium,[4] and rhenium;[5] but spectroscopic studies on solutions such as these present little of interest in the visible and ultraviolet regions.

Another limitation on the ability to study spectra of transition metal ions and of lanthanide and actinide ions in anhydrous hydrogen fluoride is that relatively few anions other than fluoride can exist as such in hydrogen fluoride. If chlorides, bromides, or iodides of heavy metals are treated with AHF, the halide ions are protonated and expelled from the solution as the gaseous hydrogen halides,[6] leaving effectively a very dilute solution of the heavy-metal fluoride, most of the metal being precipitated as fluoride. The common inorganic oxo anions undergo complete or extensive and complex solvolysis[6] while anions such as carboxylates are completely protonated to form cationic species.[6]

The most common anions other than fluoride which have separate existence in AHF are those derived from Lewis acids such as BF_3, PF_5, AsF_5, and SbF_5. Therefore solutions in AHF of some fluorometalates should be amenable to study and in fact there has been a fairly recent recording of the spectrum of K_2NiF_6 in AHF.[7] Furthermore, in principle at least, spectra of solutions of the tetrafluoroborates, hexafluoroantimonates, or similar anions associated with heavy-metal cations could be studied.

For convenience, in the studies reported here on the spectra of Ni^{2+}, Co^{2+}, Pr^{3+}, and Nd^{3+}, solutions were prepared by suspending the appropriate anhydrous metal fluoride in AHF in a Kel-F tube, applying a pressure of 2–3 atm of BF_3, and stirring magnetically at room temperature. Clear solutions were obtained in about 5 min for Ni^{2+} and Co^{2+}, but the lanthanide fluorides required overnight digestion for dissolution. Because BF_3 is a weak Lewis acid in AHF, it was necessary to maintain the pressure of BF_3 above the solutions during the filling of the cell and the spectral measurements; otherwise precipitation of the metal fluorides occurred, in part at least. Obviously, stronger and more soluble Lewis acids such as AsF_5 and SbF_5 could be used but these are moderately strong oxidants. It was decided to restrict the work to the use of the nonoxidizing acid BF_3 in the initial phase. The effects of AsF_5 and SbF_5 on fluorides of metals in higher oxidation states than those reported here are currently under study.

In a qualitative study of Lewis acidity in AHF[8] Clifford and co-workers reported in 1957 that SbF_5 in AHF caused lanthanide trifluorides to dissolve to give solutions with colors similar to those of the appropriate aqueous solutions. They said that "rare earth fluorides were prepared by suspending the simple fluorides in ethereal boron trifluoride", but when they washed out excess BF_3 with ether, their solids were insoluble in HF. They also reported that BF_3 did not cause dissolution of lanthanide fluorides in HF. Presumably their pressure of BF_3, probably at less than 1 atm, was too low. Toward the completion of the present work Court and Dove reported that both BF_3 and AsF_5 caused dissolution of CoF_2 in AHF to give red solutions and they recorded the wavelengths of the band maxima.[9]

The spectroscopic results reported below, when compared with spectra of the same cations in aqueous solution, indicate that the cations are present in AHF as simple solvated ions with similar coordination to that in water. The BF_3 dissolution process, presumably, is one in which HF-solvated cations and tetrafluoroborate anions are formed as discrete ions at the expense of the binary fluoride which, being a fluorine-bridged polymer, is very insoluble, the solubility decreasing with increasing formal charge on the cation. Thus NiF_2 and CoF_2 were much easier to dissolve in BF_3–HF than PrF_3 and NdF_3. The reprecipitation of the binary fluorides as BF_3 is removed from the system reflects the weak Lewis acidity of BF_3 and shows that, except in the presence of a strong fluoride donor such as a group 1 fluoride, fluoride ion is formed at the expense of BF_4^-.

One feature of the spectra reported initially in this program is that, in most measurements, an impurity band which has not yet been identified occurred at about 280 nm. It could be due to plasticizer or low molecular weight fluorocarbons leached from the new Kel-F body of the cell. If this is the origin of the band, it is expected that the band will be diminished and eliminated as the cell and the Kel-F tubes used for solution preparation are subjected to frequent use and become "conditioned" to AHF.

Experimental Section

Spectral Cell. The design of the cell was based on that reported in the review by Hyman and Katz.[10] The cell body was machined from a Kel-F slab, with recesses drilled to accommodate the synthetic sapphire windows. Each of these was 25 mm in diameter, 3 mm thick, and completely transparent to 220 nm.

The vacuum seal between the windows and the Kel-F body was effected by a circular ridge machined into the recesses. Each window was pressed firmly against the ridge by metal backing plates and screws. As a precaution against straining the windows, a gasket of Teflon was inserted between each plate and window. The cell body was connected to a section of $^1/_4$-in. o.d. Kel-F tubing and a Kel-F needle valve[11] by standard flare compression joints.

Two cells of this type were made, each having a path length of 6.7 mm and a volume of approximately 2 cm^3. One cell contained AHF and was used as a reference while the other contained the solution under study. Both cells were mounted over trays containing aluminum oxide powder for the purpose of absorbing liquid HF in the event of a leak occurring.

All spectra were recorded on the Cary 17 spectrophotometer. The mounted cells were secured on placers in the instrument. Both compartments were sealed against entry of extraneous light by a specially made cover. During the recording of the spectra, the compartments were flushed by dry nitrogen to remove any HF vapor should a leak occur during use.

Generally, the spectra were run from 1000 to 200 nm using chart speeds of 0.1 or 0.5 nm/s. The slit control was continually adjusted to ensure that the maximum resolution of bands was obtained; usually about 0.05–0.5 nm was appropriate.

Reagents. HF. Commercial HF was obtained from a cylinder (Matheson, 99.8%). This was purified by four trap-to-trap distillations in Kel-F apparatus using calcium chloride–water–Dry Ice constant-temperature baths (–45 °C) as the coolant.[12] The final product had a conductance of less than $1 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ at 0 °C.

NiF_2. This was prepared by the reaction of excess ClF_3 on the calculated amount of analytical reagent $NiCl_2 \cdot 6H_2O$ in a Kel-F tube. After the reaction had been completed, the volatile materials were removed under vacuum leaving the anhydrous fluoride as a free-flowing yellow powder.

CoF_2. This compound was prepared by the standard literature method.[13]

NdF_3 and PrF_3. These compounds were obtained commercially (Koch-Light, 99.9%).

BF_3. This was obtained directly from the cylinder (Matheson, 99%) and was used without purification.

Preparation of Solutions. Solutions were prepared by distilling a known amount of AHF from a storage tube onto the required amount of the anhydrous fluoride, which was contained in a Kel-F tube. The fluorides, except for NiF_2, were washed once with AHF in order to remove any loosely bound moisture which had been absorbed by the hygroscopic compounds. Boron trifluoride at a pressure between 2 and 3 atm was then applied to the suspension of the metal fluoride in AHF. The Kel-F tube containing the mixture was occasionally shaken to hasten the dissolution of the fluoride.

After the metal fluoride had dissolved, the solution was then poured into the spectral cell with care being taken to retain BF_3 pressure above the solution at all times. Some decomposition of the solution to the metal fluoride was observed if this condition was not maintained.

After being filled, the cell was removed from the vacuum line and the spectrum was recorded. At length, the cell was emptied by pouring most of the contents into a dump tube such that the windows remained wet with solution. This was done to prevent the precipitation of the fluoride onto the window surfaces. The remaining solution was removed by washing the cell compartment with a solution of BF_3 in AHF a number of times. Under these conditions no fluoride precipitate on the windows was detected.

Results and Discussion

We have measured the spectra of the four cations in AHF over the visible–ultraviolet region. For convenience the results for the transition metals and the lanthanides are discussed separately.

1. Transition Metals Co^{2+} and Ni^{2+}. The spectra of Co^{2+} and Ni^{2+} ions in AHF solution are shown in Figures 1 and 2. The positions of the peaks and their extinction coefficients are given in Tables I and II, together with the corresponding values for aqueous solutions. In AHF the bands are shifted to lower energies and the intensities are about half those in

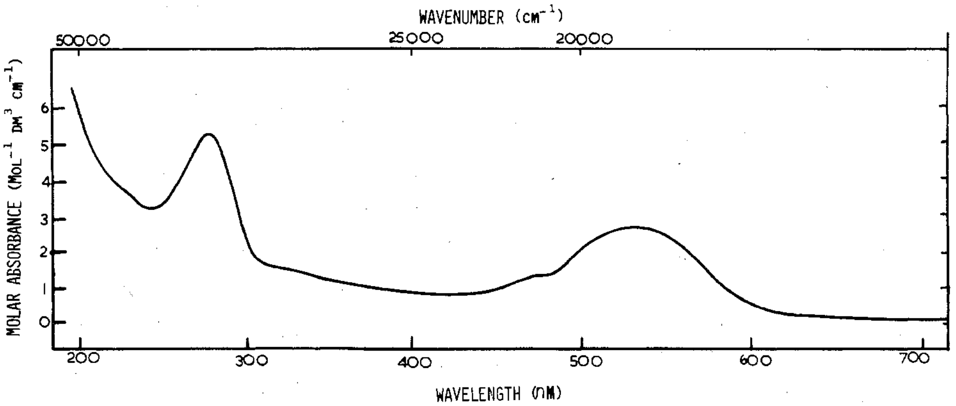

Figure 1. Electronic spectrum of Co^{2+} in AHF solution, 5×10^{-2} M.

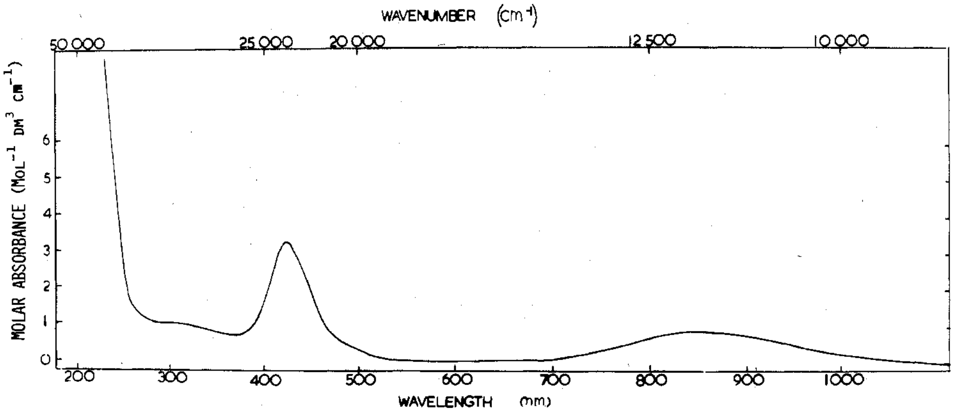

Figure 2. Electronic spectrum of Ni^{2+} in AHF solution, 5×10^{-2} M.

Table I. Spectral Data for Co^{2+} Solutions

Aqueous soln[a]		Soln in AHF			
ϵ	λ, nm	ϵ	λ, nm	E, cm^{-1}	Assignment
2.8	458 sh	1.3	471 sh	21 230	
4.5	510	2.8	532	18 800	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$

[a] Measured in this work.

Table II. Spectral Data for Ni^{2+} Solutions

Aqueous soln[a]		Soln in AHF			
ϵ	λ, nm	ϵ	λ, nm	E, cm^{-1}	Assignment
5.9	393	3.2	424	23 580	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$
1.6	654	0.8	850	11 760	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$
1.9	722				
1.9	1173				$^3A_{2g} \rightarrow {}^3T_{2g}$

[a] Measured in this work.

water. The obvious interpretation is that the metal ions are octahedrally coordinated by six HF molecules and that we are observing d–d electronic transition. The assignments shown in Tables I and II are based on analogy with the aqueous solution assignments. The shoulder on the Co^{2+} band is assumed to be due to splitting by spin–orbit coupling as in the aquo ion. The band centered at 850 nm in the Ni^{2+} spectrum in AHF is assumed to correspond to the double peak around 700 nm in the aqueous Ni^{2+} spectrum. This 850 nm band is quite broad and presumably the two peaks have not been resolved as well as in the aqueous solution.

There is a strong band probably due to charge transfer in the Ni^{2+} spectrum below 230 nm. The peak at 280 nm in the Co^{2+} spectrum is an artifact of some kind as mentioned in the Introduction. Unfortunately AHF absorbs light strongly beyond 1300 nm so we cannot observe the lower energy transitions that are predicted by crystal field theory. The two absorption bands for Ni^{2+} in AHF are in very similar positions to those for Ni^{2+} in solid $KNiF_3$.[14] A closely related spectrum has also been obtained for Ni^{2+} in a fluoride melt.[15] It appears that HF is very similar to F^- in its crystal field effects. The crystal field interpretation of Co^{2+} and Ni^{2+} spectra has been fully discussed by Ballhausen[16] and there is little need for comment on the assignments in Tables I and II.

Table III. Spectral Data for Pr^{3+} Solutions (Ground State of Pr^{3+} $^3H_4$)

Aqueous soln[a]		Soln in AHF			Pr^{3+} in LaF_3[b]	Assignment of upper state
ϵ	λ, nm	ϵ	λ, nm	E, cm^{-1}	E, cm^{-1}	
9.7	445	4.8	440	22 730	22 754	$^3P_2$
4.3	469	1.7	465	21 510	21 519	$^3P_1$, $^1I_6$
4.0	482	1.9	477	20 970	20 925	$^3P_0$
1.7	589	0.6	586	17 070	16 846	$^1D_2$

[a] Measured in this work. [b] Reference 20.

2. Lanthanide Ions Pr^{3+} and Nd^{3+}. The spectra of these ions in AHF and in water are shown in Figures 3 and 4. The positions of the peaks and their extinction coefficients are given in Tables III and IV. The resemblance between the spectra in the two solvents is even more marked here because the bands are much sharper and there are more of them to form characteristic patterns. Again the intensities are lower in AHF but the frequency shifts are quite small and to higher energies. Although the absolute intensities in AHF are lower, the relative intensities in AHF and water are remarkably similar. It is well-known that certain bands in lanthanide ion spectra are

Table IV. Spectral Data for Nd^{3+} Solutions (Ground State of Nd^{3+} $^4I_{9/2}$)

Aqueous soln[a]		Soln in AHF				
ϵ	λ, nm	ϵ	λ, nm	E, cm^{-1}	Nd^{3+} in LaF_3[b] E, cm^{-1}	Assignment of upper state
3.0	345	1.7	344	29 070		$^4D_{3/2}$, $^2I_{11/2}$; $^4D_{5/2}$, $^4D_{1/2}$; $^2L_{15/2}$
3.5	354	2.6	351	28 490		
1.5	512	0.94	507	19 720	19 607	$^2K_{13/2}$, $^4G_{7/2}$; $^4G_{9/2}$
9.5	522	2.4	519	19 270	19 230	
6.1	575	4.0	572	17 480	17 391	$^2G_{7/2}$, $^4G_{5/2}$
6.3	740	3.8	735	13 610	13 586	$^4F_{7/2}$, $^4S_{3/2}$
11.2	794	5.7	791	12 640	12 610	$^4F_{5/2}$, $^2H_{9/2}$
3.3	865	1.8	861	11 610	11 600	$^4F_{3/2}$

[a] Measured in this work. [b] Reference 19.

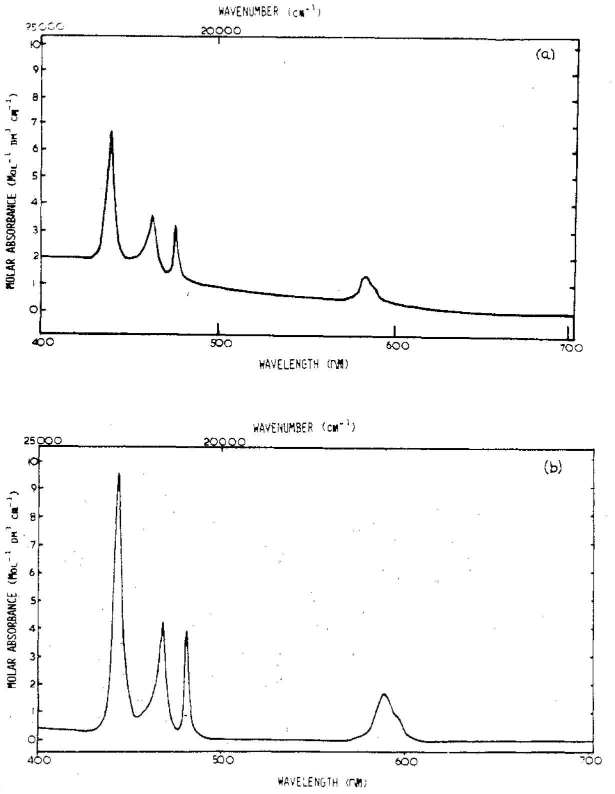

Figure 3. Electronic spectra: (a) Pr^{3+} in AHF solution, 5 × 10^{-2} M; (b) Pr^{3+} in aqueous solution, 5 × 10^{-2} M.

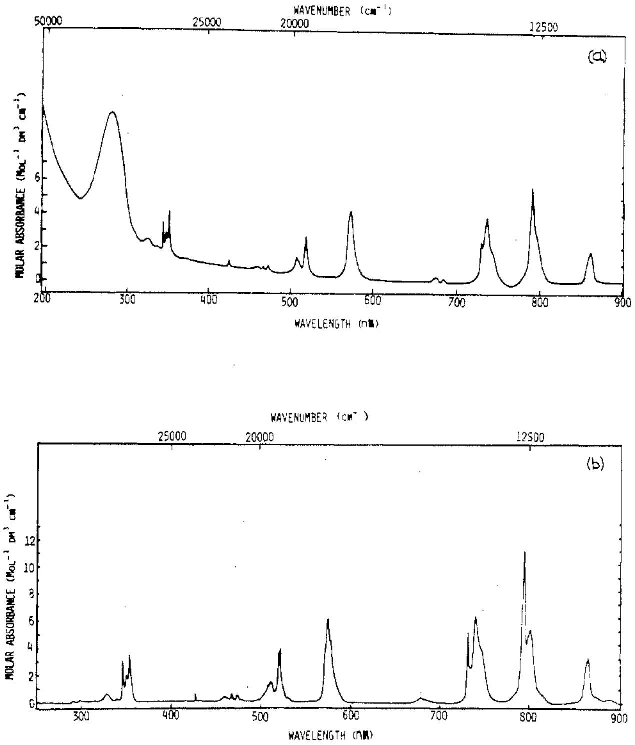

Figure 4. Electronic spectra: (a) Nd^{3+} in AHF solution, 5 × 10^{-2} M; (b) Nd^{3+} in aqueous solution, 5 × 10^{-2} M.

extremely sensitive to changes in the environment around the cation; e.g., see spectra shown by Karraker[17] and Peacock.[18] Even these bands show little change in relative intensity in the two solvents, with one exception. The shoulder which occurred at 800 nm in water for Nd^{3+} appears weaker in AHF. This may be a real alteration in intensity or the two transitions involved may have shifted closer together in energy.

The probable electronic transitions involved are also listed in Tables III and IV, based on the analogous transitions for aqueous solutions given by Carnall et al.[19] From the spectra of Co^{2+} and Ni^{2+} it has already been seen that HF produces effects very similar to those of F^-. This similarity occurs again with the lanthanides. The data for Pr^{3+} and Nd^{3+} doped into LaF_3 crystals show that the transition energies move up slightly in a fluoride environment as compared with the behavior in aqueous solution. These results are also shown in Tables III and IV, and there is close agreement with the AHF data except for one band at 586 nm in the Pr^{3+} spectrum. This discrepancy is probably not significant since the band is relatively broad and there could be an error of several nanometers in estimating the center of the band. There have been extensive studies of the intensities of lanthanide ion spectra and it has been found that intensities in a fluoride environment are about one-fourth to one-half of those for the aquo ions. Our present results for the spectra in HF are in line with this intensity ratio though we have only measured peak heights rather than oscillator strengths. So again the HF molecule is producing a very similar effect to the fluoride anion.

It is reasonable to assume that the lanthanide ions have the same coordination in AHF as in water but this is by no means certain. The two molecules HF and H_2O have rather similar sizes and dipole moments. However the energy levels in lanthanide ions are not very sensitive to changes in symmetry of their environment. Crystal field splittings might only be of the order of 100 cm^{-1} and would not be significant in the relatively broad solution spectra. The intensity patterns are probably a more sensitive indicator of changes in symmetry. The close similarity between the relative intensities in water and AHF does support the idea of the coordination being the same in the two solvents.

We are currently checking that the present technique can be applied over a wide range of transition metals and lanthanide ions. Hopefully a more detailed analysis of the various spectral parameters will then be possible and meaningful. Although we have only reported absorption spectra, it is apparent that these solutions in AHF should be amenable to study by a range of spectroscopic techniques, e.g., ESR, NMR, Raman, etc. Also there would appear to be an excellent opportunity for electrochemical investigations on these solutions.

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Registry No. Co^{2+}, 22541-53-3; Ni^{2+}, 14701-22-5; Pr^{3+}, 22541-14-6; Nd^{3+}, 14913-52-1.

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Reactions of Alkynyl- and Alkenylplatinum(II) Compounds. 1. Formation of Alkoxycarbene Ligands within the Coordination Sphere of Platinum

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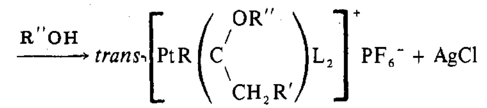
Alkynylplatinum compounds *trans*-$Pt(C{\equiv}CR)_2L_2$ and *trans*-$PtCl(C{\equiv}CR)L_2$, where R = H, Me, or Ph and L = PMe_2Ph or $AsMe_3$, have been prepared and reacted with acids HX in alcohols R′OH. When X = PF_6^- stable cationic alkoxycarbene complexes, *trans*-$[Pt(C{\equiv}CR)(C(CH_2R)OR')L_2]^+PF_6^-$ or *trans*-$[PtCl(C(CH_2R)OR')L_2]^+PF_6^-$, have been isolated for R′ = Me, Et, Pr^n, and Pr^i. When X = Cl^- or CF_3COO^-, the alkoxycarbene complex formed initially reacts to generate R′–X and the neutral acylplatinum compound. When X = CH_3COO^-, no apparent reaction occurs, although each of the weak acids nitromethane, ammonium chloride, and acetic acid react with *trans*-$Pt(C{\equiv}CH)_2L_2$ in MeOD to give *trans*-$Pt(C{\equiv}CD)_2L_2$. *trans*-$Pt(C{\equiv}CCF_3)_2(PMe_2Ph)_2$ does not react with HPF_6 in methanol; with HCl only *trans*-$Pt(CCl{=}CHCF_3)_2(PMe_2Ph)_2$ is formed. The α-chlorovinyl compounds *trans*-$PtCl(CCl{=}CHR)L_2$, where R = H and Me, react with alcohols R′OH to give *trans*-$PtCl(C(CH_2R)OR')L_2{}^+Cl^-$. The α-carbene carbon protons are acidic. For *trans*-$[PtY(C(CH_3)OMe)L_2]^+PF_6^-$ the acidity is dependent on the trans ligand Y, Y = Cl ∼ CF_3 > C≡CH > *p*-tolyl > CH_3. The α-carbene carbon protons readily exchange in MeOD, except when Y = CH_3. Addition of proton sponge to a methylene chloride solution of *trans*-$[PtY(C(CH_3)OMe)L_2]^+PF_6^-$ gives the σ-vinyl ether compounds *trans*-$PtY(C({=}CH_2)OMe)L_2$ and the ammonium hexafluorophosphate salt when Y = Cl or CF_3. When Y = *p*-tolyl, an equilibrium mixture is formed in methylene chloride: $[PtC(CH_3)OMe]^+ + \text{amine} \rightleftarrows [PtC({=}CH_2)OMe] + [(\text{amine})H]^+$. A general scheme which accounts for the formation of alkoxycarbene ligands within the coordination sphere of platinum is proposed. The reactions of platinum-stabilized vinyl carbonium ions, $PtC^+{=}CHR$, formed from (i) cationic π-acetylenic complexes, (ii) protonation of platinum acetylides, and (iii) solvolyses of α-chlorovinylplatinum(II) compounds, are discussed in the light of a number of H/D-labeled experiments.

Introduction

Cationic organoplatinum alkoxycarbene complexes have been prepared[1,2] from

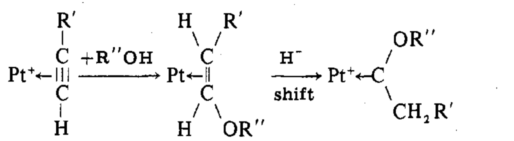
trans-$PtR(Cl)L_2 + R'C{\equiv}CH + AgPF_6$



$$\xrightarrow{R''OH} trans\text{-}\left[PtR\left(C\begin{matrix}OR''\\ CH_2R'\end{matrix}\right)L_2\right]^+ PF_6^- + AgCl \qquad (1)$$

where R = Me, Ph, $C{\equiv}CCF_3$, or CF_3; R′ = H, alkyl, or Ph; R″ = Me or Et; and L = PMe_2Ph or $AsMe_3$.

Formation of the alkoxycarbene ligand in (1) was initially considered to occur by a reaction sequence (2). Conversion



$$Pt^+ \leftarrow \begin{matrix}R'\\ C\\ |||\\ C\\ H\end{matrix} \xrightarrow{+R''OH} Pt^+ \leftarrow \begin{matrix}H\ \ R'\\ C\\ \|\\ C\\ H\ \ OR''\end{matrix} \xrightarrow[\text{shift}]{H^-} Pt^+ \leftarrow C\begin{matrix}OR''\\ CH_2R'\end{matrix} \qquad (2)$$

of a coordinated olefin to a coordinated carbene by a hydride shift, a Wagner–Meerwein rearrangement, could be the initial step in transition metal catalyzed olefin metathesis reactions.[3] However, for reactions 1 the sequence (2) was rejected[4] when stable π-vinyl ether complexes such as *trans*-$[PtMe(CH_2{=}CHOMe)(PMe_2Ph)_2]^+PF_6^-$ were isolated. This, together with other observations, led Chisholm and Clark[4,5] to propose a carbonium ion model for a number of reactions of unsaturated hydrocarbons π-bonded to organoplatinum cations. The proposed intermediate in the formation of the alkoxycarbene ligand in (1) was a platinum-stabilized vinyl carbonium ion, $PtC^+{=}CHR$.

If organoplatinum cations can induce carbonium ion reactivity in a π-bonded unsaturated hydrocarbon ligand and also stabilize the carbonium ion so formed, we anticipated that this carbonium ion character would be reflected in the reactions of unsaturated hydrocarbon ligands σ-bonded to platinum. In this paper we describe the preparation of cationic alkoxycarbeneplatinum(II) complexes from reactions of alkynyl- and alkenylplatinum(II) compounds. This work provides a new and quite general route to alkoxycarbene ligands and provides further support for the Chisholm and