

negative.¹¹ The calculations lead to a $^2J(\text{PP})$ of 346 Hz which is intermediate between the values for $\text{RN}(\text{PF}_2)_2$ (370–440 Hz) and $\text{HN}(\text{PF}_2)_2$ (154 Hz). The best agreement between calculated and experimental spectra is obtained when the two long-range coupling constants, $^4J(\text{FF})$, are assumed to have the same sign. The signs of the coupling constants $^2J(\text{PP})$ and $^4J(\text{FF})$ in $\text{MeN}(\text{PF}_2)_2$ have been shown by Rudolph and Newmark¹¹ to be positive.

The ^{19}F NMR spectrum of $\text{N}(\text{PF}_2)_3$ is complicated in appearance; it seems to correspond to an $[\text{A}(\text{X})_2]_3$ spin system. The coupling constant $^2J(\text{PP})$ is of the order of 90 Hz. This is in good agreement with estimates by Arnold and Rankin.⁴ The ^{31}P NMR spectrum was found to exhibit very broad lines, due to the quadrupole moment of nitrogen. No attempt was made to determine the δ_{P} value.

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Registry No. $\text{Me}_3\text{SiN}(\text{PF}_2)_2$, 68738-48-7; $\text{N}(\text{PF}_2)_3$, 56564-56-8; $\text{Me}_3\text{SiN}(\text{SnMe}_3)_2$, 54123-88-5; $(\text{Me}_3\text{Si})_2\text{NPF}_2$, 50732-22-4; PF_2Cl , 14335-40-1; PF_2Br , 15597-40-7; $\text{N}(\text{SnMe}_3)_3$, 1068-70-8.

References and Notes

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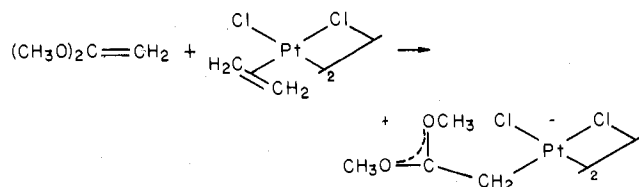
Interaction of Zeise's Dimer, *trans*- μ -Dichloro-bis(ethyleneplatinum chloride), with Polar Olefins

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Olefins can potentially coordinate to platinum halides in a η^1 or η^2 fashion, although the π complex is the most frequently observed mode of bonding for olefins and acetylenes.²

A particular example of a η^1 complex is the product isolated after treating Zeise's dimer with 1,1-dimethoxyethylene.³

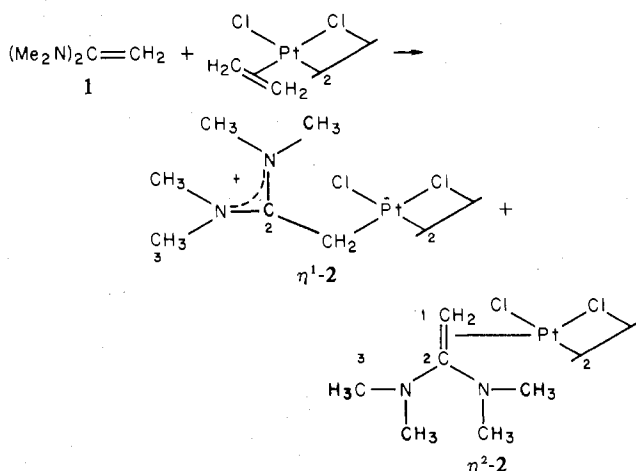


The complex can only be studied in the solid state since the ^1H NMR data show no evidence for ^{195}Pt -H coupling.

In this paper we report our results with 1,1-bis(dimethylamino)ethylene and 1,3-dimethyl-2-methyleneimidazoline with Zeise's dimer.

Results

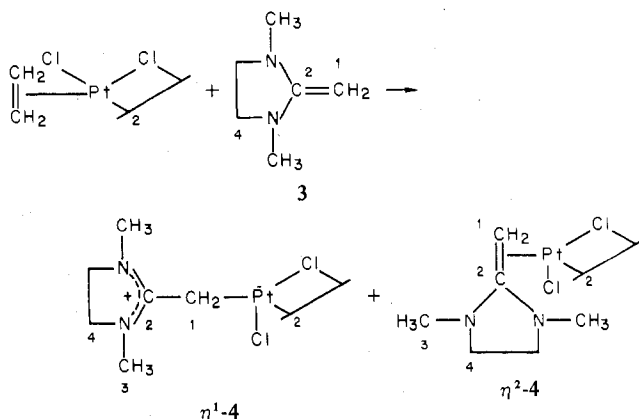
1,1-Bis(dimethylamino)ethylene and Zeise's Dimer. When a yellow-orange benzene solution of Zeise's dimer $[\text{Pt}(\text{C}_2\text{H}_4\text{Cl}_2)_2]$ is treated with 1,1-bis(dimethylamino)ethylene, $[(\text{CH}_3)_2\text{N}]_2\text{C}=\text{CH}_2$, at 5 °C, the solution becomes deep yellow and ethylene is evolved. A bright yellow solid is obtained after filtering of the solution and sublimation of the excess benzene. A ^1H NMR spectrum of this solid in benzene shows it to be a mixture of two species, η^1 -**2** and η^2 -**2**.



Structure η^1 -**2** represents a η^1 complex where the σ bond to the platinum atom describes the mode of coordination and η^2 -**2** represents a η^2 coordination of the olefin.

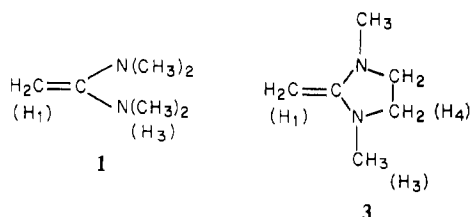
The molecular weight of the complex in benzene shows it to be dimeric, most likely with chlorine atom bridge bonds. A similar dimeric structure is observed by Paiaro et al.³ for the olefin 1,1-dimethoxyethylene and its complex with Zeise's dimer.

Similar results are obtained with the olefin 1,3-dimethyl-2-methyleneimidazoline and Zeise's dimer.



Discussion

Zeise's Dimer with 1,1-Bis(dimethylamino)ethylene. Ylides $\text{R}_3\text{P}^+-\text{CH}_2$ are highly reactive 1,2-dipolar molecules which

Table I. ^1H NMR Data for the Olefins and Their Platinum(II) Complexes

	$\delta_{\text{H}_1}^a$	δ_{H_3}	δ_{H_4}	$J_{\text{Pt-H}_1}^b$	$J_{\text{Pt-H}_3}$	$J_{\text{Pt-H}_4}$
1	3.15	2.47				
η^1 -2	3.05	2.69		104	4	
η^2 -2	4.85	2.32		47	6.7	
3	2.97	2.49	2.57			
η^1 -4	2.60	2.51	2.57	102		
η^2 -4	4.90	2.76	2.87	46		

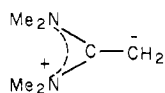
^a Chemical shifts in ppm relative to internal Me_4Si . ^b ^{195}Pt - ^1H coupling constants in Hz.

Table II. ^{13}C NMR Data for $(\text{Me}_2\text{N})_2\text{C}=\text{CH}_2$ and Its Platinum(II) Complex

	$\delta_{\text{C}_1}^a$	δ_{C_2}	δ_{C_3}	$J_{\text{Pt-C}_1}^b$	$J_{\text{Pt-C}_2}$	$J_{\text{Pt-C}_3}$
1	69.2	163.0	40.9			
η^1 -2	24.9	171.9	44.8	584	200	
η^2 -2	82.7	187.6	41	93	91	41.3

^a Chemical shifts in ppm relative to internal Me_4Si . ^b ^{195}Pt - ^1H coupling constants in Hz.

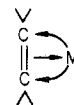
differ from other ligands in that they coordinate to metals with σ bonds between the metal atom and the carbon atom of the ylide. In the case of phosphorus ylides, the onium center remains positively charged and usually does not form a covalent bond to the metal. On the other hand, carbon onium centers are much less common and are only potentially stable when electron-releasing groups are bound to the carbon atom, as in



These polar olefinic molecules can exhibit σ - and π -complex formation to transition-metal atoms. Hydrogen atoms ($=\text{CH}_2$) in an olefinic system which are π complexed to a metal atom are normally shifted to a higher field from their positions in the free olefin.⁴ As shown in Table I, the olefinic protons in η^2 -2 occur at a lower field than the same protons in the free olefin, although the coupling constant $^2J(^{195}\text{Pt}-^1\text{H}) = 47$ Hz is typical for η^2 coordinated olefins that show ($=\text{CH}_2$) shifts to higher fields. On the other hand, the η^1 complex η^1 -2 shows the (CH_2) proton resonance at a higher field than the free olefin, which is normally the case. The coupling constant, $^2J(^{195}\text{Pt}-^1\text{H}) = 104$ Hz, is representative of hydrogen atoms of alkyl groups σ bonded to platinum.⁵

The ^{13}C NMR spectrum supports the postulate of two complexes.⁶ For instance, $J(^{195}\text{Pt}-^{13}\text{C}_1) = 584$ Hz $>$ $J(^{195}\text{Pt}-^{13}\text{C}_2) = 200$ Hz for the η^1 complex and $\Delta\sigma$ (shift relative to free olefin) C_1 ($=44.3$ upfield) $>$ $\Delta\sigma$ C_2 ($=9$ downfield). Complexes with σ bonds to the metal atom normally show large coupling constants for the carbon atom (C_1) α to the metal atom compared to carbon atoms (C_2) β to the metal. The η^2 complex shows $\Delta\sigma$ C_1 ($=13.5$ downfield) $<$ $\Delta\sigma$ C_2 ($=24.6$ downfield) and $J(^{195}\text{Pt}-^{13}\text{C}_1) = 93$ Hz $\geq J(^{195}\text{Pt}-^{13}\text{C}_2) = 91$ Hz. Both chemical shifts of C_1 and C_2 for the η^2 complex are downfield compared to those of the free olefin whereas the η^1 complex shows an upfield shift for C_1 and a downfield shift for C_2 . The N -methyl carbon atoms are relatively unchanged in their chemical shift.

Normally the upfield ^1H chemical shifts for complexed olefins imply that shielding increases with metal d to olefin π bonding, and deshielding results from olefin to metal bonding which decreases electron density on the olefin.⁴⁻⁷ Although such explanations for ^1H chemical shifts are to some extent oversimplifications, the absence of any upfield shift in the ^1H NMR resonance for the η^2 form suggests a considerable donation of electron density to the platinum atom by the olefinic ligand. This results in an excessive amount of deshielding which in turn overrides metal to ligand interactions:



In most cases there is an upfield ^{13}C NMR shift for the unsaturated carbon atoms of an olefin upon complexation to a metal. This is thought to occur because of increased metal d to olefin bonding, which increases the electron density on the olefinic carbon atoms and decreases the π carbon-carbon bond order. In another way, the decreased π -electron density results in an increase of sp^3 character of the platinum-carbon bond with a corresponding increase in the chemical shift of the metal bonded carbon atoms.^{6,8}

Yet the downfield shifts of C_1 and C_2 in the η^2 form suggest very little π back-donation, only a large decrease in electron density at the olefinic carbon atoms.⁸

The electron donation to the metal by the olefin normally is reflected in $^1J(^{195}\text{Pt}-^{13}\text{C})$ which is mainly determined by the Fermi contact term and is a measure of the σ bond between the platinum atom and the olefin. In olefin complexes this is strongly dependent on the metal s character of the bond. Thus the value of $^1J(^{195}\text{Pt}-^{13}\text{C})$ for $\text{K}[\text{PtCl}_3\cdot\text{C}_2\text{H}_4]$ is 195 Hz. This is much higher than the value of $^1J(^{195}\text{Pt}-^{13}\text{C})$ for η^2 - $(\text{Me}_2\text{N})_2\text{C}=\text{CH}_2\cdot\text{PtCl}_2$; $^1J(^{195}\text{Pt}-^{13}\text{C}) = 93$ Hz and $^1J(^{195}\text{Pt}-^{13}\text{C}) = 91$ Hz. This may suggest that 1,1-bis(dimethylamino)ethylene is much less strongly coordinated to platinum in the η^2 form than ethylene but that the overall interaction results in a deshielding of carbon atoms C_1 and C_2 .

The η^1 form shows very large $^1J(^{195}\text{Pt}-^{13}\text{C})$ values which normally suggest predominant σ -bonded forms suggested by 1. The crystal structure of the 1,1-dimethoxyethylene complex shows that such σ -complexed forms can even exist in the solid state.

Zeise's Dimer and 1,3-Dimethyl-2-methyleneimidazoline. The chemical shifts for the ^1H NMR spectrum of η^1 -4 and η^2 -4 are similar to those of η^1 -2 and η^2 -2. Again the olefinic protons in η^2 -4 (δ 4.90) are shifted to a lower field than the free olefin (δ 2.97), and the $^{195}\text{Pt}-^1\text{H}$ coupling constant is essentially the same as in η^2 -2. Moreover, the η^1 complex η^1 -4 which is also present in solution shows protons H_1 (δ 2.60, $^2J(^{195}\text{Pt}-\text{H}_1) = 102$ Hz) at a higher field than the free olefin with approximately the same coupling constant found for the complexes η^1 -2 and η^2 -2. This again suggests the postulate of σ and π forms in solution.

The ^{13}C NMR spectrum for η^1 -4 and η^2 -4 is difficult to obtain because the complex is not very soluble in either benzene or toluene. Only the peaks for C_1 (δ 83.4), C_2 (δ 170), C_3 (δ 48.0), and C_4 (δ 33.8) could be observed. The coupling constants were not resolved.

Experimental Section

Materials. Zeise's dimer is synthesized from Zeise's salt in a method described by Hartley.² The olefin 1,1-bis(dimethylamino)ethylene is synthesized according to the literature¹⁰ and handled under nitrogen. When freshly distilled it is colorless, but even when sealed under vacuum in glass ampules, it becomes a very straw yellow. The sealed vials are stored in the refrigerator at 0°C . All reactions are performed under nitrogen or argon, and solvents such as benzene are distilled

from sodium benzophenone ketyl under argon. Dichloromethane is distilled from LiAlH_4 under argon. Benzene- d_6 is obtained in ampules, and NMR samples are prepared under inert atmosphere conditions in a Vacuum Atmospheres drybox.

The infrared spectral samples are all made in a drybox and the spectra are obtained on a Perkin-Elmer 283 instrument.

The ^{13}C NMR spectra are obtained from a Varian CFT-20 instrument and the ^1H NMR spectra are recorded on a Varian XL-100 Nicolet FT-100 instrument in 5-mm tubes. Molecular weight measurements are done in benzene with equipment described by Shriver.¹¹ The mass spectrum is obtained on an AEI MS-902 double focusing spectrometer.¹²

Preparation of 1,3-Dimethyl-2-methyleneimidazoline. To a 40-mL ether suspension of 2-chloro-1,3-dimethylimidazolium chloride¹³ at -10°C is added 31.2 mL of CH_3Li in ether over a 3-h period. The mixture is stirred at 0 – 10°C for 5 h until no further methane is evolved. The mixture is filtered from LiCl and excess ether is removed under vacuum to give a pale yellow oil, 3.0 g (86%), bp 70 – 75°C . Mass spectrum at 70 eV: $(M + 1)^+$ calcd for $\text{C}_6\text{H}_{13}\text{N}_2^+$, m/e 113.1079; found, m/e 113.1074.

Zeise's Dimer and 1,1-Bis(dimethylamino)ethylene. To a yellow-orange suspension of $\text{Pt}_2\text{Cl}_4(\text{C}_2\text{H}_4)_2$ (250 mg, 0.042 mmol) in 15 mL of benzene at 5°C is added 1,1-bis(dimethylamino)ethylene (97 mg, 0.085 mmol) in 5 mL of benzene. The mixture becomes deep yellow and the $\text{Pt}_2\text{Cl}_2(\text{C}_2\text{H}_4)_2$ dissolves. After 4 h the solution is orange. It is filtered and excess benzene is sublimed away to give a bright yellow powder, 260 mg (77%), mp 111°C dec. Further recrystallization can be accomplished from dichloromethane. Anal. Calcd for $[\text{C}_6\text{H}_{14}\text{Cl}_2\text{N}_2\text{Pt}]_2$: C, 18.96; H, 3.71; Cl, 18.65; mol wt, 756. Found: C, 18.48; H, 3.36; Cl, 19.39; mol wt, 856.

Zeise's Dimer and 1,3-Dimethyl-2-methyleneimidazoline. To a yellow-orange suspension of $\text{Pt}_2\text{Cl}_4(\text{C}_2\text{H}_4)_2$ (250 mg, 0.043 mmol) in 10 mL of benzene at 5°C is added 1,3-dimethyl-2-methyleneimidazoline (209.2 mg, 1.87 mmol) in 5 mL of benzene. The mixture becomes bright yellow and the suspended material goes into solution. After 2 h the evolution of ethylene ceases, and the mixture is filtered. Sublimation of the excess benzene gives a bright yellow solid, 260 mg (79%), mp 145°C dec. Anal. Calcd for $\text{C}_6\text{H}_{12}\text{Cl}_2\text{N}_2\text{Pt}$: C, 19.06; H, 3.20. Found: C, 22.98; H, 3.26.

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Registry No. 1, 815-62-3; η^1 -2, 68757-84-6; η^2 -2, 68757-85-7; 3, 68738-47-6; η^1 -4, 68757-86-8; η^2 -4, 68757-87-9; $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]_2$, 12073-36-8; 2-chloro-1,3-dimethylimidazolium chloride, 37091-73-9.

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Complex Formation between Aluminum Ion and 5-Nitrosalicylic Acid. Mechanism and Equilibrium Constant

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The Eigen mechanism for the formation of labile complexes is today universally accepted for divalent cations; according to this mechanism, water loss from the inner coordination sphere is rate determining, and the rate constant is ligand independent.¹ Trivalent cations present a much less clear-cut picture.² For $\text{Al}(\text{III})$ there is some evidence³ that it should follow the same mechanism as the divalent cations, whereas energetic considerations argue against this dissociative mechanism.⁴ Further knowledge about the ligand dependence—or independence—of the rate constant is therefore desirable. To this aim, we consider it especially promising to compare ligands which have identical active sites and differ only in their basic strength. In this note, we report the results concerning 5-nitrosalicylic acid, to be compared with the weaker 5-sulfosalicylic,⁵ and salicylic,⁶ acids.

Experimental Section

The materials and methods were those described in our previous paper.⁵ The nitrosalicylic acid was Fluka, "purum". The ionic strength was again 0.1 M. The temperature was 25°C throughout. All measurements were carried out at 355 nm where the difference between the absorptivity of the complex and that of the ligand was found to be at its maximum.

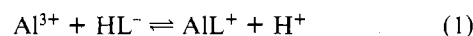
At $\text{pH} \geq 1.9$, the kinetic results were obtained by mixing two solutions, each containing one of the reactants at the appropriate pH. For runs at $\text{pH} < 1.9$, the complex present in less acid solution was decomposed by acidification. The stopped-flow technique was used when the pH was ≥ 3.1 ; at lower pH , the reaction was too slow for this method and was monitored by an ordinary spectrophotometer and recorder.⁵

Results

Equilibrium Constants. We again⁵ define an apparent, pH-dependent formation constant of our complex, which we assume to be AlL^+ , namely

$$K_{\text{app}} = \frac{[\text{AlL}^+][\text{H}^+]}{[\text{Al}(\text{III})](\text{[HL}^-] + \text{[H}_2\text{L]})} = \frac{K_1 K_{\text{H1}} [\text{H}^+]}{(K_{\text{H1}} + [\text{H}^+])(K_{\text{OH}} + [\text{H}^+])} \quad (\text{I})$$

where K_{H1} is the dissociation constant of the carboxylic group, K_{OH} the hydrolysis constant of $\text{Al}(\text{III})$, and K_1 the equilibrium constant of the reaction



(The relative concentration of L^{2-} is so small^{7,8} that its contribution to K_{app} can be neglected.)

At three values of pH —1.94, 2.13, and 2.46—the absorbance was measured at ligand concentrations of 0.5×10^{-4} or 10^{-4} M and four to five different metal ion concentrations ranging from 5×10^{-4} to 4.8×10^{-3} M. For each value of pH , K_{app} was obtained by the graphical method of our previous paper.⁵

In addition, at the same values of $[\text{H}^+]$ and reactant concentrations, we measured the pseudo-first-order rate constant, k_{obsd} , given by

$$k_{\text{obsd}} = d \ln ([\text{AlL}^+] - [\text{AlL}^+]_{\infty}) / dt = k_f a + k_d [\text{H}^+] \quad (\text{II})$$

where a is the mean concentration of $\text{Al}(\text{III})$, and k_f and k_d are the formation and dissociation rate constants, respectively,