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Effect of Trans Ligands on Iodine-129 Mössbauer Parameters in Square-Planar Platinum(II) Complexes

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Abstract: The ^{129}I Mössbauer spectra of neutral and cationic compounds of the type *trans*- $^{129}\text{IQ}_2\text{PtX}$ ($\text{X} = \text{Me}, \text{CF}_3, \text{I}; \text{Q} = \text{Me}_2\text{PhP}$) and *trans*- $^{129}\text{IQ}_2\text{PtL}^+$ ($\text{L} = \text{P}(\text{OMe})_3, \text{P}(\text{OMe})_2\text{Ph}, \text{PPh}_3, \text{AsPh}_3, \text{EtNC}, p\text{-MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{NC}$) have been recorded. The ^{129}I e^2qQ values are very sensitive to the nature of the trans ligand. For example, the total range of $e^2qQ_{(7/2)}$ values is ~ 400 MHz, and the two isocyanide ligands give significantly different $e^2qQ_{(7/2)}$ values: -1038 ± 4 MHz (EtNC) compared to -1063 ± 4 MHz (*p*-MeO \cdot C₆H₄ \cdot NC). The trans influence series is found to be $\text{Me} > \text{H} > \text{CF}_3 > \text{I}$ for the neutral compounds and $\text{P}(\text{OMe})_3 > \text{EtNC} > \text{P}(\text{OMe})_2\text{Ph} \sim p\text{-MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{NC} > \text{Ph}_3\text{As} > \text{Ph}_3\text{P}$ for the cationic complexes. This order is compared with those obtained from Pt-CH₃ nmr coupling constants, and Pt-Cl infrared stretching frequencies. Analysis of the spectra using the Williams-Bancroft analytical treatment leads to a $Q(\frac{5}{2})/Q(\frac{7}{2})$ value of 1.239 ± 0.007 , and statistically estimated errors (σ) in e^2qQ and η of ± 4 MHz and ± 0.03 , respectively.

Mössbauer spectroscopy has proved to be a very useful technique in the examination of bonding modes for a wide variety of molecules.^{1,2} We now wish to report the utilization of the 27.8-keV γ radiation from ^{129}I to elucidate the bonding in some square-planar platinum(II) complexes and in particular to examine the influence of ligands trans to the ^{129}I probe on the bonding of the iodine ligand.

The trans influence in transition metal complexes has been widely studied, using a variety of spectroscopic and other techniques, and is the subject of a recent review.³ The phenomenon has been most widely examined in platinum(II) complexes, and trans influence series have been established for a wide variety of ligands from infrared, nmr and nqr spectroscopic, and X-ray crystallographic parameters.³ The mechanism most widely invoked to explain the influence of a ligand to another trans to it in square-planar compounds is that postulated by Syrkin,⁴ where ligands trans to one another are considered to share the same hybrid orbital, which has predominantly 5d and 6s character. As a ligand L requires more d and s participation in the Pt-L bond; then the availability of these orbitals to the ligand trans to L is decreased, resulting in a weaker metal-ligand bond. The cis ligands use an independent s-d hybrid and will be affected to a lesser extent.

^{129}I Mössbauer spectra will yield less ambiguous results than those from some other Mössbauer isotopes, such as ^{119}Sn or ^{121}Sb , which have other ligands bonded to them. The parameters from the spectra of these latter elements will also reflect the bonding characteristics and structural distortions of the other ligands about the Mössbauer atom.

We have recorded the ^{129}I spectra and derived a number of spectroscopic and bonding parameters for three neutral compounds of the form *trans*- $^{129}\text{IQ}_2\text{PtX}$ ($\text{X} = \text{Me}, \text{CF}_3, \text{I}$) and six cationic complexes of the form *trans*- $^{129}\text{IQ}_2\text{PtL}^+$ ($\text{L} = \text{P}(\text{OMe})_3, \text{P}(\text{OMe})_2\text{Ph}, \text{PPh}_3, \text{AsPh}_3, \text{EtNC}, p\text{-MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{NC}$), where $\text{Q} = \text{Me}_2\text{PhP}$. The ^{129}I probe is found to be sensitive to the nature of the trans ligand and hence should be very useful in the future for studying subtle changes in iodine bonding. Since the completion of this work, the ^{129}I Mössbauer parameters for some platinum complexes of the type *cis*- and *trans*- $^{129}\text{I}_2\text{PtL}_2$ and *trans*- $^{129}\text{IHPtL}_2$ ($\text{L} = \text{neutral ligand}$) have been reported.^{5,6} A cis influence of ligands was obtained from the trans compounds, but the changes in parameters in the cis compounds are clearly due to both a cis and a trans influence.

The analysis of iodine Mössbauer spectra is still somewhat of a problem. Most recent workers have used numerical iterative methods⁷ to extract the ^{129}I Mössbauer parameters. However, the very large χ^2 values reported recently⁵ point out some of the problems associated with this method. For example, Q^*/Q —which is not yet accurately established—has to be assumed, and peak intensities have to be constrained to their expected values for random samples with no Goldanskii-Karyagin effects. In the present paper, we point out the significant advantages of the analytical method,⁸ outlined earlier, to extract our parameters. Excellent χ^2 values, a detailed analysis of the errors in the method, and the internal consistency checks which the method affords, strongly suggest that the Williams-Bancroft meth-

Table I. Physical Data for the Complexes *trans*-[ILPtQ₂]PF₆ and *trans*-IXPtQ₂ (Q = Me₂PhP)

L or X	Color	% yield	Mp, °C	Elemental analyses, %					
				C		H		I	
				Found	Calcd	Found	Calcd	Found	Calcd
EtNC	White	78	120–122	28.7	28.6	3.42	3.41	15.0	15.9
<i>p</i> -MeO·C ₆ H ₄ ·NC	White	68	184–185	32.9	32.9	3.20	3.34	13.2	13.5
P(OMe) ₃	White	65	136.5–138	27.0	26.3	3.86	3.60	14.5	14.6
P(OMe) ₂ Ph	White	85	85.5 d	31.8	31.6	3.88	3.64	13.5	13.9
PPh ₃ (sample I)	<i>a</i>	72	<i>a</i>	40.6	40.6	3.87	3.71	12.6	12.6
AsPh ₃	<i>a</i>	54	<i>a</i>	38.5	38.9	3.72	3.55	11.9	12.1
CH ₃	White	87	133–134						
CF ₃	Cream	73	126–127						
I	Yellow	90	166–167.5						

^a See text.

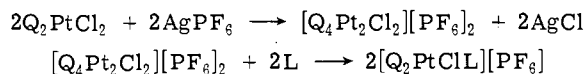
od leads to very accurate parameters with no approximations and straightforward calculations.

Experimental Section

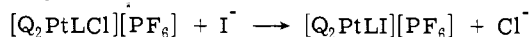
Radioactive Na¹²⁹I was purchased from the U. S. Atomic Energy Commission, Oak Ridge National Laboratory, as an aqueous solution with basic sodium metabisulfite. The Na¹²⁹I was isolated by removal of the water solvent under vacuum and extraction with several portions of acetone. The acetone was removed under vacuum, and the resulting solid was used without further purification.

The compounds *trans*-ClMePtQ₂, *trans*-I(CF₃)PtQ₂, and *cis*-Cl₂PtQ₂ (Q = Me₂PhP) were kindly donated by Dr. L. E. Manzer. The desired radioactive iodine complexes *trans*-¹²⁹I₂PtQ₂ and *trans*-¹²⁹IMePtQ₂ were prepared from the chloride precursors by metathetical reaction with a stoichiometric amount of Na¹²⁹I, and *trans*-¹²⁹I(CF₃)PtQ₂ was prepared by treatment with 1 equiv of AgClO₄, filtration to remove AgI, and addition of Na¹²⁹I. The identity and purity of the complexes were checked by comparison of melting point, ¹H nmr, and infrared data with that in the literature.^{9–12}

The cationic complexes were all synthesized by the following method, based partly on that previously used for related compounds.¹³ Typically, 0.75 mmol (408 mg) of Cl₂PtQ₂ was suspended in 30 ml of methanol, and 0.75 mmol (194 mg) of AgPF₆ dissolved in acetone was added dropwise with stirring. The precipitated AgCl was removed by centrifugation, and 0.75 mmol of the appropriate neutral ligand L was added to the pale yellow supernate and stirred for an hour. (Cleavage of the chloro-bridged dimer was also attempted using pyridine, but without success, even with heating.) The product was isolated by concentrating the solution under vacuum and crystallizing by slow addition of pentane or ether.



The iodide complexes were then synthesized from the corresponding chlorides by a metathetical reaction with sodium iodide. The appropriate chloro complex was dissolved in methanol, and an equimolar amount of sodium iodide, dissolved in acetone, was added dropwise with stirring. After several hours the solvent was removed under vacuum, and the solid was extracted with water to remove sodium chloride and any unreacted sodium iodide. The remaining solid was taken up in a minimum of dichloromethane, an equal amount of methanol was added, and the product was crystallized with pentane and cooling.



Radioactive Na¹²⁹I is expensive, so that only small amounts of the ¹²⁹I complexes were made. Satisfactory ¹²⁹I Mössbauer spectra were obtained when the final products contained 25–45 mg of ¹²⁹I.

The analytical and physical data for the iodo complexes are shown in Table I. These data refer to products synthesized using naturally occurring Na¹²⁷I. The final complexes, containing ¹²⁹I, were then made identically, and their identity and purity were checked using ¹H nmr, infrared spectra, and melting points. The physical properties shown in Table I agreed well with previous literature reports for the compounds where L = EtNC,¹³ and X = I, Me, and CF₃.^{9–12} The cationic complexes where L = *p*-MeO·C₆H₄·NC, P(OMe)₃, P(OMe)₂Ph, PPh₃, and AsPh₃ appear to

be new. Elemental analyses for all the cationic compounds are satisfactory.

Iodine-129 Mössbauer spectra were recorded with 248 channels at PCMU, Harwell on polycrystalline samples, using a ⁶⁶Zn¹²⁹Te source, with both source and absorbers at 4.2 K. The resulting spectra were fitted as the sum of nine component Lorentzian lines, by methods previously described.¹⁴ The very small ninth peak is due to adsorbed or residual Na¹²⁹I. Consequently, the peak due to this impurity was fixed at its reported¹⁵ value (−0.46 mm sec^{−1}), and the widths of all the lines were constrained to be equal. The intensity of the peak due to ¹²⁹I[−] was never greater than 1.5% of the total, but the fits to nine lines generally gave a significantly better χ² value than an eight peak fit. For example, for the compound *trans*-[¹²⁹IQ₂Pt(OMe)₃]PF₆, the peak due to Na¹²⁹I accounted for <1% of the total intensity, but the χ² improved by 50 from an eight line to a nine line fit.

Results

Structure and Nmr. The *trans* configuration for all the iodo complexes was unequivocally established by the presence of the expected¹¹ triplet of triplet proton nmr signals for the methyl groups in the Me₂PhP ligands (due to coupling with ³¹P and ¹⁹⁵Pt) (in CDCl₃ solution), except in the case of the complexes with L = Ph₃P, Ph₃As. Several pieces of evidence indicate that these compounds were a mixture of *cis* and *trans* isomers. When these compounds were crystallized from dichloromethane solutions, using pentane, they both yielded bright yellow solids which had satisfactory elemental analyses (see Table I) but which melted over ranges of ~30°. When the L = Ph₃P complex was redissolved in methanol and crystallized with ether–pentane, a pale yellow solid formed which melted over a much smaller range (126.5–133°). ¹H nmr spectra of the L = Ph₃P compound in CD₃Cl and CD₃OD solutions showed that a mixture of species was present, and the pattern of the spectra could be associated with both a *trans* (triplet of triplets) and a *cis* (triplet of triplets and triplet of doublets) isomer being present. The intensities of the signals indicated that the *trans* isomer was predominant (*trans*:*cis* approximately 3:1 in both solvents).

The ¹²⁹I spectra for L = Ph₃P (see Table II) showed a marked decrease in line width from the bright yellow (sample I) to the pale yellow (sample II) samples; though the other parameters were changed surprisingly little. Together with the melting point data and the color, this line narrowing probably indicates that sample II contained a much higher proportion of the *trans* isomer than sample I, and the derived Mössbauer parameters for sample II are probably very close to those for the pure *trans* isomer.

No sample of the L = Ph₃As compound could be obtained which melted over a small range, and, again, the ¹H nmr spectrum (in CDCl₃) indicated that both *cis* and *trans* isomers were present, with the *trans* isomer predominant. The ¹²⁹I Mössbauer spectrum for this compound was somewhat unsatisfactory in several ways. It could be computed

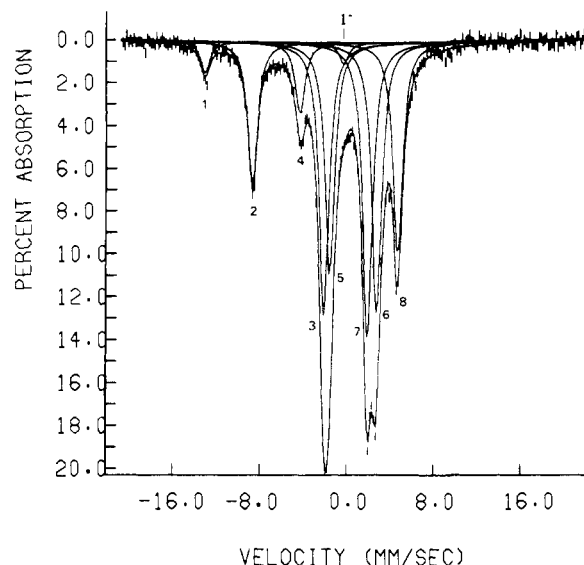


Figure 1. ^{129}I Mössbauer spectrum of $\text{trans-}[\text{}^{129}\text{IQ}_2\text{PtP}(\text{OMe})_3]\text{PF}_6$, at 4.2 K, showing the line numbering convention used and the best computed nine-peak fit.

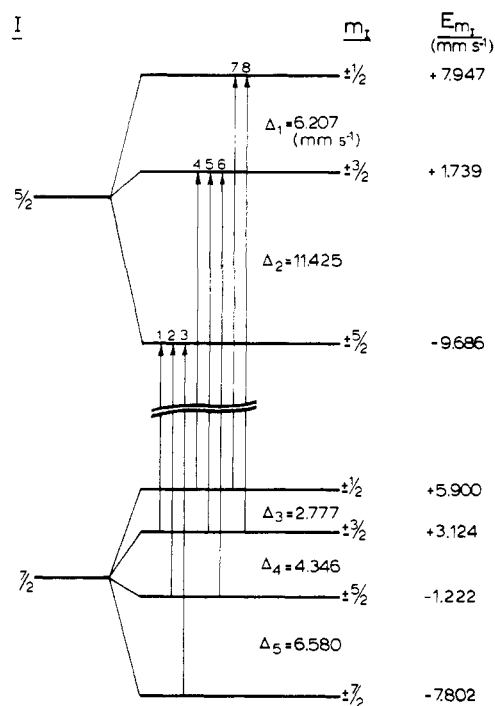


Figure 2. Nuclear energy level diagram for the ^{129}I atom in $\text{trans-}[\text{}^{129}\text{IQ}_2\text{PtP}(\text{OMe})_3]\text{PF}_6$, with the transitions numbered as for Figure 1, together with calculated energy levels and splittings.

only with some difficulty, and the best fit to the spectrum yielded unrealistic intensity ratios for some of the lines. Also, the line widths were much greater than for any of the other compounds, though the Q^*/Q value is in good agreement with our other values. Thus the calculated parameters for this compound (Table II) should be treated with some caution.

Mössbauer Spectra. The χ^2 values for the computed fits to the data, the widths of the peaks at half height, and the parameters derived from the spectra are listed in Table II. The spectrum for $\text{trans-}[\text{}^{129}\text{IQ}_2\text{PtP}(\text{OMe})_3]^+$, with the computed best fit, is shown in Figure 1. Center shift, e^2qQ , and η parameters were calculated from the computed line positions using the analytical method of Williams and Ban-

Table II. Iodine-129 Mössbauer Parameters for $\text{trans-}[\text{}^{129}\text{IXPtQ}_2]$ and $\text{trans-}[\text{}^{129}\text{LPtQ}_2]\text{PF}_6$ ($\text{Q} = \text{Me}_2\text{PhP}$)

X or L	$e^2qQ^{(1/2)}$, mm sec $^{-1}$	$e^2qQ^{(1/2)}$, ^a MHz	$e^2qQ^{(3/2)}$, ^a MHz	$Q^{(3/2)}/Q^{(1/2)}$	η^b ($^{1/2}$)	η^b ($^{3/2}$)	η^b ($^{5/2}$)	C_S^c , mm sec $^{-1}$	N_{Pz}	N_{Py}	N_{Px}	U_p	h_p	h_s	Γ_p^d , mm sec $^{-1}$	χ^2
1. CH_3	-23.77	-774.0	-969.0	1.251	0.28	0.21	-0.44	2.00	1.63	1.94	2.00	0.34	0.42	0.06	1.04	230
2. CF_3	-27.79	-905.0	-1125	1.243	0.25	0.26	-0.41	2.00	1.57	1.93	2.00	0.40	0.50	0.07	1.05	225
3. $\text{P}(\text{OMe})_3$	-31.14	-1015	-1257	1.239	0.30	0.26	-0.34	2.00	1.52	1.92	2.00	0.44	0.57	0.07	1.06	275
4. $\text{CH}_3\text{CH}_2\text{NC}$	-31.87	-1038	-1282	1.235	0.14	0.16	-0.30	2.00	1.53	1.95	2.00	0.45	0.52	0.06	0.97	204
5. $\text{P}(\text{OMe})_2\text{Ph}$	-32.30	-1052	-1304	1.239	0.27	0.31	-0.29	2.00	1.50	1.91	2.00	0.46	0.59	0.07	1.19	262
6. $p\text{-MeO-C}_6\text{H}_4\text{-NC}$	-32.62	-1063	-1316	1.239	0.16	0.13	-0.33	2.00	1.51	1.95	2.00	0.46	0.53	0.06	0.99	205
7. AsPh_3	-34.47	-1123	-1389	1.237	0.16	0.22	-0.25	2.00	1.48	1.94	2.00	0.49	0.58	0.06	1.32	325
8. PPh_3 (I)	-35.29	-1150	-1410	1.227	0.19	0.19	-0.21	2.00	1.47	1.94	2.00	0.50	0.60	0.06	1.17	290
8. PPh_3 (II)	-35.45	-1155	-1418	1.228	0.22	0.22	-0.23	2.00	1.46	1.93	2.00	0.50	0.61	0.07	0.98	215
9. I	-35.96	-1172	-1447	1.235	0.19	0.17	-0.30	2.00	1.46	1.94	2.00	0.51	0.60	0.07	1.04	260

^a ± 4 MHz. ^b ± 0.03 . ^c Relative to ZnTe at 4.2 K. ^d Peak width at half height.

croft.⁸ Generally intensities were within $\pm 20\%$ of the values expected from the Clebsch–Gordan coefficients for random samples,² except for the most intense line 3, which was consistently up to 40% less than expected, perhaps due to a saturation effect. This may account for the poor χ^2 values sometimes reported^{5,6} for ^{129}I spectra, though quite large changes in relative line intensities seem to have a much smaller effect on computed line positions. Other than for line 3, the observed intensity ratios indicated that orientation, saturation and Goldanskii–Karyagin effects are relatively small.

It can be seen from the spectrum in Figure 1 that lines 3 and 5 are poorly resolved. Since line 1 has the lowest intensity, it was often badly defined. Consequently the errors in line positions will be greatest for these three, so that calculations were performed using only the better defined line positions where a choice was possible. For example, Δ_1 (see Figure 2) is given by both $l_7 - l_4$ and by $l_8 - l_5$, but we used only the former difference to measure Δ_1 .

The following is an example of the analysis of a ^{129}I Mössbauer spectrum, using the Williams–Bancroft method, for *trans*- $^{129}\text{I}[\text{Q}_2\text{PtP}(\text{OMe})_3]\text{PF}_6$. The relevant data are shown in Table III and Figure 2, and the symbols are as defined in Figure 2. The Δ_i values are derived from the spectral line positions as differences. The nuclear energy levels are then calculated from the definitions of the Δ 's in terms of energy levels, and from the fact that for each I level, $\sum_{m_I} E_{m_I} = 0$. The secular polynomials of the determinant

$$|\mathcal{H} - E\mathbf{I}|_{ij}$$

(where $\mathcal{H} = [e^2qQ/4I(2I - 1)][3I^2 - I(I + 1) + \eta/2(I^2 + I^2)]$) are then set up for each I level, leading to cubic polynomials in μ_1 . Each of these cubic equations has three real roots for μ_1 , which will be proportional to the components of the electric field gradient¹⁶ (V_{XX} , V_{YY} , V_{ZZ}), assigned in the conventional manner so that $|\mu_{XX}| \leq |\mu_{YY}| \leq |\mu_{ZZ}|$ (where $\mu_{ii} = -eV_{ii}Q/4I(2I - 1)$). Thus V_{ZZ} , e^2qQ and η can be calculated for both $I = 5/2$ and $I = 7/2$. The e^2qQ values were converted to the usual ^{127}I megahertz scale, using the calibration factor² $e^2qQ(^{127}\text{I}) \text{ MHz} \equiv 32.58 e^2qQ(^{129}\text{I}) \text{ mm sec}^{-1}$.

The good agreement between the η values for the two energy levels (never different by more than 0.07) and the consistent value of $Q(5/2)/Q(7/2)$ (average value 1.239) from compound to compound indicates that very accurate parameters may be derived using this procedure, which is simpler than other methods used previously.^{7,17,18}

As a further test of the method we have estimated statistically the errors which would occur in the derived e^2qQ and η values as a result of errors in the line positions. This method, and its application, are outlined in a supplement to the paper. See paragraph at the end of paper regarding supplementary material. The results in Table A1 strongly suggest that e^2qQ is accurate to better than ± 4 MHz and η to better than ± 0.03 . For example, for the three compounds given in Table A1, 2σ (the 95% confidence level) is never greater than ± 7 MHz for e^2qQ and ± 0.04 for η . σ then is never larger than ± 4 MHz for e^2qQ and ± 0.03 for η . The very good agreement between the internal and external estimates of the error in η indicate that the accuracy of η values derived by the Williams–Bancroft method⁸ is limited by the accuracy of the spectroscopic data, rather than inherent inaccuracies in the treatment.

The average $Q(5/2)/Q(7/2)$ value from our data is 1.239, and the standard deviation in the nine values is 0.007. This is in very good agreement with the value (1.2385 ± 0.0011) given by Collins¹⁸ but larger than the value of 1.231 commonly used.² Alternatively, if we consider that the error in $Q(5/2)/Q(7/2)$ is due to a 4-MHz error in each of the e^2qQ

Table III. Data Used in the Analysis of the ^{129}I Mössbauer Spectrum of *trans*- $^{129}\text{I}[\text{Q}_2\text{PtP}(\text{OMe})_3]\text{PF}_6$

Line	Line position (mm sec ⁻¹) (rel to ZnTe at 4.2 K)	Cubic Equations
1	-13.204	$4\mu_{5/2}^3 - 2.857\mu_{5/2} + 0.8368 = 0$
2	-8.838	$4\mu_{7/2}^3 - 0.4244\mu_{7/2} + 0.4646 = 0$
3	-2.258	
4	-4.466	
5	-1.737	
6	+2.588	
7	+1.741	
8	+4.518	
Electric Field Gradient Components		
	$\mu_{XX}(5/2) = 0.3561$	$\mu_{XX}(7/2) = 0.1304$
	$\mu_{YY}(5/2) = 0.6088$	$\mu_{YY}(7/2) = 0.2403$
	$\mu_{ZZ}(5/2) = -0.9649$	$\mu_{ZZ}(7/2) = -0.3707$
	(where $\mu_{ii} = -eV_{ii}Q/4I(2I - 1)$)	
Derived Parameters		
	$e^2qQ(5/2) = -38.60 \text{ mm sec}^{-1}$	$\eta(5/2) = 0.26$
	$e^2qQ(7/2) = -31.14 \text{ mm sec}^{-1}$	$\eta(7/2) = 0.30$
	$CS = -0.34 \text{ mm sec}^{-1}$ (rel to ZnTe at 4.2 K)	

values, then the resultant error in the Q ratio is calculated to be 0.009. This would seem to indicate that, if anything, our estimated error of ± 4 MHz in the e^2qQ values is overly cautious.

Line positions differ from the appropriate transition energy by the amount of the center shift, *i.e.*

$$\ell_n = {}^eE_j - {}^eE_i + CS \quad (1)$$

In fact only three independent estimates of the CS result from applying the above equation to each of the eight lines of the spectrum. We averaged these three values in each case, yielding the values quoted in Table II. The values are small and negative—approaching the values observed for ionic iodides—and a relatively large error of $\pm 0.05 \text{ mm sec}^{-1}$ is associated with the CS parameters.

Discussion

The Trans Influence Series. The following equations, derived from the Townes–Dailey theory for the analysis of nqr spectra, are those normally used to calculate the U_p , N_{p_x} , N_{p_y} , N_{p_z} , h_p , and h_s parameters:

$$U_p = -e^2qQ(^{127}\text{I})/2293 \quad (2)$$

$$\eta = -\frac{3}{2}(N_{p_x} - N_{p_y})/U_p \quad (3)$$

$$U_p = -N_{p_z} + \frac{1}{2}(N_{p_x} + N_{p_y}) \quad (4)$$

$$h_p = 6 - (N_{p_x} + N_{p_y} + N_{p_z}) \quad (5)$$

$$CS(\text{ZnTe}) = -9.2h_s + 1.5h_p - 0.54(\text{mm sec}^{-1}) \quad (6)$$

Clearly there are five equations, but six variables, so that some reasonable approximation(s) must be made in order for them to be solved. The nonzero η values for the compounds show that $N_{p_x} \neq N_{p_y}$. If we assume that $U_p = h_p$, as did Parish,^{5,6} we find that the computed population of the p_x orbital, in each case, is slightly greater than two (2.02–2.04 found), which is not chemically reasonable. Consequently, we have calculated the parameters in Table II by arbitrarily setting $N_{p_x} = 2.00$.

From the treatment of Townes and Dailey,¹⁹ the iodine e^2qQ essentially reflects (1) any s character(s) in the orbital of iodine participating in the σ Pt–I bond, (2) the covalency (σ) (degree of overlap of the appropriate orbitals) of the platinum–iodine interaction, and (3) any π -character (π) in the platinum–iodine interaction; according to^{19,20}

$$(e^2qQ)_{\text{mol}} = (e^2qQ)_{\text{at}} \left[(1-s)\sigma - \frac{1}{2}\pi \right] \quad (7)$$

From the h_s values in Table II, it can be seen that the character in the iodine "sp_z" hybrid is almost constant from compound to compound and is very small. (However, eq 6 shows that even very small h_s values will have a disproportionately large effect on the CS, so that the low CS parameters measured for these compounds—almost as low as those for ionic iodides—are due, in this case, to the participation of a small amount of the iodine s orbitals in the platinum-iodine bond.) Thus we can approximate $s \sim 0$.

The nonzero η values (Table II) are not unexpected in these compounds, since the p_x and p_y orbitals do not "see" a similar environment in the square planar complexes. In addition, η would be expected to be fairly constant from compound to compound as the environment of the p_x and p_y orbitals is approximately constant, though the value of U_p is not. This can be seen from Table II, where N_{p_y} varies much less, relatively, than U_p . (The fixed value of N_{p_x} will not invalidate this conclusion, since N_{p_x} and N_{p_y} are independent variables in eq 2-6.) The actual magnitude of η will depend on its sensitivity to nonbonding interactions of the p_x and p_y orbitals with the nearby atoms, but the reduction of N_{p_y} from 2 is small, compared to that for N_{p_z} (due to the σ interaction), which would seem to indicate that any interaction of the p_y orbital with Pt d orbitals is very small and approximately constant. Consequently, $e^2qQ \propto -\sigma$ (since $(e^2q^{127}Q)_{\text{at}}$ is negative) and the e^2qQ values measured will reflect the covalent character of the platinum-iodine bond.²¹ Thus from Table II (L is a neutral or anionic ligand), e^2qQ is largest (least negative) and σ smallest for L = Me, and e^2qQ is most negative and σ greatest for L = I. Parish has reported⁶ the e^2qQ values for *trans*-[HIPtP₂] as -792 MHz for P = Ph₃P and -779 MHz for P = Et₃P. It is reasonable to assume that e^2qQ for P = Me₂PhP will lie between these values. From this result, and those which we report, the order of the trans influence for the series *trans*-[I(PMe₂Ph)₂PtL] is established to be L = Me > H > CF₃ > P(OMe)₃ > EtNC > P(OMe)₂Ph ~ *p*-MeO · C₆H₄ · NC > Ph₃As > Ph₃P > I. The sensitivity of the e^2qQ values to charge is not easy to determine, though the effect of positive charge will be to make e^2qQ values more negative in the cationic complexes relative to the neutral species. Until the magnitude of this effect can be evaluated, it may be preferable to formulate two separate series, so that the order of trans influence in these compounds will be Me > H > CF₃ >> I and P(OMe)₃ > EtNC > P(OMe)₂Ph ~ *p*-MeO · C₆H₄ · NC > Ph₃As > Ph₃P.

The ¹²⁹I Mössbauer technique appears to show good sensitivity in reflecting the different bonding characteristics of even closely related ligands. For example, there is a substantial difference between the e^2qQ values for the two isocyanide ligands, the alkyl isocyanide proving to be a better σ donor than the aryl isocyanide, as would be expected. Similarly, in the series with L = P(OMe)_nPh_{3-n} ($n = 0, 2, 3$), the range of e^2qQ values is relatively large (1015-1155 MHz for the 1/2 level) with the σ donor ability of the phosphine ligand increasing regularly as the number of methoxy groups on the phosphorus atom is increased.

Parish, in his study⁶ of the compounds *cis*-[L₂Pt¹²⁹I₂], concluded that the order of trans influence for the ligands L in these compounds is Ph₃Sb < Ph₃As < Ph₃P < RPh₂P < R₂PhP < R₃P (R = Me, Et). However, in these systems, the magnitude of the iodine e^2qQ is clearly affected by both a trans and a cis influence. In other studies of these two effects, using infrared and nmr spectroscopic and X-ray crystallographic data, it has generally been concluded³ that the magnitude of the trans influence is several times greater

than the cis influence. However, the ¹²⁹I Mössbauer study⁵ of the compounds *trans*-[L₂Pt¹²⁹I₂] (L = PEt₃, R₂S, β -picoline, py, NH₃) suggested that the influence of the cis ligands on the ¹²⁹I e^2qQ parameters is comparable to that of the trans ligand. Unfortunately, this problem cannot be resolved using our data as there is little overlap in the series of ligands studied.

With reference to previous studies of the trans influence in square planar Pt(II) complexes, our results are most directly comparable with those obtained by Fryer and Smith,^{20,22} since they used ³⁵Cl and ³⁷Cl nuclear quadrupole resonance (nqr) parameters to set various ligands into their relative orders of trans and cis influences. Unfortunately, the compounds studied by these workers do not include any series in which *only* the trans influence is varying from compound to compound but do contain the series *cis*-Cl₂PtL₂ (L = py, COD, PEt₃), analogous to the iodides studied by Parish,⁶ in which both a cis and a trans influence must be considered to be varying.

We attempted to correlate our ¹²⁹I e^2qQ values with [²J(Pt-CH₃)] parameters reported^{8,11,23} for the closely related complexes *trans*-[(CH₃)Q₂PtL] and *trans*-[(CH₃)Q₂PtL], but a linear relationship was not observed. This is, perhaps, not surprising since nmr spin-spin coupling between a central metal atom and nearby ligand atoms is commonly considered³ to be dominated by a Fermi-contact mechanism, and the observed coupling constant, J , is generally interpreted as being mainly determined by the interaction of the nuclear spin with s electrons in the overlapping metal and ligand orbitals. However, the condition for optimum overlap (and thus maximum covalency as reflected by ¹²⁹I e^2qQ values) is not, in general, that the metal hybrid orbital should have maximum s character.

One useful point to note is that the order of trans influence Me > CF₃ > I is unambiguously established. In a ¹³C nmr study²⁴ of (COD)PtX₂ (X = Me, CF₃, I), the magnitude of the coupling between ¹⁹⁵Pt and the COD olefinic carbon atoms was found to be the same for X = CF₃ and Me. This is unexpected because of the large difference in electronegativity between these ligands (as reflected by the chemical shifts of the olefinic carbon signals). However, this has recently been reinterpreted²⁵ as indicating that the J values must be of opposite sign, and only coincidentally of the same magnitude. Thus the coupling constants will also reflect the order of trans influence: Me > CF₃ > I.

It might be expected that ¹²⁹I e^2qQ values would be more consistent with the order of metal-ligand infrared stretching frequencies found for a constant ligand trans to the series of ligands being studied, as these latter parameters are dependent on both the total bond covalency and the s character of the metal hybrid orbital. However, a good correlation was not observed between ¹²⁹I e^2qQ values and ν (Pt-Cl) values observed²⁶ for the series of compounds *trans*-[Cl(PEt₃)₂PtL].

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Supplementary Material Available. The method for statistically estimating the errors in e^2qQ and η values is outlined in an appendix which will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24X reduction, negatives) containing all of the supplementary ma-

terial for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-7208.

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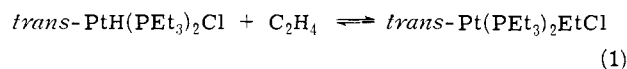
Kinetics and Mechanism of the Reaction of Methyl Acrylate with *trans*-Bis(triethylphosphine)hydridoplatinum(II) Nitrate

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Abstract: The kinetics of the reaction of HPt(PET₃)₂(NO₃) with methyl acrylate (OI) have been examined. The kinetic features have been interpreted in terms of the mechanism HPt(PET₃)₂NO₃ + OI = HPt(PET₃)₂(OI)⁺ + NO₃⁻ (*K*₁), HPt(PET₃)₂(MeOH)⁺ + OI = HPt(PET₃)₂(OI)⁺ + MeOH (*K*₂), HPt(PET₃)₂(OI)⁺ → RPt(PET₃)₂⁺ (*k*₃), RPt(PET₃)₂⁺ + NO₃⁻ = RPt(PET₃)₂NO₃, which yields a rate law $d[\text{RPt}(\text{PET}_3)_2(\text{NO}_3)]/dt = k_3 K_1 K_2 [\text{OI}][\text{Pt}]_T / (K_2 [\text{NO}_3^-] + K_1 [\text{MeOH}] + K_1 K_2 [\text{OI}])$. Values of *k*₃, *K*₁, and *K*₂ have been determined to be (5.4 ± 0.6) × 10⁻² sec⁻¹, (8.2 ± 0.9) × 10⁻², and 90 ± 17, respectively. A kinetic isotopic effect of 1.34 ± 0.06 was observed for *k*₃ (H)/*k*₃ (D). Evidence for a four-coordinate cationic intermediate, HPt(PET₃)₂(OI)⁺, is presented.

The catalytic hydrogenation and isomerization of olefins by metal complexes have been extensively studied.¹ It is generally believed² that one of the key steps in such processes is the insertion of the unsaturated molecule into the metal-hydrogen bond. Platinum(II) hydrides are particularly suitable for the studying of these types of insertion reactions, primarily because of the stabilities of the hydride and the resulting alkyl complexes. Thus far two general trends, pertinent to a consideration of the ease of the insertion reaction, have emerged. (i) The presence of catalytic amounts of a strong π -acceptor such as SnCl₂ effectively catalyzes the formation of the alkyl complex. Thus, in the absence of any catalyst, eq 1 is established under rather vigorous



conditions (95° and 80 atm),³ whereas in the presence of 1 mol % of tin(II) chloride, the equilibrium is established within 30 min at 25° and 1 atm.⁴ It has been proposed^{5,6} that the π -acceptor strength and the considerable trans influence of the SnCl₃⁻ ligand promote the formation

of a five-coordinate intermediate and the weakening of the Pt-H bond, thus enhancing the insertion reaction. Such five-coordinate intermediates (e.g., Pt(PPh₃)₂H(SnCl₃)-(C₈H₁₆)) have actually been isolated.⁷ Spectroscopic measurements indicate that both a Pt-H bond and a π bonded octene ligand are present in this compound. Kinetic measurements⁸ on reaction 1 in the presence of SnCl₂ as catalyst also support a mechanism involving a five-coordinate species, HPt(PET₃)₂(SnCl₃)(C₂H₄), as the insertion intermediate. (ii) The presence in the hydrido complex of a ligand labile to substitution greatly facilitates the insertion reaction. Thus, in the presence of Ag⁺, *trans*-HPt(PR₃)₂X (X = Cl or Br; PR₃ = PPh₃, PPh₂Me, PPhMe₂, or PET₃) reacts rapidly with olefins forming the corresponding alkyl complexes.⁹ Facile insertion also occurs when X is a good leaving group such as NO₃⁻ (eq 2).^{9,10} A four-coordi-

