R_FCO_2 group trans to triphenylphosphine should be the most labile, it may be preferentially lost as free acid. This eventuality can be accommodated by a mechanism essentially similar to that given in Scheme II and does not invalidate this discussion. We are unable to ascertain whether the step **c–d** involves simultaneous or sequential carboxylic acid loss and hydride migration. If the latter situation prevails then the following complexes could be intermediates in the reaction cycle
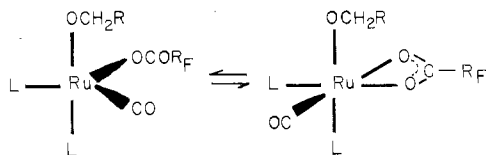
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(43) Typical data from ref 38–41: Ru–OCOMe = 2.21–2.22 Å (trans to PPh_3) and 1.96–2.09 Å (trans to OCOMe); Ru–PPh_3 = 2.35–2.37 Å (trans to PPh_3) and 2.23–2.28 Å (trans to OCOMe).

Contribution from the Lash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario, Canada M5S 1A1

^{13}C Nuclear Magnetic Resonance Studies of Organoplatinum(II) Complexes Containing Substituted Pyridine Ligands

DAVID G. COOPER and JOHN POWELL*

^{13}C NMR data are reported for the series of platinum(II) compounds *trans*-[LPtCl₂(NC₅H₄-4X)] (L = ethylene, styrene, di-*tert*-butylacetylene, or carbon monoxide; NC₅H₄-4X = a series of para-substituted pyridines), *trans*-[ZPt(NC₅H₄-4X)(PMe₂Ph)₂]BF₄ (Z = CH₃, CH₃C≡C), and [Cl(2-methoxy-5-cyclooctenyl)Pt(NC₅H₄-4X)]. These complexes provide examples of olefins, acetylenes, carbonyls, alkyls and acetylides bonded to platinum(II) in trans position to a para-substituted pyridine. Small changes in the δC and $^1J_{^{195}Pt-^{13}C}$ data of the directly bound carbon atoms as X is varied have been interpreted in terms of slight fluctuations in the σ-donor component of these platinum–carbon bonds (regardless of ligand type). The spectra of the 2-methoxy-5-cyclooctenyl complexes also demonstrate the presence of two geometrical isomers in solution contrary to previous reports.
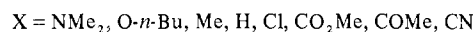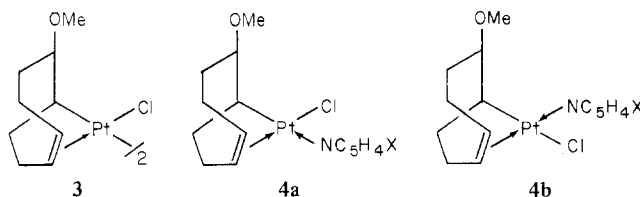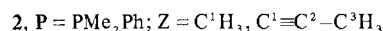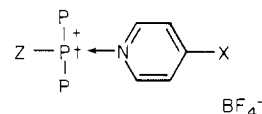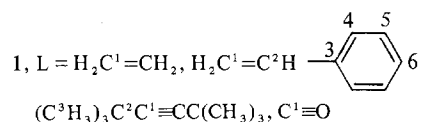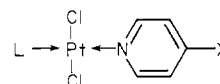
Introduction

A large amount of data have been published recently regarding the ^{13}C NMR spectra of organometallic compounds of the transition elements.[1-24] Interpretation of the reported chemical shifts is difficult because several parameters determine these values. In fact, a recent, short overview of the subject[25] concluded that it was not possible to satisfactorily explain the chemical shifts of directly bound carbon nuclei attached to transition metals using current theories. A study of trends in ^{13}C NMR data obtained from series of closely related compounds[1,2,5,24] should lead to more meaningful rationalizations. However even this approach has been only partially successful because changing only one ligand on the metal still has both an electronic and a steric effect, and in many cases, even the mode of bonding is altered.

In an attempt to circumvent these problems, we have considered series of organometallic complexes with para-substituted pyridines NC₅H₄-X as ligands. As these para substituents are varied, there should be no change in the steric parameters of the pyridine ligands near the metal, such that the *mode* of the bonding between the metal and the nitrogen should remain essentially unchanged. Thus, the only change experienced by the metal (and the trans metal–carbon bond) when the para substituent is varied will be electronic in origin.

This work considers the ^{13}C NMR data obtained for the series of platinum(II) complexes **1–4**. Platinum is an ideal metal for ^{13}C NMR studies because: (i) ^{195}Pt (33% natural abundance) couples strongly with directly bonded carbon nuclei, and (ii) it is possible to synthesize a large variety of stable platinum–carbon bonds. The series of compounds **1–4** provide examples of acetylene, olefin, carbon monoxide, methyl, and acetylide groups bound to platinum(II) in the trans position to NC₅H₄-X.

Experimental Section

Complexes of type **1** were prepared using the methods of Orchin et al.[26-29] Compounds of type **2**[2,30-32] and the dimer **3**[33] were prepared

1, L = H₂C¹=CH₂, H₂C¹=C²H

(C³H₃)₃C²C¹≡CC(CH₃)₃, C¹≡O

2, P = PMe₂Ph; Z = C¹H₃, C¹≡C²–C³H₃

3   **4a**   **4b**

X = NMe₂, O-*n*-Bu, Me, H, Cl, CO₂Me, COMe, CN

by standard methods. The complexes **4a** and **4b** were not isolated from solution; however, several of them have been characterized.[34]

The ^{13}C NMR spectra were measured at ca. 35 °C on either Varian XL-100-15 or CFT-20 spectrometers operating in the Fourier transform mode at 25.2 and 20.0 MHz, respectively. All the spectra (except **1**, L = CO) were determined with noise modulated proton decoupling.

Results

Data for complexes of type **1** are recorded in Table I.[35] Only spectral data where $^3J_{Pt-C}$ coupling to the β carbons of the pyridines is observed (ca. 35–40 Hz) are completely reliable. The complexes were recrystallized several times to remove excess pyridine which, if present, can catalyze the

Table I. ¹³C NMR Data[35] for the Complexes 1 of the Type *trans*-[(*p*-X-C₅H₄N)Pt(Cl)₂(L)] in CDCl₃ Solutions[a]

X	L = ethylene		L = (C³H₃)₃C²C¹≡CC(CH₃)₃					L = C¹O	
	δ	$^1J_{^{195}Pt-^{13}C}$	δC^1	$^1J_{Pt-C^1}$	δC^2	$^2J_{Pt-C^2}$	δC^3	δCO	$^1J_{Pt-C^1}$
N(CH₃)₂[b]	73.35	162.5	76.18	182.2	29.27	15.3	30.75		
O(CH₂)₃CH₃[b]	74.18	165.4						151.86	1649.5
CH₃[b]	75.05	164.4	76.34	183.4	29.38	16.7	30.70	151.33	1656.6
H[b]	75.23	167.9	76.40	183.5	29.58	15.7	30.75	151.10	1669.7
Cl[b]	75.12	168.8							
CO₂CH₃	75.66	(166.7)[c]							
COCH₃	75.83	(166.3)[c]						150.53	1692.2
CN	75.95	(168.9)[c]						149.70	1726.0

	L = styrene									
	Olefinic carbons				Aromatic carbons					
	δC^1	$^1J_{Pt-C^1}$	δC^2	$^1J_{Pt-C^2}$	δC^3	$^2J_{Pt-C^3}$	δC^4	$^3J_{Pt-C^4}$	δC^5	δC^6
N(CH₃)₂[b]	61.65	163.9	95.37	138.3	136.03	36.2	129.87	13.4	128.30	129.56
O(CH₂)₃CH₃[b]	61.72	166.4	96.72	138.4	135.67	35.0	129.68	12	128.37	129.68
CH₃[b]	62.09	165.8	97.59	137.6	135.49	36.2	129.92	12.8	128.37	129.92
H[b]	62.11	167.2	98.19	139.9	135.44	36.4	129.92	12.4	128.40	130.06
Cl[b]	61.84	169.5	98.32	140.9	135.28	37	129.92	12.6	128.46	130.19
COCH₃	62.28	(168.2)[c]	99.12	(135.3)[c]	135.24		130.02		128.47	130.25
CN	61.97	(170.0)[c]	100.04	(132.6)[c]	135.07		130.09		128.59	130.52

[a] δ in ppm relative internal Me₄Si, *J*'s in Hz. [b] The β carbon of the pyridine has ¹⁹⁵Pt satellites for these compounds: $^3J_{Pt-^{13}C\beta}$ = 35–40 Hz. [c] These are the largest values obtained (in the presence of [PtCl₂(C₂H₄)]₂) but they are not reliable because of fast exchange of the trans pyridines (see text). They should be regarded as minimum values.

Table II. ¹³C NMR Data[35] for Complexes of the Type *trans*-[(*p*-X-C₅H₄N)Pt(Me₂PhP)₂(Z)]⁺BF₄⁻ in CDCl₃[a]

X	Z = C¹H₃[b]		Z = C¹≡C²–C³H₃[b]					
	δC^1 [c]	$^1J_{Pt-C^1}$	δC^1 [d]	$^1J_{Pt-C^1}$	δC^2 [e]	$^2J_{Pt-C^2}$	δC^3	$^3J_{Pt-C^3}$
N(CH₃)₂	−23.60	589.4	60.90	1225.0	100.55	355.4	5.50	
O(CH₂)₃CH₃			59.66	1238	100.46	359.1	5.60	
CH₃	−23.0[f]	594[f]						
H	−22.7[f,g]	598[f,g]	58.88		100.77		5.66	27
C(O)CH₃			58.44	1251.2	100.58	362.2	5.51	27
CN	−22.80	599.9						

[a] δ in ppm relative to internal Me₄Si, *J*'s in Hz. [b] Coupling between ¹⁹⁵Pt and the pyridine β carbons ca. 30 Hz. [c] $^3J_{P-C^1}$ = 6.3 Hz. [d] $^3J_{P-C^1}$ ca. 16 Hz. [e] $^4J_{P-C^2}$ ca. 2.5 Hz. [f] Data from ref 2. [g] Solvent acetone-d_6.

exchange of the coordinated pyridine.[37,38] The most noticeable effects as the free ⇌ coordinated pyridine exchange rate increases are (i) the loss of ¹⁹⁵Pt coupling to the pyridine carbons and (ii) a small decrease (<2 Hz) in ¹⁹⁵Pt coupling to the directly bound carbon nuclei. This decrease in ¹Jₚₜ₋C may be comparable in magnitude to the variation of ¹Jₚₜ₋C with changing X (1, L = C₂H₄, styrene, acetylene). The effect of coordinated ⇌ free pyridine exchange on the chemical shifts of carbon nuclei directly bound to platinum (<0.2 ppm) is negligible compared to the changes observed within the series as the pyridine para substituent is varied. Unfortunately, for pyridines less basic than *p*-chloropyridine and for L = C₂H₄, styrene, or *t*-BuC≡C-*t*-Bu pyridine exchange in complexes 1 could not be inhibited even upon addition of K⁺[PtCl₃-(C₂H₄)]⁻ or [PtCl₂(C₂H₄)]₂ as a means of complexing free pyridine.[38] Hence it was impossible to obtain accurate ¹Jₚₜ₋C values in these cases. The data for the carbonyl carbon of 1 (L = CO) were obtained in the presence of Cr(acac)₃, a paramagnetic relaxation agent which has been shown to leave the chemical shift unaffected.[39] To further enhance the relative size of this resonance relative to the pyridine pattern, these spectra were obtained without proton decoupling.

Table II records the ¹³C NMR parameters for complexes of type 2. The data for the complexes 2 (Z = C≡CCH₃) were extremely difficult to obtain because the two carbons of interest (C¹ and C²) have long relaxation times. Even the addition of Cr(acac)₃ as a relaxation agent, which was very effective with complexes 1 (L = CO), did not help. Furthermore, it was not possible to assign $\nu_{C≡C}$ in the IR spectra of these complexes. Table III contains the data for complexes similar to type 2 where the pyridine has been replaced by other ligands.

Table III. ¹³C NMR Data for Complexes of the Type *trans*-[(C³H₃C²≡C¹)Pt(Me₂PhP)₂(Y)] in CDCl₃[a]

Y	C¹ [b]		C²		C³	
	δC^1	$^1J_{Pt-C^1}$	δC^2	$^2J_{Pt-C^2}$	δC^3	$^3J_{Pt-C^3}$
Cl	64.88	1084.0	95.19		5.72	21.7
Br	68.22	1397.4	95.05	362.4		
CCCH₃	91.23	946.1	102.07	264.4	5.86	32.2

[a] δ in ppm relative to internal Me₄Si, *J*'s in Hz. [b] $^3J_{P-C^1}$ ca. 15 Hz.

Finally Table IV records the data for the solution species **4a** and **4b**.

Discussion

(i) Olefin Complexes. As X is varied in the series of complexes 1 (L = ethylene, styrene) the observed changes in the ¹³C NMR data (Table I) are small. The variations in ¹J₁₃C₋₁H of the olefinic protons are negligible (for L = ethylene, ¹J_CH ≈ 163 Hz). Figure 1 shows a plot of the δ¹³C (olefinic carbons) and ¹J_Ptc values for the ethylene complexes against the Hammett $\sigma\rho$ constants of X.[40] (The coupling constants are not included for the pyridines less basic than *p*-chloropyridine; see Results section.) These plots generate reasonable straight lines, with ¹Jₚₜ₋C increasing slightly and the carbon nuclei being deshielded slightly, as X becomes more electron withdrawing. A similar plot of the data for C¹ and C² in the series of styrene complexes 1 (L = H₂C¹=C²HC₆H₅) is also given in Figure 1. As with ethylene, as X becomes more electron withdrawing both C¹ and C² are deshielded with C² being the more affected ($\Delta\delta$C² on going from X = NMe₂ to X = CN is ~5 ppm). The values of ¹J_Ptc do not give good

Table IV. ^{13}C NMR Data[35] for the Dimer 3 Plus Para-Substituted Pyridines, NC_5H_4X, in $CDCl_3{}^a$

X	Olefinic carbons isomer 4a				σ-Carbon 4a		Olefinic carbons isomer 4b				σ-Carbon 4b	
	δC	$^1J_{Pt-C}{}^b$	δC	$^1J_{Pt-C}{}^b$	δC	$^1J_{Pt-C}$	δC	$^1J_{Pt-C}{}^b$	δC	$^1J_{Pt-C}{}^b$	δC	$^1J_{Pt-C}{}^3$
$N(CH_3)_2{}^c$							85.98^d	$(208.2)^d$	83.46^d	$(203.4)^d$	28.98^d	681.0^d
$O(CH_2)_3CH_3$	78.48		81.91		23.36	614.8	87.55		84.77		29.38	
CH_3	78.63	(240.5)	82.46	(243.5)	23.48	613.7	88.18	(210.4)	85.50	(201.7)	30.76	$(705.6)^d$
H	78.92	(240.2)	82.93	(243.0)	23.44	614.7	88.45		85.72		30.87	
CO_2CH_3	79.25	(238.2)	83.37	(240.2)	24.14	618.0						
$COCH_3$	79.19	(238.8)	83.30	(239)	24.09	618.8	$(89.0)^d$		$(86.5)^d$		$(31.3)^d$	
CN	79.51	(238.4)	83.72		24.56	625.4						

^{a} δ in ppm relative to internal Me_4Si, J's in Hz. ^{b} The variations in these coupling constants with X are smaller than the error introduced by pyridine exchange. ^{c} Data obscured by competition of $N(CH_3)_2$ with pyridine nitrogen for donation to Pt. ^{d} Tentative assignments.

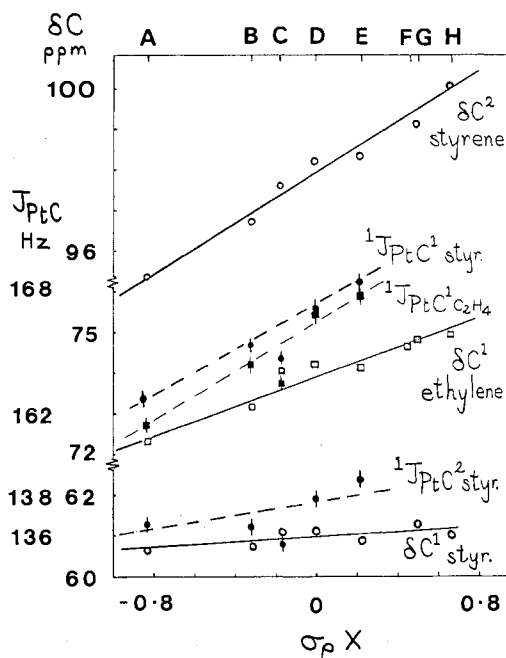Figure 1. A plot of δC and $^1J_{PtC}$ values of the olefinic carbons of 1 (L = ethylene, styrene) vs. the Hammett σρ values of X {X = NMe_2 (A), O-n-Bu (B), Me (C), H (D), Cl (E), CO_2Et (F), COMe (G), CN (H) }.
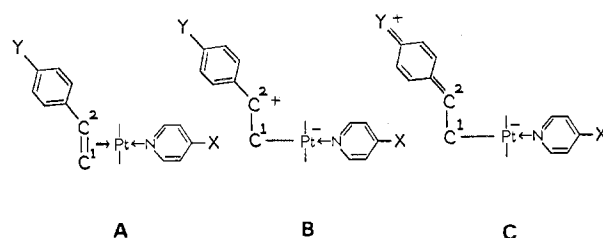

Figure 2. Valence bond representations of the styrene-Pt(II) bond.

density from the ethylene carbons causes deshielding of the ethylenic ^{13}C nuclei. At the same time there is an increase in the orbital overlap between platinum and ethylene and an increase in the S character of the platinum σ orbital.[46-48] Assuming that the Fermi contact term dominates one-bond coupling constants,[49-51] this results in the observed increase in $^1J_{Pt-C}$.

The trends in the ^{13}C NMR data for the type 1 styrene compounds behave in an analogous fashion. Thus as X becomes more electron withdrawing increased styrene → Pt donation results in an overall deshielding of C^1 and C^2. However, the increased asymmetry in the styrene bond as represented by increased contributions by the resonance structures B and C (Figure 2) causes a divergence in the chemical shifts of C^1 and C^2 as X becomes more electron withdrawing with C^2 being markedly deshielded. The effect on the phenyl ring is also consistent. As X becomes more electron withdrawing the C^3 end becomes more shielded and the C^6 end becomes more deshielded. This is consistent with an increasing polarization of electron density in the phenyl ring toward the olefin.

(ii) Di-*tert*-butylacetylene Compounds. The effect of changes in X on the ^{13}C NMR parameters of coordinated di-*tert*-butylacetylene (compounds 1, L = C_2-t-Bu_2) is much smaller than those observed in the olefin analogues. Again, the carbons bonded to platinum are deshielded, and $^1J_{PtC}$ increases as X becomes more electron withdrawing. Although the data for the *tert*-butyl substituents are almost invariant, the tertiary carbon C^2 is slightly deshielded as X becomes more electron withdrawing. These observed trends are very similar to those observed for 1 (L = C_2H_4) and can be rationalized in an analogous way.

(iii) Carbonyl Complexes. As X is varied in the series of complexes 1 (L = CO) the changes in $\delta^{13}CO$ are comparable to those observed for the ethylene analogues 1 (L = C_2H_4). The change in $^1J_{PtC}$ is appreciably larger for L = CO; however, the percentage changes are similar for the two series of compounds. A plot of the data for 1 (L = CO) vs. the σρ constants of X is shown in Figure 3. As with the series of olefin compounds, as X becomes more electron withdrawing $^1J_{PtC}$ increases. However, the carbonyl carbon becomes *more shielded*, a trend opposite to that observed for the olefin chemical shifts (see Figure 1). Furthermore as X becomes more electron withdrawing the stretching frequency, $\nu_{C\equiv O}$,

linear correlations; however, for both C^1 and C^2 there is an increase in $^1J_{Pt-C}$ as X becomes more electron withdrawing with $^1J_{PtC^1}$ being the more affected. There are also some small, but valid, trends in the chemical shift data of the phenyl ring of the coordinated styrene. As X becomes more electron withdrawing C^3 is shielded, C^4 is slightly deshielded (almost invariant), and both C^5 and C^6 are deshielded with the effect on C^6 being slightly larger (see Table I). We have previously reported on a divergence in δC^1 and δC_2 for the series of complexes 1 (L = $H_2C^1=C^2HC_6H_4$-p-Y; X = Me) as Y became more electron donating.[4,41] This was shown to be consistent with increasing contribution of the ionic resonance structures B and C (Figure 2) to the platinum–olefin bond when Y is a good electron-donating group. Similarly an *electron-withdrawing* X group on the pyridine ligand trans to the styrene should stabilize resonance structures B and C relative to A by decreasing the electron density on the platinum.

It is possible to rationalize all the above trends in complexes 1 (L = C_2H_4, styrene) by considering the relative effect of changes in X as a removal or donation of electron density through the platinum–nitrogen σ bond,[42] thereby affecting the ^{13}C NMR parameters of the trans platinum–carbon bonds. Thus the trend in the ^{13}C data of coordinated ethylene (1, L = C_2H_4) can be explained as a polarization of the ethylene to platinum σ-donor bond, induced by changes in X. As X becomes more electron withdrawing, the removal of π-electron
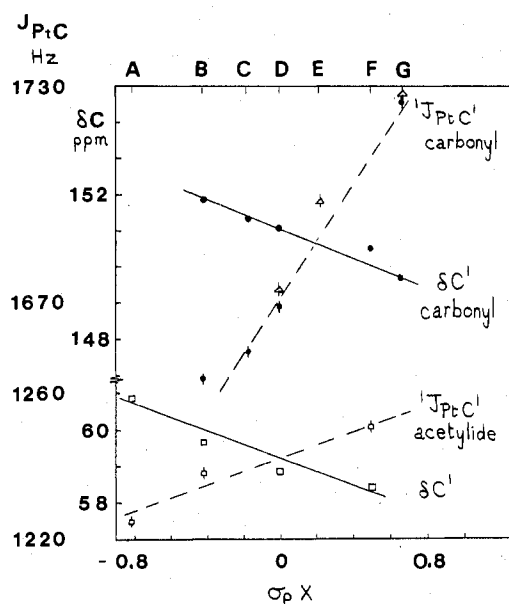
Figure 3. A plot of δC and $^1J_{PtC}$ values of the carbonyl carbon of 1 (L = CO) and the acetylide carbon of 2 (Z = C≡CCH$_3$) vs. the Hammett σp value of X {X = NMe$_2$ (A), O-n-Bu (B), Me (C), H (D), Cl (E), COMe (F), CN (G) }. (The carbonyl $^1J_{PtC}$ data points ($\triangle$) are taken from ref 36; all other data points are from this work.)
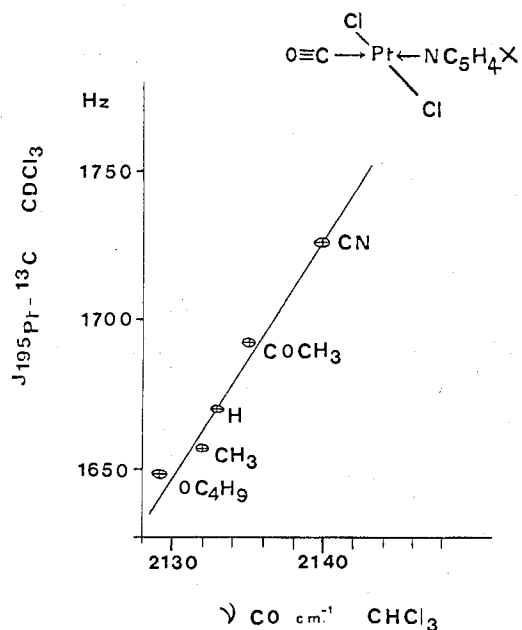

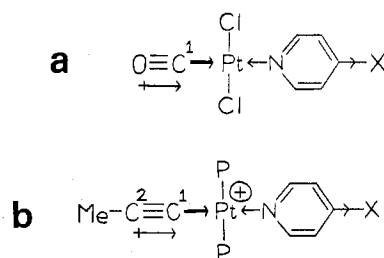Figure 4. A plot of $^1J_{PtC}$ vs. $\nu_{C≡O}$ of 1 as X is varied. (IR data taken from ref 28.)

Figure 5. A diagramatic representation of the polarization of π electrons of the carbonyl ligand of 1 (a) and the acetylide ligand of 2 (b) induced by an electron-withdrawing para X group on the trans pyridine ligand.

carbon and there is an *increased shielding* of the carbonyl carbon with electron-withdrawing X groups. Similar trends in the ^{13}C NMR and IR data of multiple bond systems have been observed and similarly rationalized for series of organic compounds containing a carbon–oxygen double bond (e.g., aldehydes, ketones, esters, etc.).[53] As more electron-withdrawing substituents are added to the ketonic carbon atom, the stretching frequency ($\nu_{C=O}$) exhibited by these organic compounds increases while in the ^{13}C NMR the ketonic carbon nucleus becomes more shielded.[53] The ^{13}C and ^{14}N NMR data for a series of nitriles (R—C≡N) have likewise been explained by polarization of the carbon–nitrogen triple bond.[54] As R becomes more electronegative, the nitrile carbon becomes more shielded and the nitrogen of the nitrile group less shielded. Yonemoto[54] concluded that this effect will be observed for any systems of the type R—A≡B or R—A=B. The type 1 complexes (L = CO) can be considered as a R—A≡B system.[55]

(iv) Methyl and Acetylide Complexes. It was of interest to look at the ^{13}C NMR data of platinum alkyl compounds with a σ-bonded carbon trans to a series of para-substituted pyridine ligands because these should exhibit trends analogous to those of the olefin complexes. Conversely, a series with platinum–acetylide bonds trans to the pyridine ligand may be considered a R—A≡B system and should exhibit trends in their ^{13}C NMR data similar to those of the carbon monoxide complexes. Unfortunately, it was necessary to alter structurally the type of compound in order to obtain stable species. The structural feature of most interest, namely a para-substituted pyridine trans to the platinum–carbon bond, is still present in compounds of type 2 (Z = CH$_3$, CH$_3$C≡C). As was expected the changes in the ^{13}C NMR data (Table II) as X is varied are very small for both series (cf. the ^{13}C NMR data in Table III and ref 2 for the magnitude of the changes when the trans ligands are markedly changed in character). The data for the methyl compounds are consistent with a polarization effect similar to that proposed for the ethylene complexes. As X becomes more electron withdrawing, the methyl group is more deshielded and $^1J_{PtC}$ increases. These changes are smaller than the comparable changes observed for the series of olefin complexes 1. This leads to the reasonable conclusion that a methyl–platinum bond is less polarizable than an olefin–platinum bond. The trends observed in the data for the methyl acetylide complexes 2 (Z = C^1≡C^{2}C^{3}H$_3$) as X is varied are analogous both in direction and magnitude to those observed for 1 (L = CO) (see Figure 3) and can be rationalized similarly (Figure 5). As X becomes more electron withdrawing, the σ-bonded acetylide carbon C^1 becomes more shielded and $^1J_{PtC^1}$ increases. These changes are large enough to be valid even though the error in the individual values is fairly substantial (>2 Hz). The data for C^2 should behave like the ^{14}N chemical shifts in the nitrile complexes.[54] Unfortunately, the effect of X on δC^2 is very small, the observed values being almost invariant within the limits of experimental error to make any definite comments

increases slightly.[26,28] A plot of $^1J_{PtC}$ vs. $\nu_{C=O}$ gives a linear correlation (Figure 4). These observations may be rationalized by considering the effect of the trans pyridine para substituents to be a polarization of electron density in the OC → Pt σ-donor bond as was proposed for the olefin complexes. Thus as X becomes more electron withdrawing an increase in the OC → Pt donor interaction results in an increase in $^1J_{Pt-C}$. However, as the carbon → platinum σ bond is polarized toward Pt, there is a concomitant polarization of the "soft" carbon–oxygen triple bond (see Figure 5). Because the carbonyl C lone pair is slightly antibonding with respect to the carbon–oxygen bond,[52] an increased polarization of these electrons toward Pt results in a slight increase in $\nu_{C≡O}$. Likewise the polarization induced in the triple bond shifts electron density from oxygen toward

concerning changes in δC^2 with changes in X. However, on going from X = NMe$_2$ to X = COMe $^2J_{Pt-C^2}$ increases by 7 Hz. This increase would be consistent with the proposed polarization arguments.

It is interesting to note that in previous studies of transition metal carbonyls where linear correlations of $\delta^{13}CO$ with $\nu_{C\equiv O}$ or force constants have been observed, these trends have, in the main, been associated with changes in the metal to carbonyl π-bonding component.[55-59] It has even been suggested that the ^{13}C NMR carbonyl shifts of closely related derivatives are a linear measure of the extent of transition metal → carbonyl π back-donation.[56] However, while the details of the transition metal–acetylide bonding mode have been the subject of some debate, recent structural studies of platinum(II)–acetylide complexes show the Pt–C$_{(sp)}$ bond length to be close to the sum of the covalent radii[60,61] (cf. Ni–acetylide bonds[62,63]) and that simple acetylides exert a large trans influence, the Pt–Cl bond length in *trans*-[PtCl(C≡CPh)-(PPhEt$_2$)$_2$] being 2.40 Å.[60] In contrast the Pt–C bond lengths of carbonyl–Pt(II) complexes are considerably less than the sum of the covalent radii and CO exhibits a weak (small) trans influence.[64] Thus in platinum(II) acetylide complexes it would appear that an acetylide ligand such as CH$_3$C≡C will behave as a strong overall donor of electron density and a poor π acceptor. (The C≡C bond length in *trans*-[PtCl(C≡CPh)(PPhEt$_2$)$_2$], 1.18 Å, is very close to that expected for the free acetylene.) Consequently, since the direction and magnitudes of the ^{13}C NMR trends for **1** (L = CO) and **2** (Z = C≡CCH$_3$) are similar and since changes in $^1J_{Pt-C}$ can be considered to be a reflection of changes in the Pt–C σ-bonding mode, an explanation involving the C → Pt σ-bonding component would appear to be more reasonable, particularly as the same explanation also rationalizes the olefin– and methyl–platinum(II) data. In several previous ^{13}C NMR studies of the effect of remote functional groups on δCO the total range of the reported δCO values is no larger than 1–2 ppm,[56,57] similar to the range observed for **1** (L = CO). Thus it could be that in these cases the *small* fluctuations in δCO and ν_{CO} are in fact symptomatic of changes in the carbonyl to metal σ-bonding component rather than the metal to carbonyl π bonding.

(v) Solution Studies of Complex 3 Plus Para-Substituted Pyridines in a 1:1 Ratio. A previous study[34] concluded that pyridines less basic than pyridine itself probably do not cleave the platinum–halide bridge because no product was isolated. Solid state IR studies of the pyridine product led the same authors to conclude that the bridge was cleaved exclusively trans to the σ-bonded carbon to give the product **4a** (X = H). The structure **4a** was later confirmed for the crystalline products by a crystal structure determination.[65] We have found that the CDCl$_3$ solution species derived from the reaction of **3** with pyridines are not this limited. The ^{13}C NMR spectra of **3** plus NC$_5$H$_4$-*p*-X (X = NMe$_2$, O-*n*-Bu, Me, H) show four types of olefinic carbons bonded to platinum and two types of σ-bonded carbons. On the basis of relative intensities these can be assigned to two different isomers each with a cyclooctenyl unit bonded to platinum. As neither set of data can be attributed to the almost insoluble dimer, **3**, it seems reasonable to conclude that the two isomers are **4a** and **4b**. When X = CO$_2$Me, C(O)Me, and CN only one isomer is observed (i.e., >95%). When these solutions were made with an excess of pyridine the rate of free pyridine ⇌ coordinated pyridine exchange remained slow on the NMR time scale, as each spectrum exhibited C$^\beta$ pyridine resonances, assignable to the free and coordinated pyridine moieties. However, the exchange was fast enough to broaden the platinum-195 satellites of the bonded pyridine spectra. For this reason the data for $^1J_{PtC}$ of the various carbons may not be reliable as
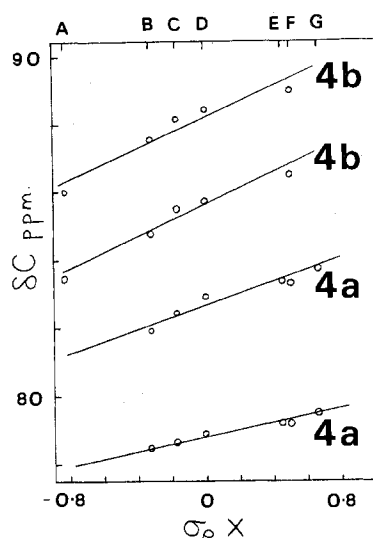

Figure 6. A plot of the δC values of the olefinic carbons of **4a** and **4b** vs. the Hammett σp values of X {X = NMe$_2$ (A), O-*n*-Bu (B), Me (C), H (D), CO$_2$Me (E), COMe (F), CN (G)}.

discussed above. The data in Table IV are incomplete due to the difficulty of assigning the resonances of the cyclooctenyl moieties unambiguously. In most cases, the pattern due to the lesser isomer **4b** was too weak to obtain the platinum-195 coupling constants. Furthermore, the chemical shifts assigned to the σ-bonded carbon of isomer **4b** are tentative as the region is complicated by the resonances of the other carbon nuclei in the cyclooctenyl ring. Finally, the spectrum with *p*-NMe$_2$-py is further complicated because the dimethylamino substituent is competitive with the pyridine nitrogen in the bridge cleavage reaction.

A plot of the olefinic carbon chemical shifts vs. Hammett's σp constants gives four linear correlations (Figure 6). In each case, as X becomes more electron withdrawing, the olefinic carbon nuclei are deshielded. Without assigning which isomer is which, it is still possible to conclude that the effect of varying the pyridine cis to the olefin is of a similar magnitude and nature to that observed when the pyridine is in a trans position. These observations are not unexpected. Polarization of the platinum–nitrogen σ bond by X alters the electron density on the platinum. This should cause comparable changes in the platinum–carbon bonds whether they are cis or trans to the pyridine.

The chemical shifts of the σ-bonded carbons in **4a** and **4b** exhibit similar trends. As X becomes more electron withdrawing, the shielding of these nuclei decreases for each isomer (Table IV). It is impossible to assign, conclusively, the structures of the two solution species as either **4a** or **4b**. However, it seems reasonable to assign the major solution species as **4a**, the product observed in the solid state.[34,56]

Conclusions

The ^{13}C NMR parameters of carbon atoms directly bound to platinum(II) and trans to a para-substituted pyridine NC$_5$H$_4$X are mildly sensitive to changes in X. The observed trends in the data may be rationalized by assuming that the primary effect that changes in X have on the carbon–platinum bond is a change in the polarization of the carbon–platinum σ-bonding component (i.e., the electronic effect of X is transmitted through the Pt–N σ-bond). The strength of this argument lies in its ability to rationalize the trends in the ^{13}C NMR data for four different bonding modes, namely olefin–, carbonyl–, methyl– and acetylide–platinum bonds. It has not been necessary to invoke π back-bonding in the case of the olefin or carbonyl complexes to account for the observed changes in the ^{13}C data. This is consistent with previous ^{13}C

NMR studies of olefin– and alkyl–platinum(II) complexes where trends in the ^{13}C NMR data with varying ligands could be most satisfactorily accounted for in terms of changes in the alkene $\pi \rightarrow$ Pt donor bond.[2,5,41] The conclusions derived from a comparison of the ^{13}C NMR data of the carbonyl and acetylide complexes open to question previous π-bonding arguments proposed to rationalize observed trends in δ[13]CO and $\nu_{C\equiv O}$ data associated with changes in remote functional groups.[56,57]

It has also been shown that all the pyridines studied can cleave the chloro-bridged dimer **3** and that for the basic pyridines both possible products (**4a** and **4b**) are present in solution, contrary to previous conclusions.

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Use of Ligand Probes in Light Scattering. 1. Structural Analysis of Some Organotin(IV) Complexes in Cyclohexane and Benzene Solutions

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Optical anisotropies have been determined for several complexes of the type R_2SnCh_2 (R = CH_3, C_2H_5; Ch^- = acetylacetonate, dibenzoylmethanate, or tropolonate) by measurement of depolarized Rayleigh-scattered light intensities at 632.8 nm. Results of studies in cyclohexane solutions confirm that several of these complexes exist as cis–trans mixtures. For example, solutions of bis(1,3-diphenyl-1,3-propanedionato)dimethyltin(IV) and bis(1,3-diphenyl-1,3-propanedionato)diethyltin(IV) have been characterized as being composed of approximately two-thirds trans and one-third cis isomers. Scattering from several benzene solutions also is consistent with the assumption of cis–trans mixtures, but in two instances involving bis(2,4-pentane-dionato)dimethyltin(IV) and bis(tropolonato)diethyltin(IV) anisotropies are believed to have been enhanced measurably by solute–solvent interaction. Advantages and limitations in the use of the depolarized-light-scattering technique for the determination of isomer distributions have been discussed.

Introduction

Neutral, monomeric, six-coordinate organotin chelate compounds of the type R_2SnCh_2 are well-known.[1-8] The substituent, R, can be a halo, alkyl, or aromatic group and the bidentate ligand, Ch^-, can be one of a variety possessing nitrogen or oxygen donors. Complexes of β-keto enols, 8-quinolinol, and tropolone have been studied most extensively. If the ligand, Ch^-, has C_{2v} symmetry, only two isomeric forms of the complex are likely, a cis and a trans. Such systems, because of their simplicity, are of special interest. Unfortunately, no simple principle has been developed which allows the prediction of the most stable isomeric form for a particular derivative and both forms have been observed.

A number of physical methods have been applied. X-ray crystal studies have shown, for example, that bis(8-quinolinolato)dimethyltin(IV), $(CH_3)_2Sn(Ox)_2$, is cis while bis-(2,4-pentanedionato)dimethyltin(IV),[9] $(CH_3)_2Sn(acac)_2$, is trans. Results of infrared, Raman, and Mössbauer studies are in substantial agreement with the findings of the x-ray work. Because of the lability of many of these complexes[10,11] in solution, NMR has been of limited use. Attempts[11] to assess the solution structure of $(CH_3)_2Sn(acac)_2$ by variable-temperature NMR, for example, have proved unsuccessful. On the other hand $Cl_2Sn(acac)_2$[12,13] and $(C_6H_5)_2Sn(acac)_2$[14] which are somewhat less labile have been shown to be 100% cis. Significantly, $CH_3ClSn(acac)_2$ is best characterized[15] in terms of a cis–trans equilibrium. Apparently conflicting data have been reported concerning $(CH_3)_2Sn(acac)_2$ in solution. Infrared[2] and Raman[2,16,17] studies have provided evidence for a predominant trans structure while dipole moment[10] and dielectric loss measurements[18] have indicated that the complex is cis or a mixture of cis and trans isomers.

Very recently, infrared spectra[19] of $(CH_3)_2Sn(acac)_2$, corresponding tropolonate and oxinate derivatives, $(CH_3)_2Sn(trop)_2$ and $(CH_3)_2Sn(Ox)_2$, and their deuteriomethyl analogues have been obtained in CS_2 solution. As expected for a cis structure[6,19] solutions of the oxinate possess two peaks at 517 and 529 cm^{-1}, assignable to the symmetrical and antisymmetrical $(CH_3)_2Sn$ skeletal stretching vibrations, which shift about 50 cm^{-1} to lower energies for the deuteriomethyl derivatives. Solutions of the corresponding tropo-lonates and acetylacetonates have been shown to possess corresponding peaks which shift in similar fashion. This indicates very strongly that a substantial amount of cis-$(CH_3)_2Sn(acac)_2$ is present in CS_2 solutions. However, the dimethyltin acetylacetonate spectra, in contrast with other spectra, include a third stronger peak at 578 cm^{-1} which also shifts 50 cm^{-1} upon deuteration. Since that peak is best assignable to the antisymmetrical stretching vibration of a linear $(CH_3)_2Sn$ moiety, it has been concluded that the dimethyltin acetylacetonate solutions are mixtures of cis and trans isomers. Dimethyltin oxinates and tropolonates[19,20] have been shown to be present exclusively as the cis isomers in solutions. Because it was not possible to determine quantitatively the relative amounts of cis and trans isomers present in equilibrium mixtures on the basis of the infrared solution study[19] and because the complexes are too labile to study effectively with NMR, it was decided to attempt another means of structural investigation capable of determining the amounts of cis and trans isomers.

A recent paper[21] reports the optical anisotropies of several ligands of C_{2v} symmetry. Because the ligands in question—acetylacetone, dibenzoylmethane, and tropolone—have very large optical anisotropies, simple complexes of the type $(CH_3)_2SnCh_2$ and $(C_2H_5)_2SnCh_2$ will have large optical anisotropies in solution. More importantly, these anisotropies will vary strongly as a function of structure. Since there is reasonable confidence[19] that the solutions are best described as possessing cis–trans equilibrium mixtures rather than single distorted intermediate type structures, apparent anisotropies, as measured in terms of the intensities of the depolarized Rayleigh scattered light, will allow calculation of the relative amounts of cis and trans isomers to be made.

This paper describes the first successful effort to determine the cis–trans isomer distributions for several highly labile complexes of type R_2SnCh_2.

Experimental Section

Light-Scattering Photometer. Intensities of Rayleigh-scattered light were measured by means of a specially constructed photometer described in detail elsewhere.[22] The instrument was equipped with a Spectra-Physics Model 122 He–Ne laser which provided vertically