Contribution from the Department of Chemistry,
The University of Western Ontario, London, Ontario N6A 3K7, Canada

Carbon-13 Nuclear Magnetic Resonance Studies of Organometallic Compounds. VIII. Platinum(II) Carbene Derivatives[1]

MALCOLM H. CHISHOLM, HOWARD C. CLARK, JOHN E. H. WARD,* and KATSUTOSHI YASUFUKU

Received June 14, 1974 AIC403758

The ^{13}C and ^{1}H nmr spectra have been obtained for a series of platinum(II) carbene complexes of the type *trans*-$[(R)Pt(Q)_2(carbene)]^+PF_6^-$, where R is an anionic ligand and Q is a neutral donor. The ^{13}C nmr parameters are discussed and compared with the ^{13}C nmr parameters derived from related platinum(II) complexes. The stereochemical orientations of the substituents on the heteroatoms of the carbene ligands are considered in detail. Finally, the ^{13}C and ^{1}H nmr parameters are briefly compared.

Introduction

There have been a variety of reports[2-11] concerning investigations of transition metal carbene complexes *via* ^{13}C nuclear magnetic resonance spectroscopy. We have previously presented[2,3] ^{13}C nmr data for seven cationic platinum(II) carbene complexes of the sort *trans*-$[RPtQ_2(carbene)]^+PF_6^-$, where R is an anionic ligand (CH_3^- or Cl^-) and Q is a neutral donor ($As(CH_3)_3$ or $P(CH_3)_2(C_6H_5)$). For several methyl(amino)carbene complexes, we noted that the values of the three bond ^{13}C–^{195}Pt coupling constants of the amino methyl groups appeared to exhibit a marked sensitivity to the orientation of those groups with respect to platinum.[2] For example, $^{3}J_{PtC}$ values of 94 (±3) and 40 (±3) Hz are observed for *trans*-$[ClPt(As(CH_3)_3)_2(:C(CH_3)(N(CH_3)_2))]^+PF_6^-$, indicating a stereospecificity of those parameters. However, in the absence of further stereochemical information, we were unable to associate each of those $^{3}J_{PtC}$ values with a specific amino methyl group.

We have now closely examined the ^{1}H nmr spectra of these and several new platinum(II) carbene complexes which reveal a dependence of the ^{1}H–^{1}H and ^{1}H–^{195}Pt coupling constants on the stereochemistries of the carbene ligands. Using this new information, the ^{1}H nmr spectra of the complexes have been completely assigned, and by selective ^{13}C-{^{1}H} decoupling experiments, the stereochemical dependences of the ^{13}C–^{195}Pt coupling constants of the carbons in the carbene ligands have been determined.

Experimental Section

All complexes were prepared as described elsewhere.[12-14] The ^{13}C nmr spectra were measured on a Varian XL-100-15 spectrometer operating in the pulsed Fourier transform mode at 25.2 MHz. All spectra were determined with noise-modulated proton decoupling. Proton-coupled ^{13}C nmr spectra were obtained by offsetting the single decoupling frequency by 1 kHz, while selective ^{13}C-{^{1}H} experiments were performed by offsetting the decoupling frequency to the desired ^{1}H nmr frequency. The spectra were usually taken on chloroform-*d*, methylene-d_2 chloride, or acetone-d_6 solutions in 5- or occasionally 10-mm sample tubes. The ^{13}C nmr spectra were calibrated using TMS as the internal reference or the solvent resonances as secondary calibration standards.[15]

The ^{1}H nmr spectra were recorded on a Varian HA-100 spectrometer; the ^{1}H chemical shifts are reported with TMS as the internal standard.

Results

The ^{13}C nmr shieldings and coupling constants obtained from the spectra of the cationic carbene complexes **1–11** are summarized in Tables I and II respectively. We have not performed relative sign determinations for the ^{13}C–^{195}Pt or ^{1}H–^{195}Pt coupling constants; thus the absolute values of those parameters are presented. Needless to say, the use of the absolute values of those coupling constants is adequate for the arguments we will present later.

In all cases, except for **9–11**, the high-field resonances in the ^{13}C nmr spectra were assigned to the platinum methyl carbons on the basis of their similarity with data for related methylplatinum(II) and methylplatinum(IV) derivatives.[1,2,16-18] The central resonances of the platinum methyl groups are flanked by ^{195}Pt satellites (*ca.* one-fourth intensity) whose separation appears to be sensitive to the nature of the Q or carbene ligands. In a similar manner, we assigned the Q methyl carbon signals.

The signals arising from the carbene carbons of **1–11** were easily assigned by their characteristic occurrence at extremely low field.[2-11] The assignments of the remaining carbons of the carbene ligands warrant special comment. The *N*-methyl and -ethyl groups of **2–4** and **9–10** may adopt cis or trans orientations with respect to the carbene methyl groups, because of restricted rotation about the C–N bond as revealed in related carbene systems.[19-21] Since the stereochemical dispositions of those groups may be established by ^{1}H nmr spectroscopy (*vide infra*), by appropriate ^{13}C-{^{1}H} decoupling experiments we have completely assigned the signals of the *N*-methylamino carbons of **3**. The carbene methyl carbon of **3** was assigned to the signal at 31.9 ppm (J_{PtC} = 51 (±1) Hz) by comparison with the signal (37.7 ppm, J_{PtC} = 58 (±1) Hz) of the carbene methyl carbon of the amino complex **1**. When the low-field *N*-methyl protons at 3.63 ppm in the ^{1}H nmr spectrum of **3** were irradiated, the multiplet of the *N*-methyl group at 50.5 ppm in the ^{13}C nmr spectrum of **3** coalesced to a sharp singlet. Thus the low-field *N*-methyl carbon is trans to the carbene methyl group and cis to the platinum atom. This assignment was confirmed by irradiating the *N*-methyl protons in the ^{1}H nmr spectrum of **3** at 3.23 ppm; the *N*-methyl carbon signals at 41.1 ppm collapsed to a singlet. Thus, the high-field *N*-methyl group in the ^{13}C nmr spectrum of **3** is cis to the carbene methyl group and trans to the platinum atom. The similar shieldings of the chloroplatinum analog **10** suggest an identical assignment. The similarity of the $^{5}J_{PtC}$ values of the *N*-methyl groups of the monomethylamino derivatives **2** and **9** to those of their dimethylamino analogs [**2**, 60 (±1) Hz, major isomer, *vs.* **3**, 66 (±1) Hz; **9**, 87 (±1) Hz, *vs.* **10**, 94 (±3) Hz] indicates that the *N*-methyl groups in **2** and **9** are trans to their respective carbene methyl groups.[22] In addition, it appears that the *N*-ethyl group in **4** is also trans to the carbene methyl group, since the J_{PtC} value (58 (±1) Hz) for the methylene group is very similar to those (60 (±1) and 66 (±1) Hz) of the *N*-methyl groups in **2** and **3** trans to the carbene methyl group. Finally, the assignments of the signals arising from the carbons of the cyclic carbene ligands in **7** and **8** follow from a comparison with the shieldings of the carbons in tetrahydrofuran as described earlier.[2] All the remaining assignments were aided by off-resonance decoupling methods and by considerations of basic ^{13}C nmr chemical shift theory.[23,24]

The ^{1}H chemical shifts and ^{1}H–^{1}H and ^{1}H–^{195}Pt coupling constants for **1–11** are assembled in Tables III and IV. These

Table I. ^{13}C Nmr Shieldings[a] for *trans*-$[(R)Pt(Q)_2(carbene)]^+PF_6^-$, **1–11**

Complex	R^-	Carbene ligand	Q	Solvent	Pt methyl carbon δ(C)	Q methyl carbons δ(C)	Carbene carbons				Other ^{13}C shieldings
							δ(C:)	$\delta(C^2)$	$\delta(C^3)$	$\delta(C^4)$	
1[b]	CH_3^-	$C^2H_3\ddot{C}NH_2$	$As(CH_3)_3$	CD_2Cl_2	−18.6	8.8	255.6	37.7			
2[b,c]	CH_3^-	$C^2H_3\ddot{C}NH(C^3H_3)$	$As(CH_3)_3$	CD_2Cl_2	−17.6	9.1	247.3	36.6	39.6		
2[b,d,e]	CH_3^-	$C^2H_3\ddot{C}NH(C^3H_3)$	$As(CH_3)_3$	CD_2Cl_2	−17.6	9.1	247.3	31.3	34.2		
3[b]	CH_3^-	$C^2H_3\ddot{C}N(C^3H_3)(C^4H_3)$	$As(CH_3)_3$	CD_2Cl_2	−19.8	9.2	245.1	31.9	50.5[f]	41.1[g]	
4[e]	CH_3^-	$C^2H_3\ddot{C}NHC^3H_2C^4H_3$	$As(CH_3)_3$	$CDCl_3$	−17.8	9.1	245.2	36.4	48.3	12.8	
5[b]	CH_3^-	$C^2H_3\ddot{C}OC^3H_3$	$As(CH_3)_3$	$(CH_3)_2CO$	−15.9	9.5	321.0	44.2	70.6		
6[e]	CH_3^-	$C^2H_3COC^3H_2C^4H_3$	$As(CH_3)_3$	$CDCl_3$	−16.5	9.4	317.8	43.7	80.5	13.9	
7[e]	CH_3^-	$:\overline{CC^2H_2C^3H_2C^4H_2O}$	$As(CH_3)_3$	CD_2Cl_2	−15.9	9.3	*h*	59.1	19.8	87.7	
8[b]	CH_3^-	$:\overline{CC^2H_2C^3H_2C^4H_2O}$	$P(CH_3)_2(C_6H_5)$	CD_2Cl_2	−10.1	12.1	299.2	57.2	18.9	87.9	$\delta(C_6H_5)$ 128.6–134.2[i]
9[e]	Cl^-	$C^2H_3\ddot{C}NH(C^3H_3)$	$As(CH_3)_3$	CD_2Cl_2		9.1	215.1	36.7	40.8		
10[b]	Cl^-	$C^2H_3\ddot{C}N(C^3H_3)(C^4H_3)$	$As(CH_3)_3$	$(CD_3)_2CO$		8.6	210.3	33.0	52.0[f,j]	41.6[g,j]	
11[b]	Cl^-	$C^2H_3COC^3H_3$	$As(CH_3)_3$	$(CD_3)_2CO$		8.7	278.3	*k*	72.1		

[a] In ppm (±0.1) (downfield positive) from TMS. [b] M. H. Chisholm, H. C. Clark, L. E. Manzer, J. B. Stothers, and J. E. H. Ward, *J. Amer. Chem. Soc.*, 95, 8574 (1973). [c] Major isomer, $N(CH_3)$ trans to $:C(CH_3)$. [d] Minor isomer, $N(CH_3)$ cis to $:C(CH_3)$. [e] This work. [f] $N(CH_3)$ group trans to $:C(CH_3)$. [g] $N(CH_3)$ group cis to $:C(CH_3)$. [h] Sample decomposed in solution; signal not observed. [i] Complex multiplet. [j] These shieldings were interchanged inadvertently in *b*. [k] This value was reported incorrectly as 9.2 ppm in *b*; signal not observed.

Table II. ^{13}C Nmr ^{13}C–^{195}Pt Coupling Constants[a] for *trans*-$[(R)Pt(Q)_2(carbene)]^+PF_6^-$, **1–11**

Complex	R^-	Carbene ligand	Q	Solvent	Pt methyl carbon $\lvert ^1J_{PtC}\rvert$	Q methyl carbons $\lvert ^2J_{PtC}\rvert$	Carbene carbons			
							$\lvert ^1J_{PtC:}\rvert$	$\lvert J_{PtC^2}\rvert$	$\lvert J_{PtC^3}\rvert$	$\lvert J_{PtC^4}\rvert$
1[b]	CH_3^-	$C^2H_3\ddot{C}NH_2$	$As(CH_3)_3$	CD_2Cl_2	380 (±1)	53 (±1)	666 (±3)	58 (±1)		
2[b,c]	CH_3^-	$C^2H_3\ddot{C}NH(C^3H_3)$	$As(CH_3)_3$	CD_2Cl_2	381 (±1)	51 (±1)	687 (±3)	50 (±1)	60 (±1)	
2[b,d,e]	CH_3^-	$C^2H_3\ddot{C}NH(C^3H_3)$	$As(CH_3)_3$	CD_2Cl_2	381 (±1)	51 (±1)	687 (±3)	*f*	*f*	
3[b]	CH_3^-	$C^2H_3\ddot{C}N(C^3H_3)(C^4H_3)$	$As(CH_3)_3$	CD_2Cl_2	385 (±5)	53 (±1)	694 (±6)	51 (±1)	66 (±1)[g,h]	20 (±1)[i]
4[e]	CH_3^-	$C^2H_3\ddot{C}NHC^3H_2C^4H_3$	$As(CH_3)_3$	$CDCl_3$	381 (±1)	51 (±1)	684 (±2)	50 (±1)	58 (±1)	0 (±1)
5[b]	CH_3^-	$C^2H_3\ddot{C}OC^3H_3$	$As(CH_3)_3$	$(CH_3)_2CO$	360 (±3)	50 (±3)	759 (±3)	86 (±3)	67 (±3)	
6[e]	CH_3^-	$C^2H_3COC^3H_2C^4H_3$	$As(CH_3)_3$	$CDCl_3$	354 (±1)	50 (±1)	756 (±2)	83 (±1)	65 (±1)	0 (±1)
7[e]	CH_3^-	$:\overline{CC^2H_2C^3H_2C^4H_2O}$	$As(CH_3)_3$	CD_2Cl_2	366 (±2)	50 (±2)	*j*	96 (±2)	17 (±2)	46 (±2)
8[b]	CH_3^-	$:\overline{CC^2H_2C^3H_2C^4H_2O}$	$P(CH_3)_2(C_6H_5)$	CD_2Cl_2	395 (±2)	40 (±2)	*f*	90 (±2)	17 (±2)	50 (±2)
9[e]	Cl^-	$C^2H_3\ddot{C}NH(C^3H_3)$	$As(CH_3)_3$	CD_2Cl_2		47 (±1)	1047 (±1)	82 (±1)	87 (±1)	
10[b]	Cl^-	$C^2H_3\ddot{C}N(C^3H_3)(C^4H_3)$	$As(CH_3)_3$	$(CD_3)_2CO$		50 (±3)	1070 (±3)	76 (±3)	94 (±3)[g]	40 (±3)[i]
11[b]	Cl^-	$C^2H_3\ddot{C}OC^3H_3$	$As(CH_3)_3$	$(CD_3)_2CO$		48 (±2)	1125 (±2)	*f*	95 (±2)	

[a] In Hz. [b] M. H. Chisholm, H. C. Clark, L. E. Manzer, J. B. Stothers, and J. E. H. Ward, *J. Amer. Chem. Soc.*, 95, 8574 (1973). [c] Major isomer, $N(CH_3)$ trans to $:C(CH_3)$. [d] Minor isomer, $N(CH_3)$ cis to $:C(CH_3)$. [e] This work. [f] ^{195}Pt satellites insufficiently intense to be observed. [g] $N(CH_3)$ group trans to $:C(CH_3)$. [h] This value was reported incorrectly as 56 (±1) in *b*. [i] $N(CH_3)$ group cis to $:C(CH_3)$. [j] Sample decomposed in solution; signals not observed.

tables also include the ^1H nmr parameters for 13 related platinum(II) carbene complexes which we have not investigated by ^{13}C nmr spectroscopy.

The arguments used to assign the platinum methyl, arsenic methyl, and phosphorus methyl proton signals of **1–24** are similar to those used to assign their respective ^{13}C nmr signals, so we will not consider them here. On the other hand, the assignments of the proton signals arising from the carbene ligands are not so straightforward.

Three rather broad signals at 2.40, 3.23, and 3.63 ppm (with ^{195}Pt satellites) in the ^1H nmr spectrum of **3** can be associated with the carbene methyl and two *N*-methyl groups. The signal at δ 2.40 was assigned to the carbene methyl protons due to the similarity of its chemical shift and $^3J_{PtCCH}$ value (15.0 Hz) to those (δ 2.43 and 15.2 Hz) observed for the carbene methyl protons of **1**, which may be unequivocally assigned. The other two signals at 3.23 and 3.63 ppm (both broad quartets with ^{195}Pt satellites) were assigned as follows: both signals gave sharp singlets when the signal at δ 2.40 was irradiated, while the signal at δ 2.40 gave the same broad quartet pattern as the undecoupled signals at δ 3.23 and 3.63 by irradiation of either of the signals at δ 3.23 or 3.63. Finally, by a triple-irradiation experiment, by irradiation at both the δ 3.23 and 3.63 signals, a sharp singlet (with ^{195}Pt satellites) was produced at δ 2.40. Thus five-bond HCCNCH coupling was clearly observed between the carbene methyl protons and the protons of both *N*-methyl groups. The observed $^5J_{HCCNCH}$ values (*ca.* 0.9 Hz for the signal at δ 3.63 and *ca.* 0.5 Hz for the signal at δ 3.23) are almost identical with those values (0.9 and 0.3 Hz) observed in methyl(dimethylamino)carbenechromium pentacarbonyl.[21] In addition, the chemical shifts of the three types of methyl groups are also close to one another: δ_{Pt} 2.40 *vs.* δ_{Cr} 2.69, δ_{Pt} 3.23 *vs.* δ_{Cr} 3.30, and δ_{Pt} 3.63 *vs.* δ_{Cr} 3.87. The similarity of all these data suggests that the chromium pentacarbonyl complex provides an excellent model on which the assignments of the ^1H nmr resonances of the methyl groups in the carbene ligand of **3** may be based. Thus, we assigned the *N*-methyl group of **3** with the $^5J_{HCCNCH}$ value of 0.9 Hz (δ 3.63) to the methyl group trans (anti) to the carbene methyl group, while the *N*-methyl group with the $^5J_{HCCNCH}$ value of 0.5 Hz (δ 3.23) was assigned to the methyl group cis (syn) to the carbene methyl group.

The ^1H nmr spectrum of the crude product **2** exhibited two different sets of carbene methyl and *N*-methyl signals in the ratio 1:5, suggesting that two isomers were present. The *N*-methyl signal of the major component occurs at 3.40 ppm ($^5J_{HCCNCH}$ = 0.9 Hz) while that signal for the minor component occurs at 3.12 ppm ($^5J_{NCCNCH}$ = 0.5 Hz). The chemical shift and five-bond ^1H–^1H coupling constant of the *N*-methyl group of the major component indicate that the

Table III. ^1H Nmr Chemical Shifts[a] and Coupling Constants[b] for *trans*-$[(R)Pt(As(CH_3)_3)_2(carbene)]^+PF_6^-$, 1–6 and 9–15

				Pt methyl protons		As methyl protons		Carbene methyl protons			
Complex	Carbene ligand	R^-	Solvent	$\delta(CH_3)$	$\lvert {}^2J_{PtCH} \rvert$	$\delta(CH_3)$	$\lvert {}^3J_{PtAsCH} \rvert$	$\delta(CH^2{}_3)$	$\lvert {}^3J_{PtCCH^2} \rvert$	$\lvert {}^4J_{H^2CCNH} \rvert$	Other ^1H nmr signals
1	$CH^2{}_3\ddot{C}NH_2$	CH_3^-	CH_2Cl_2	−0.05	50.2	1.39	23.5	2.43	15.2		
2	$CH^2{}_3\ddot{C}NH$-$CH^3{}_3$[c]	CH_3^-	$CHCl_3$	0.06	51.4	1.43	24.5	2.42	16.0	1.0	$\delta(CH^3{}_3)$ 3.40, $^4J_{PtH}$ 7.0; $^3J_{HH^3}$ 5.0; $^5J_{H^2H^3}$ ~0.9
	$CH^2{}_3\ddot{C}NH$-$CH^3{}_3$[d]	CH_3^-	$CHCl_3$	0.00	51.4	1.41	24.5	2.37	16.0		$\delta(CH^3{}_3)$ 3.12, $^4J_{PtH}$ 7.0; $^3J_{HH^3}$ 5.0; $^5J_{H^2H^3}$ ~0.5
3	$CH^2{}_3\ddot{C}N$-$(CH^3{}_3)$-$(CH^4{}_3)$	CH_3^-	$CHCl_3$	0.03	52.0	1.41	24.0	2.40	15.0		$\delta(CH^3{}_3)$ 3.63, $^4J_{PtH}$ 6.5; $^5J_{H^2H^3}$ ~0.9; $\delta(CH^4{}_3)$ 3.23, $^4J_{PtH}$ 6.8; $^5J_{H^2H^4}$ ~0.5
4	$CH^2{}_3\ddot{C}NH$-$CH^3{}_2CH^4{}_3$	CH_3^-	$CDCl_3$	0.00	50.0	1.45	23.6	2.42	17.4	1.1	$\delta(CH^3{}_2)$ 3.80, $^3J_{HH^3}$ ~5.0; $^3J_{H^3H^4}$ ~7; $\delta(CH^4{}_3)$ 1.32, $^3J_{H^3H^4}$ 7.6
5	$CH^2{}_3\ddot{C}OCH^3{}_3$	CH_3^-	$CHCl_3$	0.11	48.5	1.51	25.5	2.55	6.0		$\delta(CH^3{}_3)$ 4.86, $^4J_{PtH^3}$ 6.0; $^5J_{H^2H^3}$ ≈0.4
6	$CH^2{}_3\ddot{C}O$-$CH^3{}_2CH^4{}_3$	CH_3^-	$CHCl_3$	0.11	48.8	1.50	25.4	2.52	5.5		$\delta(CH^3{}_2)$ 5.16; $\delta(CH^4{}_3)$ 1.63, $^3J_{H^3H^4}$ 7.0
9	$CH^2{}_3\ddot{C}NH$-$CH^3{}_3$	Cl^-	CD_2Cl_2			1.52	24.1	2.57	29.4	1.0	$\delta(CH^3{}_3)$ 3.47, $^4J_{PtH^3}$ ~7; $^5J_{H^2H^3}$ ~1.0
10	$CH^2{}_3\ddot{C}N$-$(CH^3{}_3)$-$(CH^4{}_3)$	Cl^-	CD_2Cl_2			1.46	24.6	2.58	27.5		$\delta(CH^3{}_3)$ 3.83, $^4J_{PtH^3}$ 11.0; $^5J_{H^2H^3}$ 0.9; $\delta(CH^4{}_3)$ 3.38, $^4J_{PtH^4}$ 10.5; $^5J_{H^2H^4}$ 0.5
11	$CH^2{}_3\ddot{C}OCH^3{}_3$	Cl^-	CD_2Cl_2			1.59	26.0	2.70	10.9		$\delta(CH^3{}_3)$ 4.86, $^4J_{PtH^3}$ 8.8; $^5J_{H^2H^3}$ ~0.5
12	$CH^2{}_3\ddot{C}NH$-$CH^3(CH^4{}_3)_2$	CH_3^-	$CDCl_3$	0.00	51.0	1.46	24.2	2.42		1.2	$\delta(CH^3)$ 4.53, $^3J_{HCNC}$ 9.0; $\delta(CH^4{}_3)$ 1.35, $^3J_{H^3H^4}$ 6.7
13	$CH^2{}_3\ddot{C}NH$-$CH^3{}_2CH^4{=}CH^5{}_2$	CH_3^-	$CHCl_3$	0.05	49.0	1.42	23.0	2.45	16.0		$\delta(CH^3{}_2)$ 4.39; $\delta(CH^4)$ 5.70; $\delta(CH^5{}_2)$ 4.90
14	$CH^2{}_3\ddot{C}N$-$(CH^3{}_3)(CH^4{}_3)$	I^-	CH_2Cl_2			1.59	24.8	2.52	30.0		$\delta(CH^3{}_3)$ 3.80, $^4J_{PtH^3}$ 10.0; $\delta(CH^4{}_3)$ 3.38, $^3J_{PtH^4}$ 9.5
15	$CH^2{}_3\ddot{C}OCH^3{}_3$	I^-	CH_2Cl_2			1.70	24.6	2.18	14.0		$\delta(CH^3{}_3)$ 5.05, $^4J_{PtH^3}$ 10.0

[a] In ppm (±0.01) (downfield positive) from TMS. [b] In Hz. The relative errors are ±0.1 Hz for all J_{HH} values except $^5J_{HC\ddot{C}NCH}$ and $^5J_{HC\ddot{C}OCH}$ which are accurate to ±0.05 Hz. [c] Major isomer, $N(CH_3)$ trans to $:C(CH_3)$. [d] Minor isomer, $N(CH_3)$ cis to $:C(CH_3)$.

Table IV. ^{1}H Nmr Chemical Shifts[a] and Coupling Constants[b] for *trans*-$[(R)Pt(P(CH_3)_2(C_6H_5))_2(carbene)]^+PF_6^-$, 16–24

Complex	Carbene ligand	R^-	Solvent	Pt methyl protons			P methyl protons			Carbene methyl protons		Other ^{1}H nmr signals
				$\delta(CH_3)$	$\lvert ^2J_{PtCH}\rvert$	$\lvert ^3J_{PPtCH}\rvert$	$\delta(CH_3)$	$\lvert ^3J_{PtPCH}\rvert$	$\lvert(^1J + {}^3J)_{PH}\rvert$	$\delta(CH^3{}_3)$	$\lvert ^3J_{PtCCH^2}\rvert$	
16	$CH^2{}_3\ddot{C}NH_2$	CH_3^-	$CHCl_3$	−0.03	51.5	8.1	1.76	34.6	7.3	2.13	18.0	
17	$CH^2{}_3\ddot{C}NHCH^3{}_3$	CH_3^-	$CHCl_3$	0.04	51.6	8.0	1.75 1.74	34.0 34.5	7.0 7.0	2.20	19.0	$\delta(CH^3{}_3)$ 3.26, $^4J_{PtH^3}$ 8; $^3J_{H^3CNH}$ 5
18	$CH^2{}_3\ddot{C}N(CH^3{}_3)(CH^4{}_3)$	CH_3^-	$CHCl_3$	0.06	51.2	8.0	1.73 1.75	33.0 33.0	7.0 7.0	1.96	17.2	$\delta(CH^3{}_3)$ 3.48, $^4J_{PtH^3}$ 7.2; $^5J_{H^2H^3}$ ~0.4; $\delta(CH^4{}_3)$ 2.76, $^4J_{PtH^4}$ 6.7; $^5J_{PH}$ 1.3
19	$HO(CH_2)_3\ddot{C}NH_2$	CH_3^-	CH_2Cl_2	−0.02	51.2	8.2	1.74	34.4	7.0	2.40	6.0	$\delta(HOCH_2)$ ~3.40
20	$HO(CH_2)_3\ddot{C}N(CH_3)(CH_3)$	CH_3^-	CH_2Cl_2	0.06	50.0	8.0	1.75 1.76	34.8 34.0	7.0 7.0			
21	$CH^2{}_3\ddot{C}NHCH^3{}_3$	Cl^-	CD_2Cl_2				1.88 1.84	30.4 30.8		2.14	33.2	$\delta(CH^3{}_3)$ 3.18, $^4J_{PtH^3}$ 12; $^3J_{H^3CNH}$ 5
22	$CH^2{}_3\ddot{C}N(CH^3{}_3)(CH^4{}_3)$	Cl^-	CH_2Cl_2				1.96 1.92	31.5 32.0	8.2 8.2	1.95		$\delta(CH^3{}_3)$ 3.50, $^4J_{PtH^3}$ 11.0; $\delta(CH^4{}_3)$ 2.54, $^4J_{PtH^4}$ 10.0
23	$CH^2{}_3\ddot{C}N(CH^3{}_3)(CH^4{}_3)$	I^-	CH_2Cl_2				2.20 2.15	32.0 32.0	7.5 7.5	1.95		$\delta(CH^3{}_3)$ 3.70, $^4J_{PtH^3}$ 11.5; $\delta(CH^4{}_3)$ 2.55, $^4J_{PtH^4}$ 10.5
24	$:\overline{CCH^2{}_2CH^3{}_2CH^4{}_2O}$	Cl^-	CD_2Cl_2				1.92	30.0	8.8	2.20		$\delta(CH^4{}_2)$ 4.34, $^3J_{PtH^4}$ 6.0; $^3J_{H^3H^4}$ 8.0; $\delta(CH^3{}_2)$ 1.10, $^3J_{H^{2,4}H^3}$ 8.0

[a] In ppm (±0.01) (downfield positive) from TMS. [b] In Hz. The relative errors are ±0.1 Hz for all J_{HH} values except $^5J_{HC\ddot{C}NCH}$ which is accurate to ±0.05 Hz.

N-methyl group is trans to the carbene methyl group,[22] while the minor component corresponds to the cis isomer. The very broad resonance at 9.8–10 ppm in the ^{1}H nmr spectrum of **2** is assignable to the amino proton, which exhibits coupling of 5.0 Hz with the *N*-methyl protons. Deuterium exchange of this proton (with D_2O) resulted in the loss of this coupling but did not appear to cause any cis–trans isomerization of the *N*-methyl group. Substitution of the platinum–methyl group with Cl^- also proceeds stereospecifically, since the $^5J_{HCCNCH}$ value remains almost constant at 1.0 Hz. Our previous results[2] indicate that this coupling constant, which is internal within the carbene ligand, should not be particularly sensitive to alterations of the substituent trans to the carbene ligand.[25]

The ^{1}H nmr data for the methylmethoxycarbene derivative **5** clearly exhibit coupling (0.4 Hz) between the methyl and methoxyl groups. This value is identical with that for the complexes $(OC)_5MC(OCH_3)CH_3$[26] (M = Cr, W). In a previous paper,[14] we proposed that our complex existed in solution as the cis isomer; however, our careful reexamination of the ^{1}H nmr spectral data revealed that this original assignment was incorrect. This new assignment has been recently corroborated by X-ray crystallographic studies of the bis(dimethylphenylphosphine) analog of **5**.[27] In the solid state, the methoxyl group was found to adopt a trans orientation with respect to the carbene methyl group, while the plane of the carbene ligand (C–C–O–C) was found to be approximately perpendicular to the platinum square plane. Chloro substitution for the platinum methyl group of **5** gave complex **11**. The J_{HCCOCH} value (0.5 Hz) of **11** again indicates that the carbene methyl and methoxyl groups are trans to one another.

The stereochemistries of the carbene ligands of the remaining complexes were assigned by similar arguments or by methods outlined previously.[14]

Discussion

^{13}C Nmr Data. General Information. The ^{13}C nmr data obtained from complexes **1**–**11** reveal that with variations in ligands, characteristic variations in the ^{13}C shieldings and ^{13}C–^{195}Pt coupling constants may occur. For example, when the amino group in **1** is replaced by a methoxyl substituent in **5**, the ^{13}C shielding of the platinum methyl carbon *decreases* from −18.6 to 15.9 ppm, while the $^1J_{PtC}$ value of that carbon *decreases* from 380 (±1) to 360 (±3) Hz. Concomitantly, the ^{13}C shielding of the carbene carbon *decreases* from 255.6 to 321.0 ppm, while the $^1J_{PtC}$ value for the carbene carbon *increases* from 666 (±3) to 759 (±3) Hz. The ^{13}C shieldings of the arsenic methyl carbons remain relatively constant at 8.8 and 9.5 ppm, respectively, as do the $^2J_{PtAsC}$ values for those groups (*ca.* 52 (±2) ppm). Substitution of the platinum methyl group by a chloro ligand also produces significant changes in the ^{13}C nmr parameters of the remaining ligands. For example, when the platinum methyl group in the methylmethoxycarbene complex **5** is replaced by Cl^- in **11**, the shielding of the carbene carbon *increases* from 321.0 to 278.3 ppm, while the $^1J_{PtC}$ value for that carbon *increases* from 759 (±3) to 1125 (±2) Hz. The ^{13}C shieldings and ^{13}C–^{195}Pt coupling constants of the methyl and methoxyl carbons also change significantly from **5** to **11**.

^{13}C–^{195}Pt Coupling Constants. Inverse Rehybridization Scheme. We have previously noted[2] for carbene complexes of the type *trans*-$[(CH_3)Pt(As(CH_3)_3)_2(:C(CH_3)X)]^+PF_6^-$, **1**–**3** and **5**, that the $^1J_{PtC}$ values of the platinum methyl groups *increase* in the order X = OCH_3 < NR_2, while the $^1J_{PtC}$ values of the carbene carbons *decrease* in the order X = OCH_3 > NR_2. These trends were taken as support for the rehybridization concept of the nmr trans influence,[28–30] since changes at the carbene carbon, induced by changing an amino to a methoxyl substituent, apparently result in *inverse* changes in σ hybridization of the trans platinum–methyl bond.

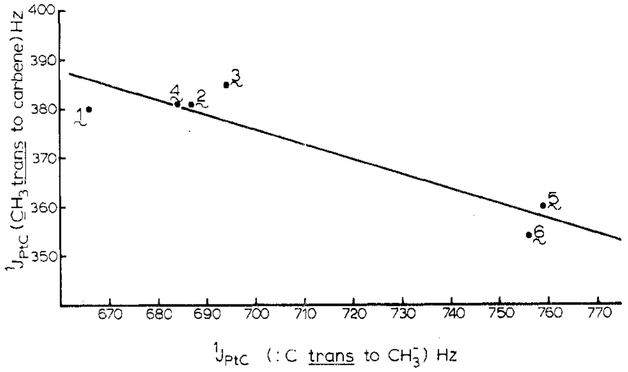


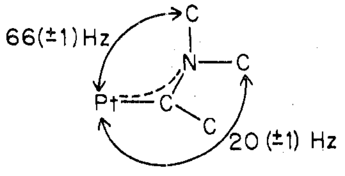
Figure 1. Plot of $^1J_{PtC}$(CH$_3$ group trans to the carbene ligand) *vs.* $^1J_{PtC}$(carbene carbon trans to the methyl substituent) for **1-6**.

We have now examined this inverse trend *quantitatively* for **1-6** by plotting the $^1J_{PtC}$ values for the platinum methyl group *vs.* the $^1J_{PtC}$ values of the carbene carbons, as shown in Figure 1. Linear regression analysis[31] of the data revealed a reasonable linear relationship shown in eq 1. It thus appears that

$$^1J_{PtC}(CH_3, \mathbf{1\text{-}6}) = [-0.30\ (\pm 0.02)]^1J_{PtC}(:C, \mathbf{1\text{-}6}) + 588\ (\pm 17) \quad r = 0.926 \tag{1}$$

there are quantitative grounds supporting the contention that the nmr trans influence should produce inverse changes in these two coupling constants. As the σ-donor ability of the carbene carbon increases (as revealed by increasing $^1J_{PtC}$(carbene) values), that carbon will compete more effectively for Pt 6s character. The increase in s character in the platinum–carbene carbon bond is obtained partially at the expense of the platinum–methyl carbon bond, and lower $^1J_{PtC}$(platinum–methyl carbon) values are observed. We should point out that this linear correlation is far from perfect, and we attribute this to the irregular changes on the carbene carbon hybridization bestowed by variations in the heteroatom substituents –OR and NR$_2$, where R = H, Me, or Et. These groups will also compete for electron density on the carbene carbon, as well as the trans and cis platinum substituents, so it is perhaps not surprising that a perfect linear correlation does not result. An excellent fit would presumably occur if the two platinum–carbon bonds were exclusively rehybridized.

Stereochemical Dependencies. Next, we will consider the angular dependencies of the three-bond PtCNC coupling constants of the amino carbene derivatives **1-4**, **9**, and **10**. The $^3J_{PtCNC}$ values of the dimethylamino complex **3** are 66 (±1) Hz for the N-methyl group trans to the carbene methyl group and 20 (±1) Hz for the N-methyl group cis to the carbene methyl group. Unexpectedly, the $^3J_{PtCNC}$ value for the N-methyl group cis to platinum is much larger than for the N-methyl group trans to platinum. A similar trend is revealed in the $^3J_{PtCNC}$ values of the chloro analog **10** (Table II). The $^3J_{PtCNC}$ values of the N-methyl groups of the monomethylamino complexes **2** and **9**, as well as the monoethyl complex **4**, follow like patterns.

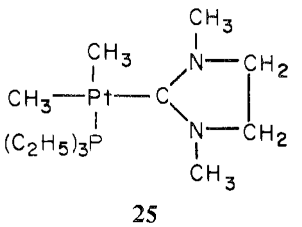


The usual trend in $^3J_{HCCH}$ values in olefins is just the reverse of the above pattern; $^3J_{HCCH}$(trans) is almost always greater than $^3J_{HCCH}$(cis). Moreover, this trend is also found for vinylplatinum compounds[32] and a variety of other vinyl-(transition metal) derivatives.[33] For *trans*-[(CH$_2$=CH)Pt(P(C$_6$H$_5$)$_3$)$_2$Br] $^3J_{PtCCH}$(H trans to platinum) = 148 Hz, while $^3J_{PtCCH}$(H cis to platinum) = 78 Hz. Assuming that these vinyl derivatives are good models for the carbene compounds examined here, our assignments would appear to be incorrect, suggesting that the close matching of the N-methyl chemical shifts and $^5J_{HCCNCH}$ values of the platinum carbenes and group VI analogs may be fortuitous.

The chemical shift variations induced by solvent changes were originally used to assign the stereochemical orientations of the N-methyl groups in pentacarbonylchromium carbene complexes[21,34] and in N,N'-dimethylamides.[35,36] While such a technique may in principle be applied to the aminocarbene complexes we are examining here, unfortunately, the appropriate derivatives are insoluble in benzene, and thus such a study could not be carried out.

If two closely related carbene complexes had unequivocally rigid cis and trans isomeric situations at the heteroatom, we could use the ^{195}Pt–^{13}C coupling constants for the carbons on those heteroatoms in order to determine if J_{PtC}(cis to platinum) is greater than J_{PtC}(trans to platinum). The methylmethoxycarbene **5** and cyclic carbene **7** complexes appear to be such a pair. Assuming that our original assignments are correct, as indicated by both nmr and X-ray crystallographic evidence, the methoxyl carbon in **5** is cis to platinum, while carbon 4 in **7** is of necessity trans to platinum. As we have shown for the N-methyl groups of **3** and **10**, J_{PtC}(cis to platinum) is greater than J_{PtC}(trans to platinum), since for **5** $^3J_{PtCOC}$ is 67 (±3) Hz, while $^3J_{PtCOC}$ for **7** is 46 (±2) Hz. However, it did occur to us that this difference may arise from the unlike substitution patterns at the carbons α to oxygen. Thus, we synthesized the methylethoxycarbene complex **6**, so that both complexes have secondary carbons α to oxygen. To our gratification, the methylene carbon in **6** exhibited coupling of 65 (±1) Hz with platinum, identical with the corresponding coupling constant (within the experimental error) in the methylmethoxycarbene complex **5**. This evidence supports our contention that $^3J_{PtC}$(cis to platinum) is greater than $^3J_{PtC}$(trans to platinum) for both the amino- and alkoxylcarbene derivatives. We should point out that it is possible that the ethoxyl group in **6** is trans to platinum, unlike its methoxyl analog, and that the combination of the additional methyl group and the change in geometry gives rise to the same $^3J_{PtCOC}$ value as found for the methoxyl analog. Since this possibility would involve a mutual canceling of two opposing factors, we feel that the former proposal is most likely. We have shown previously that the effect of replacing a methyl proton in [(1,3-cyclooctadiene)Pt(CH$_3$)$_2$] to give [(1,3-cyclooctadiene)Pt(CH$_2$CH$_3$)$_2$] does not have a gross effect on $^1J_{PtC}$(alkyl).[1] That value for the dimethyl complex is 55 (±2) Hz, while for the diethyl derivative it is 47 (±2) Hz. These data add additional support to the notion that $^3J_{PtC}$(cis to platinum) > $^3J_{PtC}$(trans to platinum) for the carbene complexes considered here. Hence, our carbene derivatives seem to exhibit nmr characteristics which deviate from those normally observed.

Ideally, this stereochemical problem could have been solved by observing the ^{13}C nmr spectra of cyclic amino analogs of the cyclic alkoxycarbenes **7** and **8**. Unfortunately, attempts to synthesize such compounds were unsuccessful. Cardin, *et al.*,[11] have obtained the ^{13}C nmr parameters of a series of carbene complexes of 1,3-diorganoimidazolidin-2-ylidenes of the sort [MX$_2$(R'$_3$E)(:C(NRCH$_2$CH$_2$NR))], A, where M = Pt, Pd; E = P, As; X$^-$ = Cl$^-$, Br$^-$, CH$_3^-$; R = CH$_3$, C$_6$H$_5$; and R' = CH$_2$CH$_3$, CH$_3$CH$_2$CH$_2$, CH$_3$CH$_2$CH$_2$CH$_2$. For a number of these trans derivatives, $^3J_{PtCNC}$(trans to platinum) varies substantially (14.6–34.2 Hz) while $^3J_{PtCNC}$(cis to platinum) is essentially invariant (*ca.* 24.2 Hz). Previous results[1,2,16-18,37] from our group suggest that both $^3J_{PtCNC}$ values should be sensitive to alterations in the ligand trans to the carbene substituent. These complexes comprise another case in which *vicinal* ${}^{13}C-{}^{195}Pt$ coupling constants do not behave in the usual manner. It is tenuous to compare directly the ${}^{13}C$ nmr parameters for these cyclic carbene complexes with those parameters obtained from our derivatives since directly analogous compounds are not available. However, the most similar derivative **25** exhibits a ${}^3J_{PtCNC}(NCH_3\text{ group})$ value of 48.8 Hz, while ${}^3J_{PtCNC}(NCH_2\text{ group})$ is 24.4 Hz, again indicating that ${}^3J_{PtCNC}(\text{cis to platinum})$ is $> {}^3J_{PtCNC}(\text{trans to platinum})$, for a carbene ligand trans to a platinum–methyl group.



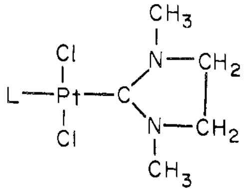
25

Comparisons with J_{PtH} Values. The ${}^1H-{}^{195}Pt$ coupling constants of the carbene ligands in **1–11** also exhibit unusual stereochemical dependencies. For example, while the ${}^3J_{PtCNC}$ values for the *N*-methyl groups of **3** and **10** are distinct (Table III), the corresponding ${}^4J_{PtCNCH}$ values for those groups are almost identical. The ${}^4J_{PtCNCH}$ coupling constants do not appear to be sensitive to the stereochemical orientations of the *N*-methyl groups. We have noted previously[1,2,16–18,37] that excellent linear relationships arise when ${}^nJ_{PtC}$ values are plotted against ${}^{n+1}J_{PtH}$ values for a variety of substituents trans to varied ligands in platinum(II) and platinum(IV) complexes.

When the ${}^{13}C-{}^{195}Pt$ coupling constants for all the methyl and methylene groups in the complexes **1–11** are plotted *vs.* their ${}^1H-{}^{195}Pt$ coupling constants, only a random array of data points results. However, a reasonable line can be drawn for the points for the carbene methyl groups and *N*-methyl groups trans to platinum. Linear regression analysis for those points yielded eq 2. Thus, the ${}^{13}C-{}^{195}Pt$ and ${}^1H-{}^{195}Pt$ coupling

$$ {}^nJ_{PtC} = [2.44\ (\pm 0.20)]\,{}^{n+1}J_{PtH} + 11.4 \qquad r = 0.964 \qquad (2)$$

constants of the carbene methyl and *N*-methyl groups cis to the carbene methyl group appear to follow similar trends for the aminocarbene derivatives. In contrast, the points for the carbene methyl groups of the alkoxycarbenes and the *N*-methyl groups trans to the carbene methyl groups of the aminocarbenes do not fall on the line described by eq 2. Since the alkoxycarbenes are a different class of compounds from the aminocarbenes, we find these deviations not entirely unexpected. As well, that the data points for the *N*-methyl groups cis to platinum do not fall on the line is somewhat reminiscent of the "anomalous" insensitivity of the ${}^3J_{PtCNC}$ values for the *N*-methyl groups of series A[11] to variations in trans ligands L. The methylene carbons of the carbene ligands in A on the other hand exhibited sensitivity of their ${}^3J_{PtCNC}$ values to alterations in L. Equation 2 then is another example demonstrating that the ${}^{13}C-{}^{195}Pt$ coupling constants of the carbons in the carbene ligands of **1–11** do not follow usual trends.



A

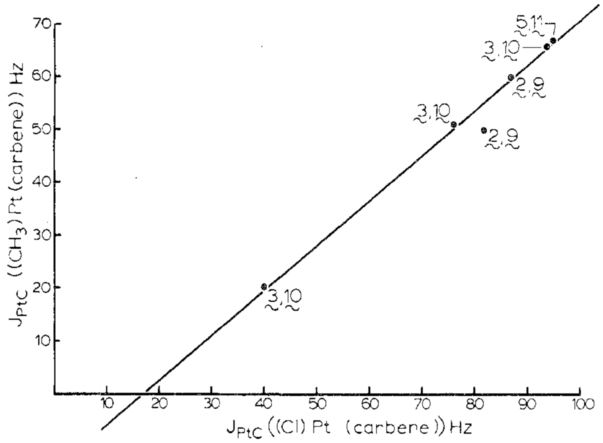


Figure 2. Plot of $J_{PtC}((CH_3)Pt(carbene))$ *vs.* $J_{PtC}((Cl)Pt(carbene))$ for the carbons of the carbene ligands of complexes bearing the same carbene ligands.

Finally, we plotted the ${}^1J_{PtC}$ values of the platinum methyl groups of the carbene complexes **1–8** *vs.* their respective ${}^2J_{PtCH}$ values. Linear regression analysis of the data yielded eq 3.

$$ {}^1J_{PtC}((CH_3)Pt, \mathbf{1\text{-}8}) = [9.1\ (\pm 1.8)]\,{}^2J_{PtCH}((CH_3)Pt, \mathbf{1\text{-}8}) - 82\ (\pm 92) \qquad r = 0.849 \qquad (3)$$

The fair linear correlation indicates that the factors giving rise to alterations in both ${}^1J_{PtC}$ and ${}^2J_{PtCH}$ values for the platinum methyl groups of **1–8** may be the same. Since the range of values is very restricted, we would anticipate that the relative errors of the ${}^{13}C-{}^{195}Pt$ and ${}^1H-{}^{195}Pt$ coupling constants would be large. This is borne out by the large errors in the slope and intercept of eq 3, and it undoubtedly contributes to the poor correlation coefficient. Nevertheless, the slope (9.1 (±1.8)) and intercept (−82 (+92)) fall within the experimental error of the average values (slope 8.2 (±0.5), intercept 19 (±35)) we have observed for three series of trans-methyl platinum complexes.[2] We concluded from those three linear relationships that both the ${}^1J_{PtC}$ and ${}^2J_{PtCH}$ values appear to be dominated by the Fermi contact mechanism.

Comparisons of Trans-Methyl and -Chloro Analogs. We have also compared the ${}^{13}C-{}^{195}Pt$ coupling constants of the carbene ligands of the trans-methyl platinum carbene complexes **2**, **3**, and **5** with the analogous ${}^{13}C-{}^{195}Pt$ coupling constants in the trans-chloro platinum carbene complexes **9–11**. A plot for the ${}^{13}C-{}^{195}Pt$ coupling constants of the carbene carbon substituents is shown in Figure 2. Linear regression analysis of the data shows that there is an excellent linear relationship (eq 4). This indicates that both series share

$$ J_{PtC}((CH_3)Pt(carbene), \mathbf{2, 3, 5}) = [0.84\ (\pm 0.13)]J_{PtC}((Cl)Pt(carbene), \mathbf{9\text{-}11}) - 14.3\ (\pm 10.3) \qquad r = 0.890 \qquad (4)$$

common factors which give rise to the changes in J_{PtC} values and also to the absolute magnitudes of those coupling constants, since the line passes relatively close to the origin.

When the three points for the ${}^1J_{PtC}$ values of the carbene carbons are included in eq 4, an even better linear correlation results, as given in eq 5. The almost perfect linear correlation

$$ J_{PtC}((CH_3)Pt(carbene), \mathbf{2, 3, 5}) = [0.661\ (\pm 0.006)]J_{PtC}((Cl)Pt(carbene), \mathbf{9\text{-}11}) - 0.08\ (\pm 1.33) \qquad r = 0.9997 \qquad (5)$$

and the fact that the plot passes through the origin adds more support to the conclusions above for eq 4.

${}^{13}C$ Shieldings. We have already discussed[2] the ${}^{13}C$ shieldings of the carbene carbons for a number of these derivatives. In a plot analogous to Figure 2 we compared the ${}^{13}C$ shieldings of the carbons of the carbene ligands for methylplatinum and chloroplatinum analogs. This relationship is shown in Figure 3 and is given by eq 6. The excellent linear

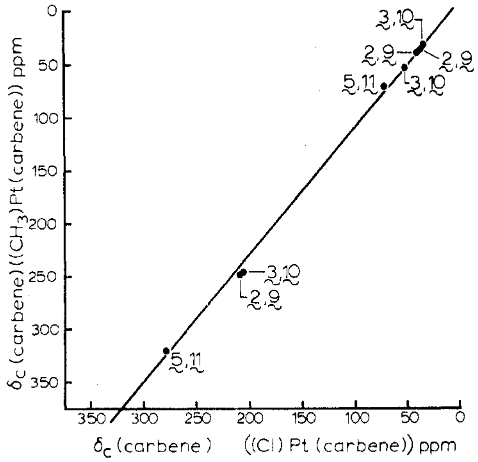


Figure 3. Plot of δ_C((CH$_3$)Pt(carbene)) *vs.* δ_C((Cl)Pt(carbene)) for the carbons of the carbene ligands of complexes bearing the same carbene ligands.

$$\delta_C((CH_3)Pt(carbene), \mathbf{2, 3, 5}) = [1.194\ (\pm 0.002)]\delta_C((Cl)Pt(carbene), \mathbf{9\text{-}11}) - 9.6\ (\pm 0.2) \quad r = 0.9997 \qquad (6)$$

relationship indicates that the factors influencing the changes in carbon shieldings of the carbons in the carbene ligands are likely very similar for both the trans-methyl and trans-chloro platinum complexes. This notion is also supported by the observation that eq 6 passes relatively close to the origin. The factors affecting the absolute magnitudes of those carbon shieldings are also likely very similar.

Variable-Temperature ^{1}H Nmr Studies. The general features of the ^{1}H nmr spectrum of the dimethylaminocarbene complex **18** obtained at 210° in nitrobenzene are the same as those features in the spectrum obtained at ambient probe temperature. This suggests that at relatively high temperatures, rotation about both the platinum–carbene carbon bond and the carbene carbon–nitrogen bond is restricted. Above 210°, decomposition occurs. For the complex *trans*-[(Cl)Pt(P(CH$_3$)$_2$(C$_6$H$_5$))$_2$(:C(OCH$_3$)CH$_3$)]$^+$PF$_6^-$, **26**,[14] variable-temperature ^{1}H nmr studies in the range −90 to +105° (in methylene-*d*$_2$ chloride and nitrobenzene solutions) exhibit only one methoxyl resonance (trans to the carbene methyl group), coalescence of the overlapping phosphine methyl triplet at 95°, and decomposition above 105°. These results suggest that rotation about the platinum–carbene carbon bond occurs rapidly on the nmr time scale above 95°.

Acknowledgment. We thank the National Research Council of Canada for financial support of this project and for the award of a postdoctoral fellowship to J.E.H.W.

Registry No. **1**, 51812-63-6; **2**, 51812-61-4; **3**, 51812-59-0; **4**, 53850-15-0; **5**, 34503-64-5; **6**, 34503-66-7; **7**, 27776-79-0; **8**, 27776-78-9; **9**, 53850-21-8; **10**, 51812-64-7; **11**, 51909-37-6; **12**, 53850-17-2; **13**, 53850-19-4; **14**, 53850-23-0; **15**, 53850-25-2; **16**, 53850-27-4; **17**, 53850-29-6; **18**, 49631-76-7; **19**, 53850-31-0; **20**, 53850-03-6; **21**, 53850-05-8; **22**, 53850-07-0; **23**, 53850-09-2; **24**, 53850-11-6; ^{13}C, 14762-74-4; ^{195}Pt, 14191-88-9.

References and Notes

(1) For the previous paper in this series see M. H. Chisholm, H. C. Clark, L. E. Manzer, J. B. Stothers and J. E. H. Ward, *J. Amer. Chem. Soc.*, **97**, 721 (1975).
(2) M. H. Chisholm, H. C. Clark, L. E. Manzer, J. B. Stothers, and J. E. H. Ward, *J. Amer. Chem. Soc.*, **95**, 8574 (1973).
(3) M. H. Chisholm, H. C. Clark, L. E. Manzer, and J. B. Stothers, *Chem. Commun.*, 1627 (1971).
(4) C. V. Senoff and J. E. H. Ward, *Inorg. Chem.*, **14**, 278 (1975).
(5) C. T. Lam, C. V. Senoff, and J. E. H. Ward, *J. Organometal. Chem.*, in press.
(6) L. F. Farnell, E. W. Randall, and E. Rosenberg, *Chem. Commun.*, 1078 (1971).
(7) C. G. Kreiter and V. Formacek, *Angew. Chem., Int. Ed. Engl.*, **11**, 141 (1972).
(8) J. A. Connor, E. M. Jones, E. W. Randall, and E. Rosenberg, *J. Chem. Soc., Dalton Trans.*, 2419 (1972).
(9) D. J. Ciappenelli, F. A. Cotton, and L. Kruczynski, *J. Organometal. Chem.*, **50**, 171 (1973).
(10) G. M. Bodner, S. B. Kahl, K. Bork, B. N. Storhoff, J. E. Weiller, and L. J. Todd, *Inorg. Chem.*, **12**, 1071 (1973).
(11) D. J. Cardin, B. Cetinkaya, E. Cetinkaya, M. F. Lappert, E. W. Randall, and E. Rosenberg, *J. Chem. Soc., Dalton Trans.*, 1982 (1973).
(12) M. H. Chisholm, H. C. Clark, W. S. Johns, J. E. A. Ward, and K. Yasufuku, following paper.
(13) M. H. Chisholm and H. C. Clark, *Chem. Commun.*, 763 (1970).
(14) M. H. Chisholm and H. C. Clark, *Inorg. Chem.*, **10**, 1711 (1971).
(15) G. C. Levy and J. D. Cargioli, *J. Magn. Resonance*, **6**, 143 (1972).
(16) H. C. Clark and J. E. H. Ward, *Can. J. Chem.*, **52**, 570 (1974).
(17) H. C. Clark, L. E. Manzer, and J. E. H. Ward, *Can. J. Chem.*, **52**, 1165 (1974).
(18) H. C. Clark, L. E. Manzer, and J. E. H. Ward, *Can. J. Chem.*, **52**, 1973 (1974).
(19) E. O. Fisher, M. Leupold, C. G. Kreiter, and J. Muller, *Chem. Ber.*, **105**, 150 (1972).
(20) E. O. Fisher, H. J. Beck, C. G. Kreiter, J. Lynch, J. Muller, and E. Winkler, *Chem. Ber.*, **105**, 162 (1972), and references therein.
(21) E. Moser and E. O. Fisher, *J. Organometal. Chem.*, **13**, 387 (1968).
(22) The structure of the bis(dimethyl)phosphine analog, **21**, of this complex has been determined by X-ray crystallography. The *N*-methyl group was revealed to adopt a trans orientation with respect to the carbene methyl group. See R. F. Stepaniak and N. C. Payne, unpublished results.
(23) J. B. Stothers, "Carbon-13 N.M.R. Spectroscopy," Academic Press, New York, N.Y., 1972.
(24) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley-Interscience, New York, N.Y., 1972.
(25) This notion follows from our observations for a series of trans-methyl platinum(II) derivatives that substitution of the ligand trans to the platinum methyl group resulted in large parallel changes in $^1J_{PtC}$ and $^2J_{PtCH}$, while $^1J_{CH}$ was invariant. Apparently changes in the s character of the hybrid Pt σ-bonding orbitals in the Pt–C bonds are mainly responsible for alterations in $^1J_{PtC}$ and $^2J_{PtCH}$.
(26) (a) E. Moser and E. O. Fisher, *J. Organometal. Chem.*, **13**, 209 (1968); (b) C. G. Kreiter and E. O. Fischer, *Angew. Chem.*, **81**, 780 (1969).
(27) R. F. Stepaniak and N. C. Payne, *J. Organometal. Chem.*, **57**, 213 (1973).
H. C. Clark and J. E. H. Ward, *J. Amer. Chem. Soc.*, **96**, 1741 (1974).
(28) A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc. A*, 1707 (1966).
(29) T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973).
(30) F. R. Hartley, *Chem. Soc. Rev.*, 163 (1973).
(31) The average deviations of the slopes and intercepts for all the linear equations presented here are calculated on the basis of the maximum possible error due to the inherent uncertainty of the experimental measurements. These errors have already been cited in Tables I–IV. It is worthwhile noting that these variations represent the maximum error in *precision* and that as such they may be generous estimates.
(32) B. E. Mann, B. L. Shaw, and N. I. Tucker, *J. Chem. Soc. A*, 2667 (1971).
(33) S. Cowley and S. S. Danyluk, *J. Phys. Chem.*, **68**, 1240 (1964).
(34) J. A. Connor and E. O. Fisher, *J. Chem. Soc. A*, 578 (1969).
(35) J. Ronayne and D. H. Williams, *J. Chem. Soc. B*, 540 (1967).
(36) P. Laszlo, *Progr. Nucl. Magn. Resonance Spectrosc.*, **3**, 231 (1967).