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The Molecular Structures and Proton Magnetic Resonance Spectra of Ethylene Complexes of Nickel and Platinum

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The result of an X-ray crystallographic study of the complex $(P(C_6H_5)_3)_2Pt(C_2H_4)$ is presented together with refined values of bond lengths and angles for the nickel analog $(P(C_6H_5)_3)_2Ni(C_2H_4)$. The solution behavior of both complexes has been studied by nmr spectroscopy and marked differences in behavior have been observed. $(P(C_6H_5)_3)_2Pt(C_2H_4)$ is undissociated in toluene solution but readily associates if excess ethylene is present; rapid exchange of ethylene between free sites and sites on the associated complex has been observed and the activation energy for the process has been found to be 11.7 kcal/mol; $(P(C_6H_5)_3)_2Ni(C_2H_4)$ dissociates in toluene solution. A mechanistic scheme incorporating associative phenomena for reactions of $(P(C_6H_5)_3)_2Pt(C_2H_4)$ with acetylenes is proposed.

Introduction

In 1968 Birk, Halpern, and Pickard[1] obtained kinetic evidence consistent with the extensive dissociation of bis(triphenylphosphine)(ethylene)platinum in benzene solution. This finding is inconsistent with the recently published[2] pmr spectrum of the compound containing ^{13}C-labeled ethylene (benzene solution) and in this, the first of two papers on this topic, we present the results of a detailed nmr spectroscopic study of bis(triphenylphosphine)(ethylene)platinum and its nickel[3] analog $(P(C_6H_5)_3)_2Ni(C_2H_4)$, as well as an X-ray crystallographic study of the former compound.

Experimental Section

Materials.—Bis(triphenylphosphine)(ethylene)platinum was prepared by the method of Cook and Jauhal;[4] bis(triphenylphosphine)(ethylene)nickel by the method of Wilke.[3]

Bis(triphenylphosphine)(ethylene-d_4)platinum was prepared with the following modifications to the method given for the undeuterated material.

A solution of bis(triphenylphosphine)(dioxygen)platinum (3.0 g) in 25 ml of absolute ethanol was placed in a 100-ml flask fitted with a pressure-equalizing funnel containing hydrazine (95%, 2 ml). Perdeuterioethylene (100 ml) in an inner-sealed bulb was then connected to the flask and the system was closed. The flask containing the oxygen adduct was cooled to −76° and the inner seal of the C_2D_4 bulb was broken. Hydrazine was then added dropwise, with magnetic stirring, at the same time allowing the contents of the flask to warm to room temperature. Upon reaching room temperature the flask was cooled to −76° again and this sequence was repeated several times until all of the hydrazine had been added. After stirring for 1 hr the white precipitate was filtered, washed with water and alcohol, and dried. The yield by this method was 60%, the same method (on $^1/_{10}$ scale) yielding an equivalent yield in the preparation of $(P(C_6H_5)_3)_2Pt(C_2H_4)$ containing ^{13}C-enriched ethylene.

Bis(triphenylphosphine)platinum was prepared by hydrazine reduction of an alcohol solution of $(P(C_6H_5)_3)_2Pt(O_2)$ in an argon atmosphere. Addition of trace amounts of sodium ethoxide to the solution increases the yield from 25 to 60%. The yellow needlelike crystals decompose at 120°. *Anal.* Calcd for $C_{36}H_{30}P_2Pt$: C, 60.66; H, 4.44. Found: C, 60.09; H, 4.20.

Technique.—An nmr tube containing a known amount of sample was preflushed with argon and deuterated solvent was distilled into the tube in an argon atmosphere (the solvent was deoxygenated by allowing it to stand over tris(triphenylphosphine)platinum for 12 hr from which it was distilled). After adding a few drops of tetramethylsilane in the argon stream (or ethylene when called for) the tube was sealed and the liquid level was marked for later calibration.

The ir spectrum of $(P(C_6H_5)_3)_2Pt(C_2H_4)$ is essentially that of triphenylphosphine. The Raman spectrum [Spex laser; excitation line at 6471 Å (Kr)] of the ^{13}C-enriched complex reveals weak absorption bands at 1525 and 1540 cm^{-1} which may be assigned to $^{13}C{=}^{13}C$ and $^{13}C{=}^{12}C$ vibrations. From these data it can be deduced that the $^{12}C{=}^{12}C$ vibration occurs at 1590 cm^{-1}, a region obscured in the spectrum by the skeletal vibrations of the triphenylphosphine rings.

The pmr spectra were obtained at various temperatures using either a Varian A-56/60D or HA 100 spectrometer. The spectra were calibrated by frequency modulation and the solutions when prepared as outlined above gave reproducible results up to 12 hr after preparation.

X-Ray Structural Determination of $(P(C_6H_5)_3)_2Pt(C_2H_4)$.—Mo K$\alpha$ X-ray radiation was used to record 4678 reflections by four-circle automated diffractometer. Of these, 4227 were measurable. No absorption corrections were made. The structure was solved from the three-dimensional Patterson function and subsequent Fourier syntheses. Refinement by full-matrix least squares using anisotropic temperature factors is virtually complete and the conventional R factor is currently 0.051.

Results and Discussion

Some years ago we published[5] without experimental details the main features of the molecular structure of $(P(C_6H_5)_3)_2Ni(C_2H_4)$. As a result of controversy arising out of an independent study[6a] of its structure, we have lately refined our earlier data[6b] and in addition completed a structural investigation of the related platinum complex $(P(C_6H_5)_3)_2Pt(C_2H_4)$. The essential details of these determinations are given in Figure 1.

It was apparent from our earlier pmr studies that the near planarity of the olefin in $(P(C_6H_5)_3)_2Ni(C_2H_4)$ was not maintained in solution and furthermore that the platinum and nickel derivatives behave differently in solution.

$(P(C_6H_5)_3)_2Pt(C_2H_4)$.—The room-temperature resonance pattern of the olefinic protons in this complex (toluene-d_8 solution) consists of a 1:4:1 broad triplet centered at τ 7.59. In the presence of free ethylene there is no change in location of the triplet and a broad signal appears corresponding in position to free ethylene (τ 4.65). On increasing the concentration of free ethylene the broad signal decreases markedly in line width.

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(2) C. D. Cook and K. Y. Wan, *ibid.*, **92**, 2575 (1970).

(3) G. Wilke and G. Hermann, *Angew. Chem.*, **74**, 693 (1962).

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(6) (a) W. Dreissig and H. Dietrich, *Acta Crystallogr., Sect. B*, **24**, 108 (1968); (b) P.-T. Cheng, C. D. Cook, C. H. Koo, S. C. Nyburg, and M. T. Shiomi, *ibid.*, in press.

TABLE I

PMR DATA AND ARRHENIUS PARAMETERS FOR A C_2H_4–$L_2PtC_2H_4$ MIXTURE IN TOLUENE-d_8 (TMS INTERNAL REFERENCE) AT DIFFERENT TEMPERATURES

$[L_2PtC_2H_4]$, M	$[L_2PtC_2H_4]$/ $[C_2H_4]$	Obsd line width of τ 4.65[a] line, Hz (temp, °K)			Arrhenius parameters		
					E_a, kcal/mol	Log A	Cor log A[c]
4×10^{-2}	4	7.0	5.2	4.2	11.67	8.76	10.20
		(341.5)	(337.5)	(330.0)			
		3.5	2.7				
		(326.0)	(322.0)				
6.6×10^{-2}	4	5.7	3.5	2.5	11.21	9.34	10.50
		(306.0)	(300.0)	(293.0)			
		1.8	1.4				
		(287.0)	(281.0)				
6.6×10^{-2}	8	14.5	11.0	7.0	12.12	9.42	10.60
		(341.5)	(337.5)	(326.0)			
		5.0	3.0				
		(318.0)	(310.0)				
1.33×10^{-1}	18[b]	1.85	1.20	0.95	11.21	9.97	10.80
		(262.5)	(255.5)	(251.0)			
		0.75					
		(244.0)					
8.3×10^{-2}	6	6.0	4.0	2.4	12.35	9.99	11.00
		(306.5)	(299.5)	(295.0)			
		1.6	1.1				
		(280.0)	(277.0)				

[a] Natural line width of C_2H_4 0.5 Hz. [b] Low C_2H_4 concentration forbids higher temperature measurements, due to a small signal to noise ratio. [c] Log A − log $[L_2PtC_2H_4]$.

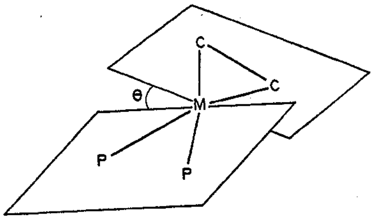

Figure 1.—Molecular parameters of the $(P(C_6H_5)_3)_2M(C_2H_4)$ complexes: M = Ni, C–C = 1.46 Å, C–M = 1.99 Å, P–M = 2.15 Å, θ = 5.0°, R = 0.095; M = Pt, C–C = 1.43 Å, C–M = 2.11 Å, P–M = 2.27 Å, θ = 1.3°, R = 0.043.

The spectrum of the deuterio derivative $(P(C_6H_5)_3)_2Pt(C_2D_4)$ containing *ca.* 0.1 equiv of added C_2H_4 is again a 1:4:1 triplet centered at τ 7.59; increasing the ethylene concentration results in spectra identical with those obtained for the undeuterated complex confirming that rapid exchange does occur.

Evaporation of a benzene solution of $(P(C_6H_5)_3)_2Pt(C_2H_4)$ *in vacuo* regenerates the olefin complex only slightly contaminated with red material ($[(P(C_6H_5)_3)_2Pt]_n$?) as noted by Ugo.[7] A benzene solution of $(P(C_6H_5)_3)_2Pt$ saturated with ethylene shows no pmr signal corresponding to coordinated ethylene.

It is apparent from the foregoing that $(P(C_6H_5)_3)_2Pt(C_2H_4)$ does not dissociate in solution; indeed the spectral observations point to an associative process with exchange of free ethylene with coordinated ethylene *via* a diolefin complex (assuming 1:1 molecular association).

The kinetically labile complex $(P(C_6H_5)_3)_2Pt(C_2H_4)_2$ evidently resembles the tetrakis-phosphine complex, $(P(C_6H_5)_3)_4Pt$, inasmuch as in solution both are dissociated to the three-coordinated complex; they differ in that the latter is stable enough to be isolated.

In an effort to obtain more information on the slow (nmr time scale) exchange process between free and complexed ethylene the system was studied at different temperatures with varying C_2H_4:$(P(C_6H_5)_3)_2Pt(C_2H_4)$ concentration ratios. The results are contained in Table I. From the relationship $k_{\text{obsd}} = \pi(W - W_0)$, where W is the observed line width of "free" ethylene when exchange is occurring and W_0 is the natural line width, a series of rate constants (k_{obsd}) has been calculated[8] and used to obtain Arrhenius parameters. Assuming slow exchange between two sites,[9] calculations indicate an enthalpy of activation of about 12 kcal/mol and an entropy of activation of about −14 eu. These values enable a rough estimate to be made of the coalescence temperature; the 140–160° calculated is not attainable since the complex in solution begins to decompose rapidly at about 70°.

Association in solution of ethylene with coordinatively unsaturated complexes has been observed previously, the complex $Ir(Cl)(C_2H_4)_3$ being detected by means of pmr spectroscopy.[10]

Another point of interest in such systems is the possible rotation[11] of the ethylene molecule about the metal–olefin axis. The spectrum of $(P(C_6H_5)_3)_2Pt(C_2H_4)$ in toluene is unaltered over the temperature range +25 to −60° and consists of the expected triplet (33% ^{195}Pt isotope), each peak in the triplet consisting of a sharp doublet sandwiching a broad unresolved signal (Figure 2). The ^{19}F nmr spectrum of $(P(C_6H_5)_3)_2Pt(C_2F_4)$ was interpreted on the basis of an A_4X_2 system (C_{2v} symmetry) for which each peak of the triplet is split into a quartet, the inner pair being broader than the outer.[12] Substitution of F for H in the olefin significantly alters the platinum–olefin bond (it being stronger in the latter case), yet in terms of their magnetic environment, F and H are equivalent provided that rotation of the C_2H_4 ligand does not occur. Although the larger $J_{\text{Pt-F}}$ compared to $J_{\text{Pt-H}}$ separates

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[9] K. Vrieze, H. C. Volger, and P. W. N. M. van Leeuwen, *Inorg. Chim. Acta Rev.*, **3**, 109 (1969).

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[12] M. Green, R. B. L. Osborn, A. J. Rest, and F. G. A. Stone, *J. Chem. Soc. A*, 2525 (1968).

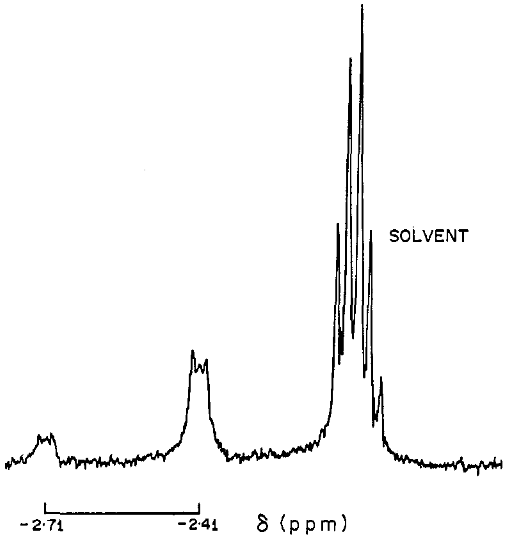

Figure 2.—Pmr spectrum of $(P(C_6H_5)_3)_2Pt(C_2H_4)$ in toluene-d_8 (100 MHz; TMS as internal reference).

the components of each peak in the spectrum of $(P(C_6H_5)_3)_2Pt(C_2F_4)$, compared with what is observed for $(P(C_6H_5)_3)_2Pt(C_2H_4)$, the basic similarities of the two spectra are very evident, and we conclude that over the temperature range studied no ligand rotation occurs. The separation of the outer sharp peaks, which is the sum $J_{\text{cis PH}} + J_{\text{trans PH}}$, is approximately 3 Hz.

$(P(C_6H_5)_3)_2Ni(C_2H_4)$.—In addition to the multiplet arising from the phenyl protons the pmr spectrum of the compound consists of a single line at τ 7.45 of line width 1.7 Hz. At −75° there is only a small chemical shift change but the line broadens to 18–20 Hz; variations in concentration (3×10^{-3} to 1.5×10^{-2} *M*) do not alter the above values. On cooling the solution, a marked color change (red to yellow) is observed which can be reversed on warming. Passage of argon through the solution results in the loss of the τ 7.45 signal and finally the formation of a dark brown precipitate.

If excess ethylene is present, the solution remains yellow at room temperature, and increasing the free ethylene concentration results in a progressive downfield shift of the olefin resonance toward τ 4.65 together with a sharpening of the line. At lower temperatures the same sequence is observed, but the lines are broadened. In contrast to $(P(C_6H_5)_3)_2Pt(C_2H_4)$, no phosphorus–proton coupling was observed in the spectrum of the nickel compound despite cooling to −80°. It would thus appear that a rapid exchange between free and coordinated ethylene occurs in solution and that in the absence of additional ethylene $(P(C_6H_5)_3)_2Ni(C_2H_4)$ dissociates to $(P(C_6H_5)_3)_2Ni$ and C_2H_4. We are, of course, unable to determine whether or not the coordinated ethylene is rotating about the metal–ligand axis.

If we assume that C_2H_4 is shifting from coordinated site A to uncoordinated site B, we can obtain quantitative information on the process by measuring line widths at various C_2H_4 concentrations and employing Gutowsky's equation[13]

$$k_{\text{obsd}} = 2\pi P_A P_B (\delta\nu)^2 [W - W^0]^{-1}$$

where P_A and P_B are the fractional populations at the two uncoupled sites (A (complexed) and B (free)), $\delta\nu$ is the chemical shift difference of sites A and B, and W and W^0 are the line widths during and in the absence of exchange, respectively. P_A and P_B are related to the chemical shifts of the A and B sites by the relationship

$$\delta_{\text{obsd}} = P_A\delta_A + P_B\delta_B$$

The results of these studies are contained in Table II.

TABLE II

PMR DATA[a] FOR C_2H_4–$L_2NiC_2H_4$ MIXTURES AT VARIOUS TEMPERATURES[b]

$[C_2H_4]/[L_2NiC_2H_4]$	$10^3[L_2NiC_2H_4]$, *M*	Temp, °K: 306	257.5	246	223	212
0	9.60	153.0	155.0	157.0	159.0	160.0
		1.7	3.3	4.0	9.0	12.0
		...	...	...	...	...
		(43.7)[c]	(15.5)[c]	(11.80)[c]	(5.88)[c]	...
1	...	250.0	252.0	253.0	...	...
		1.5	3.2	4.0	...	...
		60.0	60.6	60.8	...	...
		39.5	14.6	10.6	...	...
1.25	4.12	257.0	260.0	264.0	270.0	...
		1.5	3.0	3.5	6.5	...
		64.0	65.6	67.7	70.9	...
		38.0	14.5	11.4	5.4	...
8	7.27	292.0	293.0	295.5	298.0	...
		1.5	2.1	2.5	3.5	...
		85.8	86.3	87.7	88.8	...
		20.0	11.9	8.5	5.3	...
9	1.40	298.0	298.5	299.0	304.0	305.8
		1.5	2.0	2.4	3.3	4.0
		89.5	89.7	89.9	93.0	93.5
		15.7	9.9	7.5	3.7	2.8
12	3.74	303.0	303.5	305.0	307.0	309.0
		1.4	1.8	2.2	3.1	4.0
		92.6	92.8	93.7	94.6	95.5
		11.3	8.3	5.4	3.1	2.0
∞	...	315.0	315.0	315.0	315.5	316.0
		0.5	0.5	0.5	0.6	0.7
		...	...	...	...	...
		...	...	...	...	...

[a] TMS as internal reference. L = triphenylphosphine. [b] Chemical shift, line width, P_B, and 10^3k are arranged in vertical sequence in the temperature columns. [c] Extrapolated from log k_{obsd} *vs.* $[C_2H_4]/[L_2NiC_2H_4]$ plot.

The data obtained for this system are difficult to interpret and are probably semiquantitative at best since it is impossible to obtain an accurate value for δ_A due to dissociation of $(P(C_6H_5)_3)_2Ni(C_2H_4)$. Also for a given temperature k_{obsd} does not follow changes in C_2H_4 but more nearly changes in the ratio $[(P(C_6H_5)_3)_2Ni(C_2H_4)]/[C_2H_4]$. This implies a mixed-order reaction and it is possible that the following equilibrium plays a contributing part, the bimolecularity of the reverse reaction leading to the observed dependence on [complex]/[ethylene] ratio[9]

$$(P(C_6H_5)_3)_2Ni(C_2H_4) \rightleftharpoons (P(C_6H_5)_3)_2Ni + C_2H_4$$

Qualitatively it would appear, however, that $(P(C_6H_5)_3)_2Ni(C_2H_4)$ and its platinum analog behave differently in solution with the nickel compound dissociating[14] in solution and exchange occurring between free and dissociated ethylene. A log k_{obsd} *vs.* $[C_2H_4]/[(P(C_6H_5)_3)_2Ni(C_2H_4)]$ plot with extrapolation to zero ethylene concentration yields a rate constant for the dissociative process of about 4×10^4 mol^{-1} sec^{-1}.

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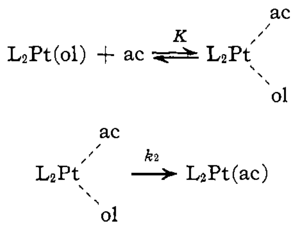
(14) Dr. C. A. Tolman has kindly informed us of his studies (see *Inorg. Chem.*, **9**, 2350, 2354 (1970)) on this and related systems which point to an irreversible decomposition of $(P(C_6H_5)_3)_2Ni(C_2H_4)$ in solution. While admitting the possibility of this complication, we suggest that under the conditions employed for the pmr study the rate of decomposition is sufficiently slow for it not to interfere with the exchange process described above.

Conclusion

The main purpose of this study was to obtain further information on the behavior of olefinic complexes of the type $(P(C_6H_5)_3)_2M(C_2H_4)$ in solution. It is apparent from the above material that under the conditions used by Halpern, *et al.*,[1] for their kinetic studies (*i.e.*, excess ethylene present) the complex $(P(C_6H_5)_3)_2Pt(C_2H_4)$ is associated in solution, presumably to $(P(C_6H_5)_3)_2Pt(C_2H_4)_2$. A reasonable *associative* scheme for the reaction of an acetylene (ac) with the olefin (ol) complex can be written as[15]



$$L_2Pt(ol) + ac \overset{K}{\rightleftharpoons} L_2Pt\genfrac{}{}{0pt}{}{ac}{ol}$$

$$L_2Pt\genfrac{}{}{0pt}{}{ac}{ol} \xrightarrow{k_2} L_2Pt(ac)$$

where $L = P(C_6H_5)_3$. For this scheme the rate is given by

$$k_{obsd} = \frac{k_2K[ac]}{1 + K[ac]} \qquad (1)$$

This can be compared with the equation derived by Halpern for the same reaction

$$k_{obsd} = \frac{k_1k_2'[ac]}{k_{-1}[ol] + k_2'[ac]} \qquad (2)$$

for which the following stages were proposed

$$L_2Pt(ol) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PtL_2 + ol$$

$$L_2Pt + ac \xrightarrow{k_2'} L_2Pt(ac)$$

these stages being preceded by an immeasurably fast reaction. Equations 1 and 2 are identical with equations derived for SN2IP and SN1CB reaction pathways for Co(III) complexes,[16,17] the associative (IP) and dissociative (CB) processes both being consistent with the kinetic results. For $(P(C_6H_5)_3)_2Pt(C_2H_4)$, however, the additional pmr evidence is so strongly supportive of the associative process that we feel the kinetic data must be interpreted in terms of a bimolecular mechanism.

Allen and Cook[18] first proposed $(P(C_6H_5)_3)_2Pt$ as the intermediate in substitution reactions of $(P(C_6H_5)_3)_2Pt(ac)$ complexes, but recent synthetic work by Tripathy and Roundhill[19] and spectral observations of Greaves, Lock, and Maitlis[20] have cast some doubt on the validity of the proposal. In addition, Halpern[21] has shown that oxidation of $(P(C_6H_5)_3)_3Pt$ to $(P(C_6H_5)_3)_2Pt(O_2)$ does not involve the bis(phosphine)platinum intermediate. In view of the increasingly precarious position occupied by $(P(C_6H_5)_3)_2Pt$ in mechanistic schemes we have reexamined substitution reactions of $(P(C_6H_5)_3)_2Pt(ac)$ complexes and these studies will form the basis of the second paper on this general topic.

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(15) If free ethylene is present in the solution, there will be competition for the fourth coordination site between the acetylene and ethylene. However, the argument is unaffected provided that $L_2Pt(ol)(ac)$ is the predominant intermediate. In view of the relative coordinating abilities of olefins and acetylenes to zerovalent platinum this seems to be a reasonable supposition.

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The Luminescence of Platinum(II) Complexes

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Emission spectra of eight σ complexes of Pt(II) in the solid state are reported. The complexes are of two types, those whose lowest energy absorptions include d ← d transitions and those which show only CT bands at usual spectral concentrations. For the latter, new weak bands to the red of the first apparent band are reported and the possible origin of these is discussed. The emissions of three of the compounds in alcoholic solution are also presented.

While complexes of Pt(II) are among the earliest known luminophores,[1] they are also among the least studied. This is perhaps unfortunate since information yielded by comparison of absorption and emission spectra might prove useful in clarifying the unsettled problem of the assignment of electronic energy state levels in such compounds. One of the problems associated with making such assignments is that the uv absorption spectra do not always contain a sufficient number of clearly resolved bands in order to furnish the ligand field parameters necessary for calculations. In compounds where molecular symmetry is reduced from the convenient O_h or T_d to some lesser group, more than just $10Dq$ is required to describe splitting of the d orbitals. Thus further information is needed to provide the basis for reasonable energy schemes. In connection with this problem we have observed that a number of Pt(II) complexes are luminescent at low temperature. (We have already reported the emission of K_2PtCl_4 and have inferred from this something of the nature of the lowest excited state.[2]) This paper is the preliminary report on the new emissions.

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