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Carbon-13 Nuclear Magnetic Resonance Studies of Platinum(II)–Olefin Bonds

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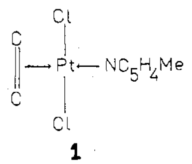
^{13}C NMR data are reported for the series of platinum(II) compounds *trans*-$[(olefin)PtCl_2(NC_5H_4Me)]$, $K[(olefin)PtCl_3]$, and $[(olefin)PtCl(NH_3)_2]BF_4$ (where olefin may be *p*-$YC_6H_4CH{=}CH_2$, $RCH{=}CH_2$, $RHC{=}CHR$, or $CH_2{=}CH(CH_2)_nX$). The observed trends in $^1J^{195}Pt-^{13}C$ and δ_C values of the olefinic carbon atoms are discussed in terms of the nature of olefin–platinum(II) bonding. The data can be rationalized qualitatively using a valence-bond description of the bonding. In terms of the Chatt–Dewar model of the bonding, the data support the view that donation from olefin π to a platinum σ orbital is the predominant component of the olefin–metal bond. The data also illustrate the varied effects of olefin substituents on the nature of platinum(II)–olefin bonds.

Introduction

Recent years have seen a rapid growth in the application of ^{13}C NMR to bonding and structural studies in organometallic chemistry. While ^{13}C NMR investigations of π-bonded olefin–transition metal complexes are now commonplace,[1–21] there is still considerable uncertainty and controversy concerning the unusual magnitudes of the ^{13}C coordination chemical shifts of olefins and the possible relationship with π-back-bonding effects.[2,3,5,16,17,20–22] Recent studies of organoplatinum compounds clearly emphasize the importance of systematic studies of closely related series of compounds and the added advantages of studying systems where both olefinic carbon shieldings and metal–olefinic carbon coupling constant data are available.[2–6]

In this paper we report a systematic ^{13}C NMR spectroscopic study of both functionally substituted olefins and simple alkenes coordinated to platinum(II) in the three series of complexes **1–3**. These series provide examples of olefin coordination to neutral, anionic, and cationic platinum(II).



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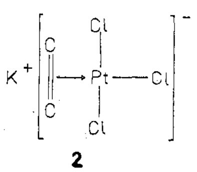

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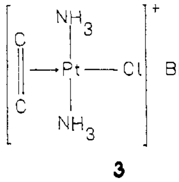

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In view of the extensive studies by Orchin and others of complexes of type **1** and thus the available literature data[23–31] the major portion of our studies has been confined to series **1** compounds with anionic **2** and cationic **3** analogues being studied for particularly interesting cases.

Very few of the previously reported ^{13}C NMR studies have concentrated on the effects of functional substitution of the olefin on coordination chemical shifts and metal–carbon coupling constants.[4,5,21]

Experimental Section

Complexes of the type *trans*-$[(olefin)PtCl_2(NC_5H_4Me)]$ were prepared using the method of Orchin et al.[23] The anionic complexes $K[(olefin)PtCl_3]$ were prepared via the method of Saika et al.[32] The cationic derivatives *trans*-$[(olefin)PtCl(NH_3)_2]BF_4$ were prepared according to the method of Gel'fman and co-workers[33] with the exception that we have used $AgBF_4$ in place of $AgNO_3$ and used acetone as the solvent in lieu of water. Acetone–dichloromethane was found to be an excellent solvent for the recrystallization of these compounds.

The ^{13}C NMR spectra were measured on either a Varian XL-100-15 or a Varian CFT-20 spectrometer operating in the Fourier transform mode at 25.2 and 20.0 MHz, respectively. All spectra were determined with noise-modulated proton decoupling. Proton-coupled spectra were recorded where necessary for assignment purposes. In order to obtain accurate $^1J_{PtC}$ values it was frequently necessary to recrystallize the type **1** complexes several times in order to ensure that the samples contained no excess picoline.[28,29] The observation of well-resolved ^{195}Pt satellite resonances for the β carbon of the coordinated picoline indicated that picoline exchange was slow on the NMR time scale. In most cases the effect of repeated recrystallizations was an increase in $^1J^{195}{}_{Pt-olefinic}\ {}^{13}C$ values of ca. 1 Hz.

Results and Discussion

^{13}C NMR data for a variety of simple alkenes coordinated to the "*trans*-$PtCl_2(NC_5H_4Me)$" moiety (type **1** complexes) are tabulated in Table I. Corresponding data for series of para-substituted styrenes coordinated to either type **1** complexes or to type **2** ($PtCl_3^-$) or type **3** (*trans*-$PtCl(NH_3)_2^+$) are given in Table II. Table III contains the data for complexes of functionally substituted olefins generally of the type $CH_2{=}CH(CH_2)_nX$ where X is an electronegative substituent (e.g., OH, OMe, OPh, Cl) and $0 \leq n \leq 4$. Table IV lists a few examples of olefins, other than styrenes, coordinated to type **2** or type **3** complexes.

Complexes of Simple Alkenes. Upon coordination, upfield shifts ($\Delta\delta_C$) ca. 30–55 ppm are observed for the olefinic carbon atoms of the simple alkenes. Platinum–olefinic carbon coupling constants are in the range ca. 150–160 Hz.

For complexes of cis- or trans-1,2-dialkyl-substituted olefins, values of $^1J_{^{195}Pt-^{13}C}$ of ca. 150–160 Hz and upfield shifts $\Delta\delta_C$ of ca. 30–37 ppm are observed for the olefinic carbons. The only noticeable difference between complexes of the cis-1,2- and trans-1,2-disubstituted olefins is to be found in the platinum-195 coupling to the α and β carbons of the alkyl side chains. For example, for the cis-1,2-disubstituted olefins $^2J_{Pt-C^\alpha}$ is ca. 15–22 Hz; for the complexes of the corresponding trans olefins $^2J_{Pt-C^\alpha}$ is larger, ca. 26–35 Hz. The different magnitudes of $^2J_{Pt-C^\alpha}$ for complexes of cis or trans olefins probably reflect either a distortion about the Pt–olefin bond which is only possible for the trans olefins (i.e., a preferred orientation of the olefin away from one that is perpendicular to the coordination plane) or a distortion about the C=C axis of the double bond which may occur with complexes of the cis olefins (rotation of substituents away from the metal). Such distortions have been previously postulated to account for $^2J_{Pt-C-H}$ data for complexes of this type[31,34,35] and receive some corroborative support in the solid state from x-ray structural studies.[36,37] Distortions of this type, if present, are not reflected by the $^1J_{Pt-C}$ values for the coordinated olefinic carbons. This is consistent with the current view that $^1J_{Pt-C}$ coupling constants are dominated by the Fermi contact term[38,39] and, while sensitive to changes in trans ligands and rehybridization at carbon, are probably not very sensitive to distortions of the type mentioned.

Platinum coupling to the β carbon of an alkyl side chain varies from ca. 0 for coordinated cyclopentene and cyclohexene through values of 30–40 Hz (linear alkenes) to ca. 40 Hz for coordinated cycloheptene and cyclooctene. This wide variation clearly indicates a marked conformational dependence with respect to the magnitude of $^3J_{Pt-C^\beta}$ with $^3J_{Pt-C^\beta}$ being ca. 0 when C^β is oriented close to the coordinate plane. While a detailed explanation is not readily apparent, conformational dependence for three-bond platinum coupling constants has been previously observed for $^3J_{Pt-P-C-H}$ in $[(Me_2PhP)PtI(O_2CR)]_2$.[40] Platinum coupling to C^γ or subsequent carbons in alkyl side chains has not been observed for any of the simple alkenes.

For a series of cyclic olefin complexes of type **1** the $\Delta\delta_C$ and $^1J_{Pt-C}$ values for the olefinic carbons are noticeably less for cyclopentene (29.8 ppm and 150 Hz) and cyclohexene (32.0 ppm and 146 Hz) relative to those of the cycloheptene (36.6 ppm and 162.7 Hz) and cyclooctene (36.1 ppm and 161.8 Hz) complexes. The lower values of $\Delta\delta_C$ and $^1J_{PtC}$ may well reflect a weaker olefin–Pt bond. X-ray structural studies of $[Pt_2Cl_4(olefin)_2]$ (olefin = cyclopentene or cycloheptene) have shown the Pt–C(olefin) distances in the cyclopentene complex to be 2.20 (1) Å—a value 0.08 Å (3σ) greater than the mean value of the Pt–C(olefin) distance (2.12 Å) reported for the cycloheptene complex.[41] The type **1** complexes of terminal alkenes of general formula *trans*-$[(RCH_2C^2H{=}C^1H_2)PtCl_2(NC_5H_4Me)]$ (R = alkyl) have very similar ^{13}C NMR parameters, typically $^1J_{Pt-C^1} \approx 160$ Hz, $^1J_{Pt-C^2} \approx 157$ Hz, $^2J_{Pt-C^\alpha} \approx 21$–$24$ Hz, $^3J_{Pt-C^\beta} \approx 30$–$35$ Hz, $\Delta\delta_{C^1} \approx 44.5$ ppm, and $\Delta\delta_{C^2} \approx 35.5$ ppm.

The data of the *tert*-butylethylene complex *trans*-$[(Me_3CCH{=}CH_2)PtCl_2(NC_5H_4Me)]$ deviate considerably from this general pattern of behavior. The lower $^3J_{Pt-C^\beta}$ (20.4 Hz) for this complex probably reflects the expected conformational dependence, i.e., at least one of three C^β's must be oriented close to the coordination plane for which a much smaller coupling constant is expected (cf. $^3J_{PtC} \approx 0$ for the analogous cyclopentene complex). A particularly odd feature is that $^1J_{Pt-C}$ for the *tert*-butyl-substituted olefinic carbon C^2 (152.5 Hz) is slightly greater than that observed for C^1 (147 Hz) although the observed coordination shifts $\Delta\delta_{C^1} = 44.7$ ppm and $\Delta\delta_{C^2} = 33.0$ ppm are reasonably consistent with the general pattern. The data for the propene complex *trans*-$[(CH_3CH{=}CH_2)PtCl_2(NC_5H_4Me)]$ are also slightly out of line relative to the general trends in that $^1J_{Pt-C^2}$ is 151 Hz which is ca. 6 Hz less than that observed for the 1-butene, 1-hexene, 5-methylhex-1-ene, 4-methylpent-1-ene, and 4,4-dimethylpent-1-ene analogues. In fact, a comparison of complexes with methyl olefinic substituents with the analogous complexes with ethyl olefinic substituents indicates that a slightly lower $^1J_{Pt-C}$ value for the methyl-substituted olefinic carbon ($\sim$151 Hz) relative to its "ethyl analogue" ($\sim$158 Hz) may be a general observation (see Table I). While a rationalization of this observation is not readily available, it should be noted that replacement of a methyl substituent with an ethyl substituent frequently increases the stability of the olefin–metal bond.[42,43] Correlations of this type are *not* apparent in the corresponding $\Delta\delta_C$ data. Brown et al.[11] have previously commented on the possible significance of the coordination chemical shifts of coordinated propene. It was suggested that larger mean upfield coordination chemical shifts and smaller values of $(\delta_{C^2} - \delta_{C^1})$ would be indicative of increased π back-bonding. A smaller value for $(\delta_{C^2} - \delta_{C^1})$ for increased π back-bonding is anticipated on the basis that the chemical shifts of saturated "sp^3 C atoms" are less sensitive to methyl substitution of H relative to an olefinic "sp^2 atom". Furthermore, on going from ethylene to propene in $[(olefin)_2Rh(acac)]$ complexes (acac = acetylacetonate) the value of $\Delta\delta_C$ of the double-bond carbons decreases from 85.8 ppm to a mean value of 57.6 ppm, respectively. This reduction has been ascribed to an expected relative decrease in π back-bonding for the propene complex.[21]

A similar consideration of *trans*-$[(olefin)PtCl_2(NC_5H_4Me)]$ complexes shows that the mean values of $\Delta\delta_C$ for the propene complex (39.8 ppm) and for the hex-1-ene complex (40.20 ppm) are closer to that of the ethylene complex (47.3 ppm). A comparison of the $\Delta\delta_C$ values and $(\delta_{C^2} - \delta_{C^1})$ for the propene complex of type **1** with the values reported by Brown et al.[11] is given in Table V. In view of the similarity of the $\Delta\delta_C$ values of the ethylene and propene type **1** complexes and the large value of $(\delta_{C^2} - \delta_{C^1})$ (cf. data for $[Ag(propene)_2]^+$ with those of *trans*-$[(CH_3CH{=}CH_2)PtCl_2(NC_5H_4Me)]$) one would have to conclude on the basis of Brown's criteria that either (i) π back-bonding is not a major parameter in the bonding of alkenes to "$PtCl_2(NC_5H_4Me)$" or (ii) π back-bonding in olefin–platinum(II) compounds is not reflected very strongly by trends in the ^{13}C data or (iii) both (i) and (ii).

Previous studies[2,5] lend considerable support to conclusion (iii) with respect to the ^{13}C NMR data for platinum(II)–olefin complexes. Previous observations of parallel trends in the shielding of the σ-bonded carbons C^1 and the olefinic carbons C^2 and C^3 in complexes of type **4**[5] and the two analogous series of complexes **5** (*trans*-$[CH_3Pt(As(CH_3)_3)_2L]^+$) and **6**[2] strongly suggest that a major and possibly predominant

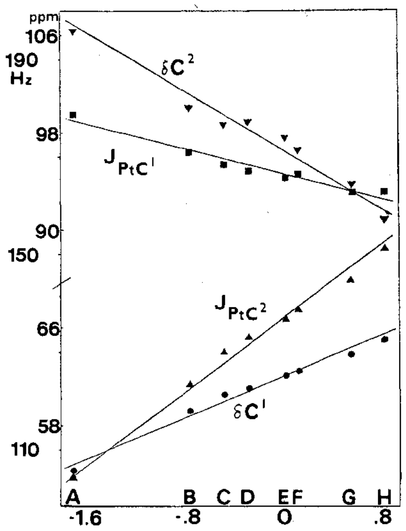


Figure 1. Plots of δ and $^1J_{^{195}Pt-^{13}C}$ of the vinylic carbons of $[(p\text{-}CH_3C_5H_4N)PtCl_2(p\text{-}Y\text{-}sty)]$ vs. Brown's σ_p^+ constants for Y: δ_{C^1}, ●; $^1J_{^{195}Pt-^{13}C^1}$, ■; δ_{C^2}, ▼; $^1J_{^{195}Pt-^{13}C^2}$, ▲ (A = $N(CH_3)_2$, B = OCH_3, C = OC_6H_5, D = CH_3, E = H, F = Cl, G = $COCH_3$, H = NO_2).

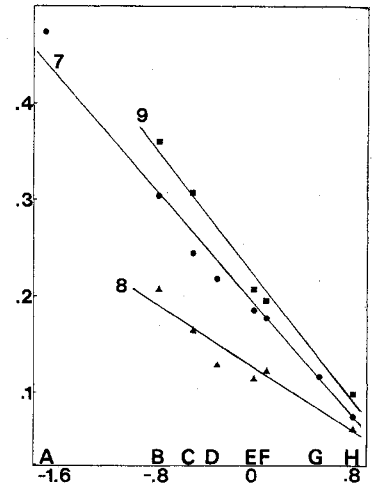
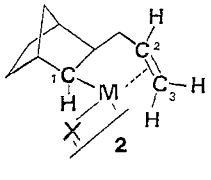


Figure 2. Plot of $[(^1J_{^{195}Pt-^{13}C^1}) - {}^1J_{^{195}Pt-^{13}C^2})]/[\text{average } ^1J_{^{195}Pt-^{13}C} \text{ (for Y} = NO_2)]$ vs. σ_p^+ for complexes 7 (●), 8 (▲), and 9 (■) (A = $N(CH_3)_2$, B = OCH_3, C = OC_6H_5, D = CH_3, E = H, F = Cl, G = $COCH_3$, H = NO_2).



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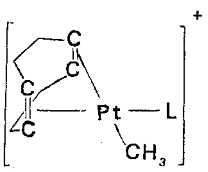

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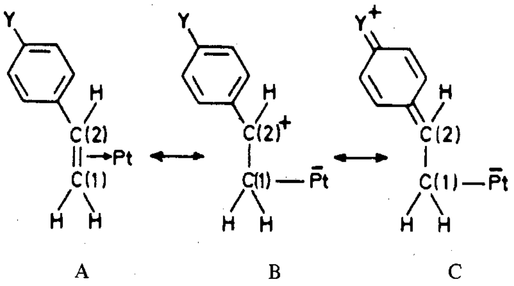


Figure 3. Valence bond representations of the styrene–platinum(II) bonding.

component of the observed changes in the ^{13}C NMR parameters of these closely related series of platinum(II) complexes may be accounted for in terms of nonbonding paramagnetic and/or diamagnetic neighbor anisotropy effects associated with platinum. Such correlations are understandable if the major component in alkene–platinum(II) bonding is filled olefin π to empty metal σ donation.

Para-Substituted Styrene Complexes.[44] The ^{13}C NMR data for the series of complexes *trans*-$[(p\text{-}YC_6H_4CH{=}CH_2)PtCl_2(NC_5H_4Me\text{-}p)]$ (7) {Y = NMe_2, OEt, OPh, Me, H, Cl, COMe, NO_2}, $K[(p\text{-}YC_6H_4CH{=}CH_2)PtCl_3]$ (8), and *trans*-$[(p\text{-}YC_6H_4CH{=}CH_2)PtCl(NH_3)_2]BF_4$ (9) {Y = OEt, OPh, Me, H, Cl, NO_2} are tabulated in Table II. Plots of $^1J_{Pt-C}$ and δ_C (the chemical shift of the coordinated olefinic carbons) for C^1 and C^2 of 7–9 vs. Brown's σ_p^+ constants for Y gave reasonably linear correlations (e.g., see Figure 1). Figure 2 illustrates the linear σ_p^+ correlations obtained for $\Delta^1J_{Pt-C}/J_{mean(Y=NO_2)}$ (the difference between $^1J_{PtC^1}$ and $^1J_{PtC^2}$ for a given Y divided by the mean $^1J_{PtC}$ value of the *p*-nitrosytrene analogue). Values of $^1J_{C-H}$ for a representative selection of olefinic C–H bonds in complexes of type 7 is given in Table II. $^1J_{C-H}$ values of the coordinated styrenes are rather insensitive to changes in the nature of the para substituent Y. They are also slightly larger than the values found for the uncoordinated styrene.

By comparison with the previously reported ^1H NMR data for the series of compounds of structure 8,[32] it is apparent that the ^{13}C NMR spectra of coordinated styrenes are far more sensitive to changes in Y than the corresponding ^1H NMR spectra. The following trends are clearly apparent in the data (see Figure 1): (i) for each styrene in the three series of complexes $^1J_{Pt-C^1} > {}^1J_{Pt-C^2}$, $\delta_{C^1} < \delta_{C^2}$ (i.e., C^1 is more shielded) and $\Delta\delta_{C^1} > \Delta\delta_{C^2}$; (ii) the differences in the NMR parameters of C^1 and C^2 are greatest for electron donor Y groups and least for electron acceptor Y groups; (iii) $^1J_{Pt-C}$ and δ_C of C^2 are more sensitive to changes in Y than are the C^1 values; (iv) electron donor Y groups decrease markedly both the shielding of C^2 and $^1J_{Pt-C^2}$ while increasing both the shielding of C^1 and $^1J_{Pt-C^1}$; (v) Δ^1J_{Pt-C} for a given styrene decreases in the order complex 9 > 7 > 8; (vi) the slopes of the plots of $\Delta J/J_{mean(Y=NO_2)}$ vs. σ_p^+ (Figure 2) also decrease in the order 9 > 7 > 8. Polarization of the olefin π electrons by Y, as represented by the VB (valence-bond) representations A, B, and C (Figure 3) provides a reasonable rationalization of (i)–(vi). Electron donor Y groups would increase the percent contribution of B and/or C to the overall styrene–platinum bonding. It is a reasonable assumption that for B and C, $^1J_{Pt-C^1} \gg {}^1J_{Pt-C^2}$ and $\Delta\delta_{C^1} > \Delta\delta_{C^2}$. Thus as the π-donor ability of Y increases, the equilibrium position of Pt relative to the styrene C=C bond will lie closer to C^1. This will result in an increase in the shielding of C^1 and will also increase $^1J_{Pt-C^1}$ owing to an increase in Fermi contact (s-orbital overlap). Concomitantly the shielding of C^2 and $^1J_{Pt-C^2}$ will decrease.

Previously Ray et al.[49] have reported a good linear correlation between the δ_{C^1} values for the trityl carbonium ions $[(p\text{-}YC_6H_4)_3C^1]^+$ and the σ_p^+ constants of Y. The three series of styrene complexes studied provide data for complexation to cationic platinum(II) 9, neutral platinum(II) 7, and anionic platinum(II) 8. While the absolute magnitude of $^1J_{Pt-C^1}$ and $^1J_{Pt-C^2}$ will be a function of several factors and will be particularly sensitive to the nature of the trans ligand, it is a reasonable assumption that the ratio $\Delta J/J_{mean(Y=NO_2)}$ will be more indicative of the extent of polarization (ionic contributions) within the three series of compounds. For a given styrene decreasing the electron density on the platinum should result in increased ionic contributions to the styrene–platinum bond and hence a larger $\Delta J/J_{mean}$ ratio. This rationalization is consistent with the magnitude of the observed values (see Figure 2) which decrease in the order 9 (cationic) > 7 (neutral)

Table I. ^{13}C NMR Data for Complexes of Type **1**, (olefin)PtCl$_2$(p-CH$_3$-C$_5$H$_4$N) in CDCl$_3$^{a,h}

	Vinylic carbons						Carbons in olefin substituents (R)^c					C^β of p-CH$_3$-C$_5$H$_4$N^d
	=CH$_2$			=CHR			C^α		C^β		C^γ, etc.	
Olefin	δ_{C^1}	$\Delta\delta^b{}_{C^1}$	$^1J_{^{195}Pt-^{13}C^1}$	δ_{C^2}	$\Delta\delta^b{}_{C^2}$	$^1J_{^{195}Pt-^{13}C^2}$	$\delta_{C\alpha}$	$^2J_{^{195}Pt-^{13}C\alpha}$	$\delta_{C\beta}$	$^3J_{^{195}Pt-^{13}C\beta}$	$\delta_{C\gamma}$	$^3J_{^{195}Pt-^{13}C\beta}$
Ethylene^g	75.05	47.35	164.4									37.5
Propene^g	71.54	43.46	158.9	99.20	36.10	151.3	21.20	23.3				36.6
But-1-ene^g	69.52	42.88	160.0	105.06	34.24	157.9	28.11	23.2	14.06	36.4		35.9
cis-But-2-ene^g				90.75	32.95	149.8	15.60	21.6				*e*
trans-But-2-ene^g				92.69	30.41	152.0	20.42	34.0				*e*
Hex-1-ene	69.61	44.54	159.9	103.40	35.83	157.0	34.23	21.9	31.37	33.7	22.10; 13.74	36.0
cis-Hex-3-ene				95.71	35.33	155.8	22.65	20.1	13.33	32.5		35.8
trans-Hex-3-ene				97.11	33.90	161.0	27.46	28.4	14.39	39.7		35.6
4-Methylpent-1-ene	70.49	45.01	159.6	102.20	35.77	157.4	43.62	22.0	28.52	31.7	23.14,^{f} 21.66^f	36.9
5-Methylhex-1-ene	69.80	44.15	160.1	103.98	35.38	156.4	32.79	23.3	38.66	33.2	23.90; 22.83,^{f} 22.25^f	35.6
3,3-Dimethylbut-1-ene	64.18	44.73	146.8	116.62	33.05	152.0	35.56	17.7	29.59	20.4		37.0
4,4-Dimethylpent-1-ene	71.29	45.07	159.8	100.71	35.40	158.4	48.20	21.2	31.46	30.0	29.41	37.0
Cyclopentene				100.95	29.78	150.0	32.47	17.9	23.07			37.3
Cyclohexene				95.04	32.02	146.0	26.80	14.9	21.32			37.6
Cycloheptene				95.63	36.59	162.7	28.24	16.1	24.64	39.0	32.99	34.0
Cyclooctene				93.84	36.13	161.8	28.0	17.6	29.23	43.8	26.21	34.2

[a] δ's in ppm relative to internal TMS; J's in Hz. [b] $\Delta\delta$ is the upfield shift from the free olefin. [c] Whenever possible these assignments were made on the basis of ^{1}H-coupled spectra. For cases where this did not distinguish C^α from C^β assignments were made on the basis of platinum coupling. In every case where an unambiguous assignment could be made (including several examples in Table III) $^3J_{^{195}Pt-^{13}C\beta} > {}^2J_{^{195}Pt-^{13}C\alpha}$. [d] Complete data for p-CH$_3$-C$_5$H$_4$N is not given because the parameters do not change as the olefin is varied. Representative data for ethylene are $\delta_{C\alpha}$ 150.51, $^2J_{^{195}Pt-^{13}C}$ = 12.3; $\delta_{C\beta}$ 126.20, $^3J_{^{195}Pt-^{13}C}$ = 37.5; $\delta_{C\gamma}$ 152.74; δ_{CH_3} 21.38. [e] ^{195}Pt satellites were apparent but too broad to report a meaningful value for the coupling constant. [f] The two methyl carbons in the configuration –CH(CH$_3$)$_2$ become nonequivalent upon complexation of the olefin. [g] Data for free olefin are from D. E. Dorman, M. Jautelat, and J. D. Roberts, *J. Org. Chem.*, **36**, 2757 (1971). [h] Changes in $^1J_{^{13}C-^1H}$ were found to be relatively small, and, hence, these data are not recorded. Typically $^1J_{^{13}C-^1H}$ for the vinylic carbons was ca. 160 Hz (usually there was a slight increase from the values for the free olefins).

Table II. ^{13}C NMR Data for Para-Substituted Styrenes Coordinated to Platinum(II)^a (Tabulated in Order of Increasing $\sigma_p{}^+$ of Y)

	=CH$_2$			=CHR			$C^{\alpha c}$		$C^{\beta c}$		$C^{\gamma c}$	$C^{\delta c}$		C^β of p-CH$_3$-C$_5$-H$_4$N^b
Y	δ_{C^1}	$\Delta\delta_{C^1}$	^1J-$_{^{195}Pt-^{13}C^1}$	δ_{C^2}	$\Delta\delta_{C^2}$	^1J-$_{^{195}Pt-^{13}C^2}$	$\delta_{C\alpha}$	^2J-$_{^{195}Pt-^{13}C\alpha}$	$\delta_{C\beta}$	^3J-$_{^{195}Pt-^{13}C\beta}$	$\delta_{C\gamma}$	$\delta_{C\delta}$	Y^c δ	$^3J_{^{195}Pt-^{13}C}$
							7, *trans*-(p-Y-sty)PtCl$_2$(p-CH$_3$-py) in CDCl$_3$							
N(CH$_3$)$_2$^{d}	54.44	54.86	178.9	106.36	30.31	104.6	122.04	36.3	132.04	15.7	111.33	151.74	CH$_3$, 40.00	37.5
OCH$_2$CH$_3$	59.09	52.08	171.1	100.65	35.46	123.4	127.41	*f*	131.72	12.2	114.36	160.64	CH$_2$, 63.46; CH$_3$, 14.74	37.4
OC$_6$H$_5$	60.51	52.28	168.4	98.60	37.44	130.0			131.67	12.6	117.71	159.20	C$_6$H$_5$, 155.89, 129.73, 124.04, 119.79	37.8
CH$_3$	60.96	52.45	167.2	98.84	38.01	132.9	132.55	36.4	129.92	12.3	129.20	140.39	CH$_3$, 21.61	38.0
H	62.09	51.64	165.8	97.59	39.34	136.7	135.40	36.2	129.92	12.0	128.37	128.37		38.6
Cl	62.37	51.96	166.6	95.55	40.10	138.6	133.99	36.6	131.06	13.0	128.66	135.85		38.0
C(O)CH$_3$	63.87	52.04	162.8	93.70	42.37	144.4	140.46	~35	129.89		128.26	137.36	C(O), 197.87; CH$_3$ 25.22	38.9
NO$_2$^{e}	65.02	53.40	162.7	90.85	44.01	150.9	142.59	36.2	130.44	12.6	123.49	147.98		40.0
trans-β-CH$_3$-sty {C^1, CH$_3$	84.03		158.1				20.31	31.4						37.1
trans-β-CH$_3$-sty {C^2, C$_6$H$_5$				93.24		135.2	136.03	44.4	129.09	14.0	128.42	128.42		

							8, $K^+[(p\text{-Y-sty})PtCl_3]^-$ in Acetone-d_6						
OCH_2CH_3	56.56	54.61	201.0	88.01	48.10	162.2	130.21	*f*	131.67	13.5	114.86	159.98	CH_2, 63.99; CH_3, 15.06
OC_6H_5	57.52	55.27	198.9	86.23	49.81	168.0	133.20	~40	131.84	13.6	118.65	158.11	C_6H_5, 130.76, 124.43, 119.92
CH_3	57.91	55.50	196.0	86.52	50.33	171.9			130.95		129.48	138.17	CH_3, 21.28
H	58.01	55.72	195.4	86.03	50.90	173.7	138.38	*f*	130.28	15.6	128.81	128.81	
Cl	58.49	55.83	197.4	84.01	51.64	174.4	133.79	*f*	131.54		128.82	137.40	
NO_2	59.79	58.63	192.7	80.93	53.93	181.0	146.08	*f*	131.02	~14	123.71	147.55	
							9, $[trans\text{-}(p\text{-Y-sty})Pt(NH_3)_2Cl]^+BF_4^-$ in Acetone-d_6						
OCH_2CH_3	58.49	52.68	201.0	92.14	43.97	138.4	127.90	39.6	130.80		116.53	161.65	CH_2, 64.35; CH_3, 14.97
OC_6H_5	59.18	53.61	197.6	90.33	45.71	144.0							
H	60.35	53.38	190.8	89.88	47.05	154.6	137.63	*f*	130.76		129.11	129.11	
Cl	60.10	54.22	187.7	87.89	47.76	153.5	134.65	~40	130.35		130.35	135.94	
NO_2	62.51	55.91	182.8	85.43	49.43	165.3	143.11	*f*	130.30	~14	125.54	149.22	

[a] See Table 1, footnote *a*. [b] See Table 1, footnote *d*. [c] Assignments based on those for the free styrenes; see ref 47. [d] $^1J_{^{13}C-^1H}$ for =CHR 159.2 Hz; average value for =CH_2 157 Hz. [e] $^1J_{^{13}C-^1H}$ for =CHR 161.4 Hz; average value for =CH_2 158 Hz. [f] C^α has a relatively long relaxation time resulting in a week signal for which the ^{195}Pt satellites were unobserved.

Table III. ^{13}C NMR Data for Complexes of Type **1**, (olefin)$PtCl_2(p\text{-}CH_3\text{-}C_5H_4N)$ in $CDCl_3$[a]

Olefin	Vinylic carbons						Carbons in olefin substituents (R)[c]					C^β of $p\text{-}CH_3\text{-}C_5H_4N$[d]
	=CH_2			=CHR			C^α		C^β		C^γ, etc., δ	
	δ_{C^1}	$\Delta\delta^b{}_{C^1}$	$^1J_{^{195}Pt-^{13}C^1}$	δ_{C^2}	$\Delta\delta^b{}_{C^2}$	$^1J_{^{195}Pt-^{13}C^2}$	$\delta_{C\alpha}$	$^2J_{^{195}Pt-^{13}C\alpha}$	$\delta_{C\beta}$	$^3J_{^{195}Pt-^{13}C\beta}$		$^3J_{^{195}Pt-^{13}C}$
Vinyl methyl ether[f]	44.44	38.76	193.1	144.16	8.14	88.4					CH_3, 60.73	35.7
Allyl methyl ether	70.64	46.21	157.8	93.02	41.88	175.2	72.46	21.0			CH_3, 58.59	37.2
But-3-enyl methyl ether	71.22	45.19	158.7	98.93	36.37	161.7	34.84	22.7	71.38	34.3	CH_3, 58.70	36.7
Pent-4-enyl methyl ether	70.02	44.71	159.4	102.58	35.72	158.7	31.40	23.2	29.34	32.8	71.90; CH_3, 58.50	36.1
Hex-5-enyl methyl ether	69.96	44.30	159.6	102.91	35.51	158.0	34.31	22.8	26.05	34.2	29.15; 72.36; CH_3, 58.49	35.8
Vinyl acetate	52.86	44.53	164.5	111.08	30.45	171.0					CH_3, 21.30; CO_2, 167.96	37.2
Allyl acetate	71.33	46.81	154.8	89.29	43.13	181.6	64.02	17.8			CH_3, 21.35; CO_2, 170.42	39.6
But-3-enyl acetate	71.47	45.61	159.8	96.57	37.40	165.9	33.50	22	62.99	34.8	CH_3, 21.29; CO_2, 170.89	37.0
Pent-4-enyl acetate	70.41	44.89	160.0	101.47	36.10	161.9	31.06	21.8	28.42	31.4	CH_3, 21.29	36.2
Hex-5-enyl acetate	70.12	44.43	160.1	102.24	35.78	160.2	34.10	21.6	26.09	35.0	CH_3, 21.49	35.6
Allyl alcohol	67.36	47.74	155.5	100.27	37.27	159.3	63.40	24.1				*e*
1-Buten-4-ol	71.45	45.63	158.6	99.11	36.02	160.5	37.54	22.9	61.55	34.2		*e*
1-Penten-5-ol	69.51	45.33	159.3	102.25	36.12	157.3	29.81	22.6	31.45	26.9	61.03	35.9
1-Hexen-6-ol	69.80	44.46	159.2	102.78	35.64	158.6	33.81	22.7	25.15	33.2	31.75; 61.79	36.2
3-Methylbuta-1,2-diene	35.84	36.79	112.2	157.73	49.51	277.5	110.00	36.9	23.51, 20.69	41.5, 42.6		*e*
4-Methylpenta-1,3-diene	61.55	53.05	172.2	98.41	28.06	119.8	126.18	44.2	159.06		26.57, 18.75	35.4
5-Methylhexa-1,4-diene	69.32	44.83	160.1	101.38	36.19	157.7	33.89	21.6	120.61		36.89; 134.47; 25.78, 18.15	35.3
Allylbenzene	69.16	56.41	159.2	99.82	39.98	162.7	40.34	23.5	138.32		126.40; 128.47; 128.63	36.7
Allyl chloride	66.09	52.45	145.6	90.29	43.68	175.1	42.73					37.4
Allyl phenyl ether	70.92	44.14	156.0	90.47	42.70	180.0	67.90	20.0			C_6H_5, 114.96; 121.03; 129.29; 158.35	37.3

[a] See Table I, footnote *a*. [b] See Table I, footnote *b*. [c] Assignments were made on the basis ^{1}H-coupled spectra (see Table 1, footnote *c*) as well as the distinctive chemical shifts caused by an adjacent oxygen. [d] See Table I, footnote *d*. [e] See Table I, footnote *e*. [f] Data for free olefin were from K. Hatada, K. Nugata, and H. Yuki, *Bull. Chem. Soc. Jpn.*, 43, 3195 (1970).

Table IV. ^{13}C NMR Data for Complexes of Types **2** and **3** in Acetone-d_6 [a]

Olefin	=CH$_2$ δ_{C^1}	=CH$_2$ $^1J_{^{195}Pt-^{13}C^1}$	=CHR δ_{C^2}	=CHR $^1J_{^{195}Pt-^{13}C^2}$	C$^\alpha$ $\delta_{C\alpha}$	C$^\alpha$ $^2J_{^{195}Pt-^{13}C\alpha}$	C$^\beta$ $\delta_{C\beta}$	C$^\beta$ $^3J_{^{195}Pt-^{13}C\beta}$	C$^\gamma$, etc., δ
				2, K$^+$[(olefin)PtCl$_3$]$^-$					
Ethylene	66.89	195.2							
5-Methylhex-1-ene	65.05	190.9	91.54	192.3	38.93	36.1	32.21		28.34; 23.01,[b] 22.41[b]
Allyl phenyl ether	65.16	184.9	80.30	212.2	68.41				159.53; 130.24; 121.57; 115.64
				3, *trans*-[(olefin)Pt(NH$_3$)$_2$Cl]$^+$BF$_4^-$					
5-Methylhex-1-ene	67.75	177.6	95.72	174.2	39.06	40.4	32.66	24.5	28.39; 22.83,[b] 22.40[b]
Allyl phenyl ether	64.93	170.6	87.16	188.7	68.29	27.4			158.42; 130.43; 122.59; 115.77

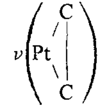
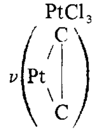
[a] See Table I, footnote *a*. [b] See Table I, footnote f.

Table V. Values of $\delta_{C^2(HCH_3)} - \delta_{C^1(CH_2)}$ and $\overline{\Delta\delta}$ for Free and Coordinated Propene in Several Transition Metal Complexes

Complex	$\overline{\Delta\delta}$, ppm	$\delta_{C^2} - \delta_{C^1}$, ppm
Propene		18.2[a]
[Ag(propene)$_2$]$^+$BF$_4^-$	3.3	29.1[a]
[Fe(C$_5$H$_5$)(CO)$_2$(propene)]$^+$CF$_3$CO$_2^-$	45.2	30.8[a]
Rh(acac)(propene)$_2$	57.6	11.4[a]
(p-CH$_3$-C$_5$H$_4$N)Pt(Cl)$_2$(propene)	39.8	27.6

[a] From ref 11.

Table VI. Selected Ir Data for Conplexes of Types **7** and **8**[a]

	7, (p-Y-sty)-PtCl$_2$(p-CH$_3$-C$_5$H$_4$N) 		**8**, K$^+$[(p-Y-sty)-PtCl$_3$]$^-$ 			
Y	Sym	Asym	Sym	Asym	ν(Pt-Cl)[b]	σ_P^+
N(CH$_3$)$_2$		480	531	507	297	−1.7
OCH$_2$CH$_3$	506	425	510	441	303	−0.78
OC$_6$H$_5$			509	426	301	−0.5
CH$_3$	482		495	400	311	−0.311
H	481	417	492	392	310	0
Cl	465	415	467	367	312	0.114
C(O)CH$_3$	458	392				0.57
NO$_2$	449	388	463		314	0.790

[a] Nujol mulls; data reported in cm^{-1}. [b] Platinum-chloride bond trans to sytrene.

> **8** (anionic) and with the observation that the sensitivity of $^1J_{Pt-C}$ to changes in Y also decreases in the same order.

For the series of styrene complexes **7** $^3J_{Pt-N-C^\beta}$ values of the coordinated picoline increase from 37.5 Hz (Y = NMe$_2$) to 40 Hz (Y = NO$_2$). While this change is a small one, it is consistent with a greater styrene trans influence and a weaker Pt–N bond for the case where Y = NMe$_2$ which is compatible with the bonding description (Figure 3) and ir data for complexes of type **8** (see below).

Support for the above rationalization of the observed ^{13}C NMR data together with an indication of the structural and electronic significance of the changes induced in the styrene–platinum bond by changes in the para substituent is to be found in the following observations:

(i) Infrared Spectroscopic Studies. Table VI contains the frequencies assigned to the more important vibrational modes. Assignment of the ν_{Pt-Cl} modes of **8** has been confirmed by comparison with the ir spectra of the corresponding bromide analogues. The two "ν_{PtC_2}-ring" modes, which are expected in the region 400–500 cm^{-1},[50] were assigned on the basis of comparisons within a series of complexes and with the spectra of the uncomplexed styrenes. Owing to the lack of a solvent suitable for the study of the ionic complexes at wavelengths below 500 cm^{-1} the ir spectra of all the complexes were run as Nujol mulls.

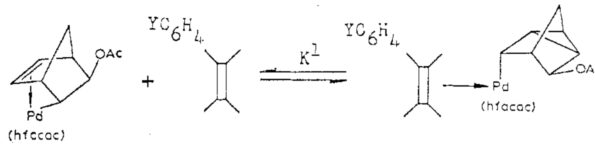
Plotting the data for ν_{Pt-Cl} and symmetric and asymmetric "ν_{PtC_2}-ring" modes against σ_p^+ gave reasonably linear correlations. As Y becomes more electron donating, ν_{Pt-Cl} (trans to styrene) for the complexes K[PtCl$_3$(p-Y-sty)] (sty = styrene) decreases from 314 cm^{-1} (Y = NO$_2$) to 297 cm^{-1} (Y = NMe$_2$). The increasing ionic nature of the styrene–platinum bond (see Figure 3), as Y becomes a better π donor, places more electron density on the metal. This results in a weakening of the trans Pt–Cl bond thereby decreasing ν_{Pt-Cl}; i.e., the styrenes exhibit an increased trans influence as Y becomes more electron donating. Increasing ionic contributions to the overall sty–Pt bond as Y becomes a better donor would imply an increase in the Pt–sty bond strength. Consistent with this is the observed increase in the ν_{PtC_2} modes as Y becomes a better donor. Again the change in ν_{PtC_2} on going from Y = NO$_2$ to Y = NMe$_2$ is considerable ($\Delta\nu_{PtC_2}$ is ca. 80–100 cm^{-1}). Vibrational modes reflective of $\nu_{C=C}$ (coordinated olefin) are difficult to identify positively in the series of complexes **7**–**9**.

(ii) pK_a Measurements. Gel'fman et al.[33] have published pK_a data for the coordinated H$_2$O in the series of complexes *trans*-[Pt(NH$_3$)$_2$(H$_2$O)(p-Y-sty)](BF$_4$)$_2$ (Y = Cl, H, OMe), i.e., for

$$[Pt(NH_3)_2(H_2O)(p\text{-}Y\text{-}sty)]^{2+} \rightleftharpoons [Pt(NH_3)_2(OH)(p\text{-}Y\text{-}sty)]^+ + H^+(aq)$$

the pK_a's are 3.18, 3.28, and 3.42 for Y = Cl, H, and OMe. The acidity of the complexes decreases in the order Y = Cl > H > OMe; i.e., as the styrene places more electron density onto the platinum, the acidity of the trans water molecule becomes less.

(iii) Equilibrium Studies of the Relative Thermodynamic Stabilities of Styrene–Palladium(II) Bonds. The assumption that increased ionic character should strengthen the sty–Pt(II) bond is supported by previously reported equilibrium studies of the complexation of styrene to norbornenylpalladium(II) hexafluoroacetylacetonate derivatives,[43] viz.



$\Delta G°$ for the reaction was found to vary linearly with σ_p^+ of Y. Good donor Y groups favor complexation of the styrene, coordination being enthalpy favored but entropy unfavored.

(iv) X-Ray Structural Studies. In 1955 Baenziger and Holder[51] reported the structural details of [Pd$_2$Cl$_4$(sty)$_2$] as determined by x-ray crystallography (see Figure 4). The structure as reported has considerable asymmetry in the sty–Pd bond with the olefinic CH$_2$ carbon atom being considerably closer to the Pd than the PhCH carbon atom. While this

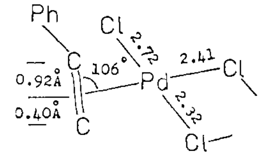


Figure 4. Pertinent crystallographic data for the dimer [(sty)-PdCl$_2$]$_2$.[51]

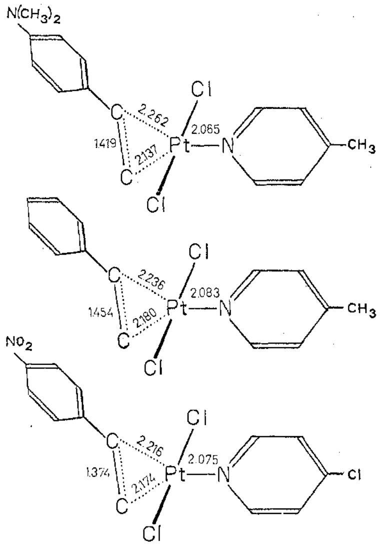


Figure 5. Pertinent bond length data for [(p-NMe$_2$sty)PtCl$_2$-(p-Me(py))], [(sty)PtCl$_2$(p-Me(py))], and [(p-NO$_2$sty)PtCl$_2$(p-Cl(py))].

structure has frequently been cited as an example of steric effects on olefin–metal bonds, it is clear from the above discussion that such a structure could at least in part be symptomatic of an ionic contribution to the sty–Pd bond.

The longer μ-PdCl bond trans to styrene relative to μ-PdCl trans to Cl implies a considerable trans influence associated with the coordinated styrene. X-ray structural studies of complexes **7** (Y = NMe$_2$ and H) and the complex *trans*-[(p-NO$_2$C$_6$H$_4$CH=CH$_2$)PtCl$_2$(NC$_5$H$_4$Cl)],[52] **10**, have been carried out by Nyburg and co-workers.[53] Some of the more pertinent bond length data are given in Figure 5. As expected the bond length data for the Pt–C^2 (2.262 Å) and Pt–C^1 (2.137 Å) distances in **7** (Y = NMe$_2$) are considerably different (>7σ) with Pt–C^1 being relatively short and Pt–C^2 being considerably larger than the average olefin–Pt(II) bond length (ca. 2.15–2.16 Å). In contrast, the corresponding bond length data for Pt–C^1 and Pt–C^2 in *trans*-[p-NO$_2$C$_6$H$_4$CH=CH$_2$)PtCl$_2$(NC$_5$H$_4$Cl)], **10**, are more symmetrical, being 2.174 (13) and 2.216 (11) Å, respectively. On going from Y = NMe$_2$ to Y = H to Y = NO$_2$, Pt–C^2 becomes shorter, Pt–C^1 becomes longer, and, with the notable exception of **7** (Y = H), C^1–C^2 becomes shorter. For all three complexes the position at which the PtCl$_2$N coordination plane bisects the styrene C=C bond is displaced from the midpoint toward the CH$_2$ group by 0.2113 Å [**7** (Y = NMe$_2$)], 0.1165 Å [**7** (Y = H)], and 0.0852 Å (**10**). These distortions within the sty–Pt bond are in the main consistent with the valence bond description of the bonding given in Figure 3.[55]

(v) Optical Inversion and Substitution of Coordinated Styrenes in *trans* (*N*)-Chloro-L-prolinatostyreneplatinum(II) Complexes.[56] The rate of inversion of coordinated styrenes in the complexes *trans*(*N*)-[(p-YC$_6$H$_4$CH=CH$_2$)PtCl(L-pro)] (pro = prolinate) has been found to be quite sensitive to the nature of the para Y substituent increasing in the order Y = MeO < Me < H < Cl < NO$_2$. While the details of the mechanism of this inversion reaction are still unknown, it has been suggested that the reaction proceeds via a solvolytic displacement of the coordinated styrene. The observed dependence of the rate on Y is consistent with a stronger Pt–sty bond for Y = OMe, consistent with the data above and the bonding scheme in Figure 3.

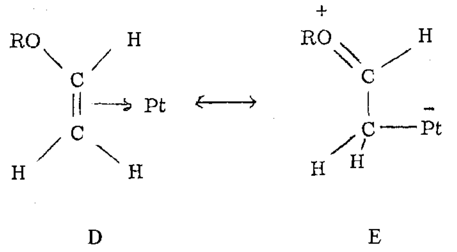


Figure 6. Valence bond representation of vinyl alcohol- or vinyl ether-platinum(II) bonding.

(vi) Stability Constant Studies of Some Styrene–Platinum Compounds. In 1959 Roy and Orchin[57] reported details of a spectroscopic study of the system [(1-dodecene)PtCl$_2$]$_2$ + 2HCl + styrene in ethanol. It was suggested that the predominant solution equilibrium could be written

$$YC_6H_4CH{=}CH_2 + [(C_{12}H_{24})PtCl_3]^- \overset{K}{\rightleftharpoons} C_{12}H_{24} + [(YC_6H_4CH{=}CH_2)PtCl_3]^- \qquad (1)$$

It was found that the values of K so obtained did not give a linear correlation with Hammett σ or σ^+ constants. Instead, $K_{Y=OMe} \approx K_{Y=NO_2} > K_{Y=H}$ In view of the consistency of the ^{13}C NMR data and the data in (i)–(v) above, the observed trends in K (eq 1) as a function of Y are surprising. It may be that the solution equilibria are more complex than that represented in eq 1. A reasonable possibility may be solvolysis of the Cl trans to the styrene (particularly for Y = OMe). This added solution equilibrium could easily account for the apparent anomalous behavior of this system.

***trans*-[(*trans*-β-Me-sty)PtCl$_2$(NC$_5$H$_4$Me)].** This complex has ^{13}C NMR parameters that are reasonably similar to the corresponding styrene complex, e.g., $^1J_{Pt-C^2}$ = 135 and 137 Hz, $^1J_{Pt-C^1}$ = 158 and 166 Hz, respectively. The lower value of $^1J_{Pt-C^1}$ for the β-methylstyrene derivative is consistent with the effect of methyl substitution on simple alkenes, cf. **1** (olefin = ethylene and propene).

***trans*-[(CH$_2$=CHOMe)PtCl$_2$(NC$_5$H$_4$Me)].** X-ray structural studies of [(CH$_2$=CHOH)PtCl(acac)][54] and *cis*-dichloro[(*R*)-α-methylbenzylamine][(*S*)-1,2,2-trimethylpropyl (*R*)-vinyl ether]platinum(II)[58] have shown a marked difference in the two olefinic carbon–platinum bonds in both cases, with the oxygen-substituted carbon being further away from the platinum. A valence bond model for the bonding invokes a considerable contribution from the ionic resonance structure E (Figure 6), thereby accounting for the large differences in the Pt–C bond lengths and the distortion in the olefin–platinum bonding. ^{13}C NMR data for the complex *trans*-[(CH$_2$=CHOMe)PtCl$_2$(NC$_5$H$_4$Me)] (see Table III) shows $^1J_{Pt-C^2}$ (88 Hz) $\ll$ $^1J_{Pt-C^1}$ (193 Hz) which is clearly consistent with a comparable asymmetry in the vinyl methyl ether–platinum(II) bond. In contrast, the corresponding vinyl acetate does *not* reflect any appreciable asymmetry in the olefin–platinum bond ($^1J_{Pt-C^1}$ = 164.5; $^1J_{PtC^2}$ = 171.0 Hz). This is probably due to the fact that the "lone pair of electrons" on the acetate oxygen attached to the vinyl group are effectively delocalized in the π orbitals of the carboxylate group and hence are less available to contribute significantly to structural representations such as E.

An η^2-Coordinated 1,3-Diene. A comparison of the ^{13}C data for the olefinic carbons of η^2-coordinated 4-methyl-1,3-pentadiene in the complex *trans*-[(Me$_2$C=CHCH=CH$_2$)-PtCl$_2$(NC$_5$H$_4$Me)] with those of the closest alkene analogue

Table VII. ^{13}C NMR Data for Complexes (acetylene)$PtCl_2(p\text{-}CH_3\text{-}C_5H_4N)$ in $CDCl_3$[a]

		≡CR			C^{α}		C^{β}			C^{β} of p-CH_3-C_5H_4N
Acetylene	R	δ	Δδ[b]	$^1J_{^{195}Pt-^{13}C}$	δ	$^2J_{^{195}Pt-^{13}C}$	δ	$^3J_{^{195}Pt-^{13}C}$	C^{γ}, etc., δ	$^3J_{^{195}Pt-^{13}C}$
$C_6H_5C{\equiv}CC_6H_5$	C_6H_5	72.69	16.62	165	122.07	26.8	132.05	23.3	130.05, 128.97	40.5
$C_6H_5C{\equiv}CCH_3$	C_6H_5	72.90	12.69	132	122.10		131.94	22.6	129.19, 128.49	39.1
	CH_3	65.79	14.84		9.05	24.6				
$CH_3C{\equiv}CC(CH_3)_3$	CH_3	65.83	3.92	141.1	8.41	27.8				38.2
	$C(CH_3)_3$	75.37	12.55		30.08		30.75	18.2		
$(CH_3)_3CC{\equiv}CC(CH_3)_3$	$C(CH_3)_3$	76.34	10.91	183.4	29.38	16.6	30.70	17.0		37.8

[a] See Table I, footnote *a*. [b] See Table I, footnote *b*.

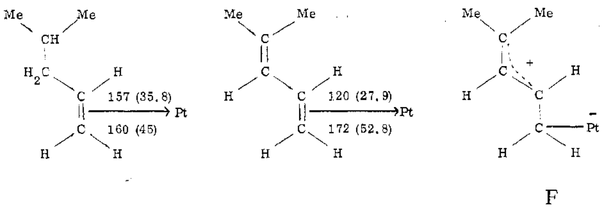


Figure 7. ^{13}C NMR parameters for C^1 and C^2 of $C^1H_2{=}C^2HCH{=}CMe_2$ and $C^1H_2{=}C^2HCH_2{-}CHMe_2$ coordinated to platinum. $^1J_{^{195}Pt-^{13}C}$ is in Hz with $\Delta\delta_C$ in ppm in parentheses.

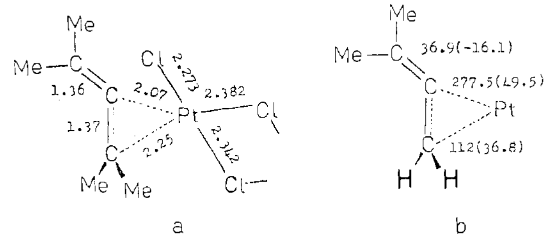


Figure 8. (a) Pertinent bond length data for the complex $[(Me_2C{=}C{=}CMe_2)PtCl_2]_2$.[61] (b) ^{13}C NMR parameters given as $^1J_{^{195}Pt-^{13}C}$ in Hz with $\Delta\delta_C$ in ppm in parentheses for the complex *trans*-$[(Me_2C{=}C{=}CH_2)PtCl_2(NC_5H_4Me)]$.

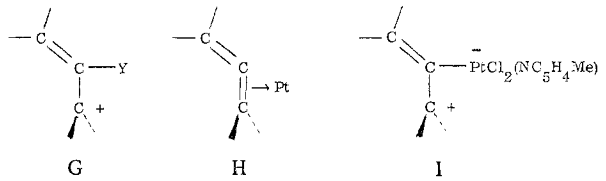


Figure 9. Possible significant valence bond representations of the η^2-allene-platinum(II) bond.

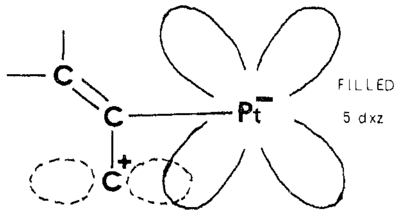


Figure 10. Possible through-space stabilization of the ionic valence representation I (Figure 9) by the filled $5d_{xz}$ of platinum.

4-methylpent-1-ene (see Figure 7) suggest considerable asymmetry in the η^2-1,3-diene–platinum(II) bond on the basis of the considerably lower values of $\Delta\delta C^2$ and $^1J_{Pt-C^2}$ and higher $\Delta\delta_{C^1}$ and $^1J_{Pt-C^1}$ values relative to the 4-methylpent-1-ene case.[59] A significant contribution to overall η^2-1,3-diene–platinum bonding by the ionic valence bond representation F (Figure 7) provides a reasonable and consistent rationalization of these observations. It is interesting to note that an x-ray structural determination of the complex $[(Me_2C{=}CHCH{=}CH_2)_2RhCl]_2$ has shown the coordinated olefinic CH_2 carbon to be closer to the Rh atom than the coordinated RCH carbon.[60] Although previously ascribed to steric effects, it appears more than likely that this distortion in the olefin–rhodium bond is in fact electronic in origin.

An η^2-Coordinated 1,2-Diene. Several x-ray structural studies of platinum,[61,62] palladium,[63] and rhodium[61] complexes containing a coordinated η^2-allene moiety have shown that the central allenic carbon atom has a noticeably shorter metal–carbon distance relative to that of the coordinated terminal carbon. This asymmetry in the allene–platinum(II) bond is reflected quite markedly in the ^{13}C NMR parameters of the complex *trans*-$[(Me_2C{=}C{=}CH_2)PtCl_2(NC_5H_4Me)]$ (Figure 8b). The nonequivalence of the methyl carbons indicates that the coordinated 3-methyl-1,2-butadiene is nonfluxional and that the "$CH_2{=}C$" segment bonds to the Pt, consistent with previous ^{1}H NMR studies. It has been suggested that the geometry and binding of coordinated allenes may be accounted for in terms of the Chatt–Dewar bonding model by the incorporation of an additional π-back-bonding overlap between the filled metal d_{xy} orbital and the empty orthogonal π^* orbital of the uncoordinated olefin.[61] However, it should be noted that coordinated allenes exhibit a noticeable trans influence (cf. μ-Pt-Cl data in Figure 8a[61]) which suggests a strong allene $\pi \rightarrow$ metal donor interaction. It has also been noted that the ability of the allene to coordinate to certain palladium(II) compounds is increased by methyl substitution on the allene (e.g., $Me_2C{=}C{=}CH_2 > MeHC{=}C{=}CHMe > MeHC{=}C{=}CH_2 > H_2C{=}C{=}CH_2$).[64] Crandall and Sojka,[65] on the basis of MO calculations and ^{13}C NMR studies, have shown that the π-electron density at the central carbon atom increases with increasing methyl substitution.

Also, of possible relevance to the nature of η^2-allene–platinum(II) bonds, it is interesting to note that addition of "soft" electrophiles (Y^+) such as Br^+, I^+, RS^+, and RSe^+ to allenes occurs at the central carbon atom to give a postulated carbonium ion intermediate of structure G (nonallylic).[66-68]

In view of the above observations and the reasonable success of a simple qualitative VB approach in rationalizing the structural and spectroscopic properties of coordinated styrenes and vinyl ethers (alcohols) it is tempting to suggest that an ionic representation I, similar to G, may make a considerable contribution to the η^2-allene–platinum(II) bond (see Figure 9). The stability of carbonium ion resonance structures such as G and I may be enhanced by a "through-space interaction" between the carbonium ion center and filled d orbitals on either Y or Pt as illustrated schematically in Figure 10. A similar through-space stabilization has been previously postulated to account for the stability of $[(\pi\text{-}C_5H_5)Fe(C_5H_4CH_2)^+)]$.[68]

Coordinated Allylic Derivatives ($CH_2{=}CHCH_2X$). Table III contains ^{13}C NMR data for a series of terminal alkene complexes containing substituents of varying electronegativity on a side chain carbon atom of the coordinated olefin. The

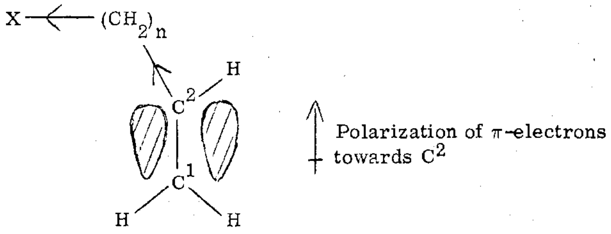


Figure 11. Schematic representation of a through-bond polarization of olefin π-electron density by an electronegative side-chain substituent.

presence of a methoxy group on the olefin (e.g., the vinyl methyl ether complex, see above) causes $^1J_{PtC^1} \gg {}^1J_{PtC^2}$. Removal of the methoxy group to an α-C position as in the allyl methyl ether complex *trans*-[(MeOCH$_2$CH=CH$_2$)-PtCl$_2$(NC$_5$H$_4$Me)] results in a reversal such that $^1J_{PtC^2}$ (175.2 Hz) > $^1J_{PtC^1}$ (157.8 Hz). This is true for all the platinum complexes in Table III containing olefins of the type CH$_2$=CHCH$_2$X, where X is an electronegative substituent. This is demonstrated by the following list of X ($\Delta'J$), where $\Delta'J$ is the difference $^1J_{PtC^2} - {}^1J_{PtC^1}$: X = Cl (29.5) ≳ OAc (26.8) ≳ OPh (25.4) > OMe (17.4) ≫ OH (3.8)[69] > Ph (3.5) > CH$_3$ (−2.1) ≳ CH=CMe$_2$ (−2.4) ≳ CH$_2$CH$_2$CH$_3$ (−2.9) > H (−7.6).

A reasonable explanation of the relative order of the observed $^1J_{Pt\text{-}C}$ and δ_C values of the complexes containing a coordinated CH$_2$=CH(CH$_2$)$_n$X (n = 1–4) is an induced, ground-state, through-bond polarization of the olefin π electrons by the electronegative substituent X, as illustrated schematically in Figure 11. Such an effect should be greatest for n = 1 and should also be apparent in the free olefin. δ_C values of the free olefinic carbons as a function of n show similar trends to those exhibited by the δ_C and $^1J_{PtC}$ values of the series of coordinated olefins (n = 1–4). For the complex *trans*-[{CH$_2$=CH(CH$_2$)$_n$X}PtCl$_2$(NC$_5$H$_4$Me)] the effect of X on the relative magnitudes of the olefinic δ_C and $^1J_{Pt\text{-}C}$ values rapidly diminishes as n increases and is insignificant for $n \geq 4$. For X = OMe $\Delta'J$ (Hz) = 17.4, n = 1; 3.0, n = 2; −0.7, n = 3; −1.6, n = 4. For X = OAc $\Delta'J$ (Hz) = 26.8, n = 1; 6.1, n = 2;, 1.9, n = 3; 0.1, n = 4. Polarization of π electrons as illustrated in Figure 11 has also been postulated to rationalize the ^{13}C NMR data of the ketonic carbon in molecules of the type X$_n$CH$_{3-n}$C(=O)Y (Y = Me, OH)[70] and the ^{13}C and ^{14}N NMR data of organic nitriles.[71]

This effect of electronegative substituents on the ^{13}C NMR parameters of the coordinated olefin is also observed for compounds of types **2** (anionic) and **3** (cationic). Table IV contains data for the olefin CH$_2$=CH—CH$_2$—O—C$_6$H$_5$ coordinated to platinum showing that $^1J_{PtC^2} > {}^1J_{PtC^1}$ for both types of complex. When the olefin has an alkyl substituent (i.e., CH$_2$=CH(−CH$_2$−)$_2$CH(CH$_3$)$_2$), the difference between $^1J_{PtC^2}$ and $^1J_{PtC^1}$ is negligible (<2 Hz; Table IV).

Coordinated Acetylenes. A limited amount of ^{13}C NMR data for coordinated acetylenes in complexes of the type *trans*-[R^{1}C≡CR^2)PtCl$_2$(NC$_5$H$_4$Me)] are presented in Table VII. $^1J_{PtC}$ data are difficult to obtain owing to (i) the long relaxation times associated with acetylenic carbon nuclei and (ii) the marked tendency for complexes not containing *tert*-butyl-substituted acetylenes to undergo decomposition.[42] Upon coordination, there is an upfield shift of the acetylenic carbon resonances of 12–17 ppm. $^1J_{PtC}$ values for the acetylenic carbon atoms are in the range 132–183 Hz, the largest coupling constant being observed for the di-*tert*-butylacetylene complex which is the most stable with respect to decomposition in solution. The range of $^1J_{PtC}$ values is very similar to those observed for the complexes *trans*-[(olefin)PtCl$_2$(NC$_5$H$_4$Me)]. This contrasts with previously reported data for the complexes *trans*-[PtMeL(PMe$_2$Ph)$_2$]PF$_6$ and [PtL(PPh$_3$)$_2$] (L = C$_2$H$_4$ or MeC≡CMe) where $^1J_{PtC}$ values for the coordinated acetylene were 60–70% less than the corresponding values for the ethylene analogues.[3]

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Registry No. *trans*-[(ethylene)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 53532-78-8; *trans*-[(propene)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59350-46-8; *trans*-[(but-1-ene)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59367-99-6; *trans*-[(*cis*-but-2-ene)-PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 33151-88-1; *trans*-[(*trans*-but-2-ene)-PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 33151-87-0; *trans*-[(hex-1-ene)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59350-08-2; *trans*-[(*cis*-hex-3-ene)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59367-86-1; *trans*-[(*trans*-hex-3-ene)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59433-25-9; *trans*-[(4-methylpent-1-ene)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59367-85-0; *trans*-[(5-methylhex-1-ene)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59367-84-9; *trans*-[(3,3-dimethylbut-1-ene)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59350-05-9; *trans*-[(4,4-dimethylpent-1-ene)-PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59350-34-4; *trans*-[(cyclopentene)PtCl$_2$-(*p*-CH$_3$-C$_5$H$_4$N)], 59389-69-4; *trans*-[(cyclohexene)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59367-98-5; *trans*-[(cycloheptene)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59350-10-6; *trans*-[(cyclooctene)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59367-83-8; *trans*-(*p*-N(CH$_3$)$_2$-sty)PtCl$_2$(*p*-CH$_3$-py), 59350-04-8; *trans*-(*p*-OCH$_2$CH$_3$-sty)PtCl$_2$(*p*-CH$_3$-py), 59367-97-4; *trans*-(*p*-OC$_6$H$_5$-sty)PtCl$_2$(*p*-CH$_3$-py), 59367-95-2; *trans*-(*p*-CH$_3$-sty)PtCl$_2$(*p*-CH$_3$-py), 59367-82-7; *trans*-(*p*-H-sty)PtCl$_2$(*p*-CH$_3$-py), 59350-03-7; *trans*-(*p*-Cl-sty)PtCl$_2$(*p*-CH$_3$-py), 59350-02-6; *trans*-(*p*-C(O)CH$_3$-sty)-PtCl$_2$(*p*-CH$_3$-py), 59350-01-5; *trans*-(*p*-NO$_2$-sty)PtCl$_2$(*p*-CH$_3$-py), 59350-33-3; *trans*-(*trans*-β-CH$_3$-sty, C^1 = CH$_3$)PtCl$_2$(*p*-CH$_3$-py), 59367-89-4; *trans*-(*trans*-β-CH$_3$-sty, C^2 = C$_6$H$_5$)PtCl$_2$(*p*-CH$_3$-py), 59367-96-3; K$^+$[(*p*-OCH$_2$CH$_3$-sty)PtCl$_3$]$^-$, 43186-75-0; K$^+$[(*p*-OC$_6$H$_5$-sty)PtCl$_3$]$^-$, 59389-57-0; K$^+$[(*p*-CH$_3$-sty)PtCl$_3$]$^-$, 33221-84-0; K$^+$[(*p*-H-sty)PtCl$_3$]$^-$, 12080-15-8; K$^+$[(*p*-Cl-sty)PtCl$_3$]$^-$, 33112-97-9; K$^+$[(*p*-NO$_2$-sty)PtCl$_3$]$^-$, 33042-14-7; [*trans*-(*p*-OCH$_2$CH$_3$-sty)Pt-(NH$_3$)$_2$Cl]$^+$BF$_4^-$, 59367-88-3; [*trans*-(*p*-OC$_6$H$_5$-sty)Pt-(NH$_3$)$_2$Cl]$^+$BF$_4^-$, 59367-94-1; [*trans*-(*p*-H-sty)Pt(NH$_3$)$_2$Cl]$^+$BF$_4^-$, 59433-24-8; [*trans*-(*p*-Cl-sty)Pt(NH$_3$)$_2$Cl]$^+$BF$_4^-$, 59433-23-7; [*trans*-(*p*-NO$_2$-sty)Pt(NH$_3$)$_2$Cl]$^+$BF$_4^-$, 59350-00-4; *trans*-[(vinyl methyl ether)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59349-98-3; *trans*-[(allyl methyl ether)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59350-42-4; *trans*-[(but-3-enyl methyl ether)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59350-32-2; *trans*-[(pent-4-enyl methyl ether)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59367-92-9; *trans*-[(hex-5-enyl methyl ether)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59367-91-8; *trans*-[(vinyl acetate)-PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59350-14-0; *trans*-[(allyl acetate)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59350-18-4; *trans*-[(but-3-enyl acetate)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59350-43-5; *trans*-[(pent-4-enyl acetate)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59350-41-3; *trans*-[(hex-5-enyl acetate)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59350-09-3; *trans*-[(allyl alcohol)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59367-90-7; *trans*-[(1-buten-4-ol)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59350-13-9; *trans*-[(1-penten-5-ol)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59350-12-8; *trans*-[(1-hexen-6-ol)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59350-17-3; *trans*-[(3-methylbuta-1,2-diene)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59350-45-7; *trans*-[(4-methylpenta-1,3-diene)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59349-97-2; *trans*-[(5-methylhexa-1,4-diene)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59368-00-2; *trans*-[(allylbenzene)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59350-11-7; *trans*-[(allyl chloride)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59350-40-2; *trans*-[(allyl phenyl ether)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59350-39-9; K$^+$[(ethylene)PtCl$_3$]$^-$, 12012-50-9; K$^+$[(5-methylhex-1-ene)PtCl$_3$]$^-$, 59389-59-2; K$^+$[(allyl phenyl ether)PtCl$_3$]$^-$, 59389-58-1; [*trans*-(5-methylhex-1-ene)Pt-(NH$_3$)$_2$Cl]$^+$BF$_4^-$, 59350-16-2; [*trans*-(allyl phenyl ether)Pt-(NH$_3$)$_2$Cl]$^+$BF$_4^-$, 59350-07-1; *trans*-[(C$_6$H$_5$C≡CC$_6$H$_5$)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59350-44-6; *trans*-[(C$_6$H$_5$C≡CCH$_3$)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59350-38-8; *trans*-[(CH$_3$C≡CC(CH$_3$)$_3$)PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59350-37-7; *trans*-[((CH$_3$)$_3$CC≡CC(CH$_3$)$_3$)-PtCl$_2$(*p*-CH$_3$-C$_5$H$_4$N)], 59368-10-4; ^{13}C, 14762-74-4.

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Single-Crystal Vibrational Spectrum of Bis(dimethyl sulfoxide)dichlorocopper(II) and Infrared Spectra of Some Hexakis(dimethyl sulfoxide) Complexes

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All of the skeletal internal modes of $CuCl_2(DMSO)_2$ have been assigned from the evidence of single-crystal ir and Raman spectra at liquid nitrogen temperature. $\nu(Cu–O)_s$, $\nu(Cu–O)_a$, $\nu(Cu–Cl)_s$, and $\nu(Cu–Cl)_a$ are at 481, 496, 229, and 286 cm^{-1}, respectively. An outline assignment is given for ir (powder) data for $[M(DMSO)_6]^{2+}$ types.

Introduction

Most studies of the vibrational spectra of inorganic coordination complexes are of dissolved or polycrystalline samples. Data are usually incomplete and, where complex polyatomic ligands are involved, assignments are chiefly restricted to metal–ligand stretching modes. The spectra of powder samples (usually obtained at ambient temperature only) also generally show substantially fewer than the number of bands predicted by factor group analysis (fga) thereby inviting oversimple assignments.

In this paper we report a single-crystal ir and Raman study at liquid nitrogen temperature of $CuCl_2(DMSO)_2$ and its