length to indicate a predominantly ionic bond. For a central atom surrounded symmetrically in a plane by three anions or ligands and having a fourth anion perpendicular to the plane of the ligands an EFG tensor component can pass through zero and exhibit a sign change as the central atom–anion distance changes. In view of this we believe that this apparent abnormality in the order of the frequencies is due to the particular bond lengths that occur in the compounds and does not represent any deviation from normal concepts regarding electronegativity. Consideration of the copper–halogen bond as being predominantly ionic is supported by the low value of the bromine resonances (38.838 and 46.588 MHz) in Cu(etu)$_2$Br. A Townes–Daily calculation using Br$_2$ as the 100% covalent reference indicates 78% ionic character for the Cu–Br bond.

(4) The observed resonance frequencies for the dimethyl- and ethylenethiourea compounds are in general higher than for the thiourea compounds. The higher frequencies exhibited by the substituted thiourea compounds are probably due to the inductive effect of the substituents on the thiourea ligand. The stability of thiourea resonance forms having a partial negative charge on the sulfur atom is highest for the unsubstituted thiourea; hence it can donate more electron density to the copper atom thereby resulting in a lower p-electron defect and a lower coupling constant.

Acknowledgment.—The authors wish to thank the National Science Foundation for support of this work through Grants GP-9243 and GP-13973. We also thank Dr. G. V. Gibbs and the Virginia Tech Department of Geology for providing necessary X-ray diffraction powder patterns.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY,
KYOTO UNIVERSITY, KYOTO, JAPAN,
AND KOBE UNIVERSITY, KOBE, JAPAN

Reorientation of Styrene Groups in Styreneplatinum(II) and -palladium(II) Chlorides

BY T. IWAO, A. SAIKA,* AND T. KINUGASA

Received February 15, 1972

In a previous paper[1] we have reported nuclear magnetic resonance studies of mono-styrene derivative complexes of platinum, and the present work is concerned with similar studies of bis-styrene derivative complexes of platinum and palladium. In the bis-styrene complexes, it is known from infrared spectroscopic studies by Chatt[2] and X-ray investigation by Baenziger[3] (Figure 1) that the coordination about the metal atoms is square planar, the terminal and bridge chlorine atoms lie in the plane, and the olefin groups are oriented at right angles to the plane in the trans position in the solid state. Ethylenic proton magnetic resonance spectral lines have been found broader for styreneplatinum(II) chlorides than for styrenepalladium(II) chlorides. The phenomenon is interpreted to show that reorientation of the styrene groups about the coordination bond occurs more slowly in platinum(II) chlorides than in palladium(II) chlorides.

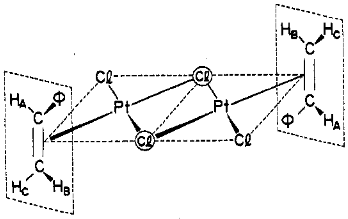

Figure 1.—Structure of styreneplatinum(II) chloride.

Experimental Section

The proton nmr spectra were recorded at 60 MHz on JNM-3H-60 and Varian A-60 spectrometers and calibrated by the usual side-band technique. Styreneplatinum(II) chlorides were stable in acetonitrile solutions for about 1 hr, except 2,3,5,6-tetramethylstyreneplatinum(II) chloride which was stable for a few hours. Styrenepalladium(II) chlorides in chloroform solutions precipitated palladium chloride in 0.5 hr. It was possible, however, to make nmr measurements without any detectable change in chemical shifts and coupling constants before precipitation. Other solvents tried were not suitable for lack of either solubilities or stabilities of the complexes in them. Palladium satellites could not be observed due to the rapid quadrupole relaxation of ^{105}Pd.

p-Methoxy-,[4] *p*-methyl-,[5] *p*-chloro-,[6] and *p*-bromostyrenes[7] were prepared by previously reported methods. 2,3,5,6-Tetramethylstyrene and 2,3,4,5-tetramethylstyrene were supplied by K. Nakamura. All the styrenes were used after redistillation.

Zeise's salt and ethyleneplatinum(II) chlorides were prepared according to the method of MacNevin[8] and of Chatt,[9] respectively. Styrene-, *p*-methoxystyrene-, and *p*-methylstyreneplatinum(II) chlorides were synthesized according to Anderson's method[10] as modified by Orchin.[11]

Di-μ-chloro-dichlorobis(*p*-bromostyrene)diplatinum(II).—*p*-Bromostyrene (0.5 g, 3 mmol) was added to a saturated solution of ethyleneplatinum(II) chloride (0.6 g, 1 mmol) in benzene at room temperature. The solution was concentrated under reduced pressure (15 mm) to give an orange powder. It was washed with petroleum ether (bp 30–70°) and then recrystallized from benzene, yielding orange-yellow crystals. *Anal.* Calcd for $C_{16}H_{14}Cl_4Br_2Pt_2$: C, 21.4; H, 1.6. Found: C, 21.1; H, 1.8.

Di-μ-chloro-dichlorobis(*p*-chlorostyrene)diplatinum(II) was prepared similarly to the *p*-bromostyrene complex. The product is orange-yellow crystals. *Anal.* Calcd for $C_{16}H_{14}Cl_6Pt_2$: C, 23.7; H, 1.7. Found: C, 23.5; H, 1.9.

Di-μ-chloro-dichlorobis(2,3,5,6-tetramethylstyrene)diplatinum(II) monobenzene was prepared similarly to the *p*-bromostyrene complex. The product is orange-yellow crystals. *Anal.* Calcd for $C_{30}H_{38}Cl_4Pt_2$: C, 38.7; H, 4.1. Found: C, 38.4; H, 4.3.

Di-μ-chloro-dichlorobis(2,3,4,5-tetramethylstyrene)diplatinum(II) was prepared similarly to the *p*-bromostyrene complex. The product is orange-yellow crystals. *Anal.* Calcd for $C_{24}H_{32}Cl_4Pt_2$: C, 33.8; H, 3.8. Found: C, 33.5; H, 4.0.

For the preparation of the palladium complexes, the method of Kharasch[12] was followed.

---

* To whom correspondence should be addressed at Kyoto University.

[1] T. Kinugasa, M. Nakamura, H. Yamada, and A. Saika, *Inorg. Chem.*, **7**, 2649 (1968).

[2] J. Chatt and A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

[3] J. N. Dempsey and N. C. Baenziger, *J. Amer. Chem. Soc.*, **77**, 4984 (1955).

[4] C. Walling and K. B. Wolfstirn, *ibid.*, **69**, 852 (1947).

[5] M. Sutzbacher and E. Bergmann, *J. Org. Chem.*, **13**, 303 (1948).

[6] L. A. Brooks, *J. Amer. Chem. Soc.*, **66**, 1295 (1944).

[7] C. G. Overberger and R. E. Allen, *J. Amer. Chem. Soc.*, **68**, 722 (1946). Their method for *p*-cyanostyrene was applied.

[8] W. MacNevin, A. Giddings, and A. Foris, *Chem. Ind.* (*London*), 577 (1958).

[9] J. Chatt and M. L. Searle, *Inorg. Syn.*, **5**, 210 (1957).

[10] J. S. Anderson, *J. Chem. Soc.*, 1042 (1936).

[11] J. R. Joy and M. Orchin, *J. Amer. Chem. Soc.*, **81**, 305 (1959).

[12] M. S. Kharasch, R. C. Seyler, and F. R. Mayo, *J. Amer. Chem. Soc.*, **60**, 882 (1938).

TABLE I

CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR ETHYLENIC PROTONS IN STYRENEPLATINUM(II) AND -PALLADIUM(II) CHLORIDES

Substituent	Complex						Free ligand						Shift diff[c]		
	Chem shift[a]			Coupling const[b]			Chem shift[a]			Coupling const[b]					
	δ_A	δ_B	δ_C	J_{AB}	J_{AC}	J_{BC}	δ_A	δ_B	δ_C	J_{AB}	J_{AC}	J_{BC}	$\Delta\delta_A$	$\Delta\delta_B$	$\Delta\delta_C$
Platinum(II) Chlorides															
p-CH_3O	5.38	3.60	3.02	14.8	8.2		5.27	4.18	3.68	17.1	10.6		−0.12	0.58	0.67
p-CH_3	5.35	3.90	3.30	15.6	8.7		5.28	4.25	3.73	17.7	10.6		−0.07	0.35	0.43
H	5.30	3.77	3.17	14.8	8.1		5.35	4.35	3.82	17.5	10.7		0.05	0.58	0.65
p-Cl	5.23	3.75	3.20	14.5	8.6		5.30	4.32	3.83	17.6	10.6		0.07	0.57	0.63
p-Br	5.20	3.73	3.18	14.1	8.8		5.32	4.35	3.83	17.4	10.5		0.12	0.62	0.65
2,3,5,6-Tetramethyl	5.21	3.84	3.57	15.0	8.6	1.6	5.35	3.65	4.10	17.9	11.4	2.5	0.15	−0.19	0.53
Palladium(II) Chlorides															
p-CH_3	5.82	3.96	3.71	15.5	8.6	1.0	5.29	4.24	3.73	17.5	10.8	1.2	−0.53	0.28	0.03
H	5.70	4.06	3.79	15.9	9.2	0.9	5.32	4.30	3.80	18.1	10.5	1.3	−0.38	0.25	0.02

[a] In ppm downfield from cyclohexane as internal standard at 60 MHz. [b] In Hz. [c] $\Delta\delta \equiv \delta_{\text{free}} - \delta_{\text{complex}}$.

Di-μ-chloro-dichlorobis(styrene)dipalladium Monobenzene.—Styrene (0.15 g, 1.5 mmol) was added to a saturated solution of dibenzonitrilepalladium(II) chloride (0.4 g, 1 mmol) at room temperature. On standing, the product slowly crystallized. It was separated by filtration, washed with petroleum ether, and dried under reduced pressure (15 mm) for 1 hr, yielding brown crystals. *Anal.* Calcd for $C_{22}H_{22}Cl_4Pd_2$: C, 41.1; H, 3.4. Found: C, 40.7; H, 3.7.

Di-μ-chloro-dichlorobis(p-methylstyrene)dipalladium monobenzene was prepared similarly to styrenepalladium(II) chloride. The product is brown crystals. *Anal.* Calcd for $C_{24}H_{26}Cl_4Pd_2$: C, 36.6; H, 3.4. Found: C, 36.3; H, 3.4.

To determine the ratio of benzene to styrene contained in these palladium complexes, they were dissolved in acetonitrile. By ligand exchange, styrene and benzene were isolated, and their quantities were determined by bromometry and gas chromatography, respectively. It was also confirmed by nmr spectroscopy.

Other substituted styrenepalladium(II) complexes were also prepared, but they could not be subjected to nmr studies owing to their sparing solubilities in ordinary solvents.

Results and Discussion

The nmr spectra of the styrene derivative complexes of platinum and palladium were examined in 0.07 *M* acetonitrile and deuteriochloroform solutions, respectively, with cyclohexane as internal standard, since tetramethylsilane accelerated the decomposition of the complexes. The ethylenic proton absorption lines for platinum(II) chlorides were too broad to show the fine structure, and use had to be made of rapid exchange between coordinated and free styrenes to determine the chemical shifts and coupling constants in the complexes. Various known amounts of styrenes, enough to sharpen the absorption lines, were added. Then the observed shifts should be given by

$$\delta_{\text{obsd}} = \frac{\delta_\pi M_\pi + \delta_f M_f/2}{M_\pi + M_f/2}$$

where M_π and M_f are moles for the complexes and free ligands, respectively, and δ_π and δ_f respective shifts. Linear relationships are therefore expected for plots of δ_{obsd} *vs.* mole fractions of free ligands, and the plotted straight lines extrapolated to zero fractions give shift values for the complexes. The coupling constants can be obtained similarly except for J_{BC}; the lines are still too broad (with a width of 3–4 Hz) to observe J_{BC}. The spectra for palladium(II) chlorides are sharp enough (with a width of 0.6 Hz) to permit us to obtain the magnetic parameters directly.

The nmr spectral parameters thus determined at 60 MHz are in Table I. These results may be compared with those previously obtained for potassium (para-substituted styrene)trichloroplatinate(II).[1] The shift differences defined by $\Delta\delta \equiv \delta_{\text{free}} - \delta_{\text{complex}}$ are $\Delta\delta_A \simeq 0.7$ ppm and $\Delta\delta_B \simeq \Delta\delta_C \simeq 1$ ppm for mono-styrene complexes, while $\Delta\delta_A \simeq 0$ ppm and $\Delta\delta_B \simeq \Delta\delta_C \simeq 0.6$ ppm for styreneplatinum(II) chlorides, and $\Delta\delta_A \simeq -0.5$ ppm, $\Delta\delta_B \simeq 0.3$ ppm, and $\Delta\delta_C \simeq 0$ ppm for styrenepalladium(II) chlorides. Generally speaking, upfield shifts by complexing are roughly 0.5 ppm less for bis-styrene complexes of platinum than for mono-styrene complexes, and further 0.5 ppm less for bis-styrene complexes of palladium. In addition, the decrease in the coupling constants on complexing follows similar trends; the decrease is the largest for mono-styrene complexes and the smallest for palladium complexes. These changes resulting from complexing can be considered to reflect the decreased double-bond character in the complexes.[1] Accordingly it appears that the bonding with the metal atoms is weaker in the dimeric complexes than in the monomeric forms, and it is the weakest for the palladium(II) complexes. This conjecture is in accord with relative stabilities of the complexes in solution as observed in the present experiment.

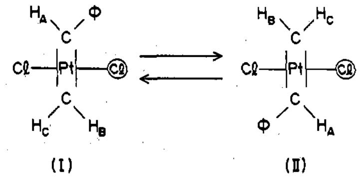

Figure 2.—Reorientation of styrene in styreneplatinum(II) chloride: Cl, terminal chlorine; (Cl), bridge chlorine.

The chemical shifts of 2,3,5,6-tetramethylstyrene and its complex may merit some comments. In this particular styrene H_B is more shielded than H_C, while in its complex H_C is more shielded than H_B as in other styrenes and their complexes (Figure 1). It may be interpreted in terms of steric effects. The phenyl ring of 2,3,5,6-tetramethylstyrene is more likely to be perpendicular to the ethylenic plane because of the methyl groups at both ortho positions. On complex formation, however, the ring plane may be forced back to be coplanar with the ethylenic plane. Consequently the time-average orientation of the phenyl ring with respect to the ethylenic plane may be appreciably different in the free ligand and the complex. In case the phenyl ring is perpendicular to the ethylenic plane, H_B is closer to the shielding region due to the phenyl ring anisotropy than H_C, and this may bring about part of the upfield shift for H_B in the free ligand.

Finally it is to be noted that only the dimeric complexes of platinum show broad ethylenic proton resonance signals. Of several possible mechanisms[13] for the broadening, exchange and reorientation of the styrene group are likely. The exchange mechanism can be excluded by the following observation. In contrast to the ethylenic proton resonance, the phenyl proton resonance is narrow. If the exchange mechanism were responsible, the latter would be expected to be as broad as the former, because shift differences between the free ligands and complexes are of the same order of magnitude for both proton groups.

It is apparent from Figure 2 that the reorientation mechanism can be responsible for the line broadening in the dimeric complexes. In the orientation (I), H_A and H_C are closer to the terminal chlorine atoms, while H_B is closer to the bridge chlorine atoms, and in (II) the situation is reversed. The terminal and bridge chlorine atoms must have spatially[8] and electronically different characters, and hence each proton should experience different magnetic fields in (I) and (II). If the reorientation rate with the coordination bond as axis is comparable to the shift difference in (I) and (II), which may be probably of the order of 10 Hz, line broadening will be observed. This may be considered to be the case with styreneplatinum(II) chlorides; the phenyl proton signals remain narrow, since their shifts are presumably unaffected by reorientation, those protons being significantly remote from the chlorine atoms. For the same reason such broadening was observed also for the proton resonance of the dimer of Zeise's salt in acetonitrile and acetone solutions, which indicates also that the broadening is not due to specific solvent interactions.

On the other hand, styrenepalladium(II) chlorides give narrow proton resonance signals. It can be understood if we consider that the reorientation rate of the styrene groups is faster in the palladium complexes owing to the weaker coordination bonds discussed above. The proton resonance signals of Zeise's salt and its homologs are also narrow. In the case of these monomeric forms, each proton does not experience nonequivalence by reorientation. Thus no line broadening could occur irrespective of the reorientation rate, and nmr spectra are of no direct use in studying this rate process. However, it is felt that the reorientation rate may actually be slower for the monomers in view of their probably stronger coordinative bonding.

Because of their limited solubilities at low temperatures and instabilities at high temperatures, variable-temperature experiments could not be performed to confirm the above discussions on the reorientation of ethylene groups in these complexes. So an attempt has been made to prepare a sterically hindered complex. Di-μ-chloro-dichlorobis(2,3,5,6-tetramethylstyrene)diplatinum(II) provides such an example. Reorientation of the styrene group in the molecule would be difficult due to the bulky substituents on the phenyl ring, and narrow absorption lines are expected if the above views are valid. Indeed such a spectrum has been observed, enabling us to detect ^{195}Pt satellites with $J(\text{Pt–H}_A) = 62$ Hz, $J(\text{Pt–H}_B) = 70$ Hz, and $J(\text{Pt–H}_C) = 74$ Hz. Although the dimeric complex of 2,3,4,5-tetramethylstyrene with a substituent at only one ortho position was also prepared, its low solubility did not allow an nmr observation.

Acknowledgment.—We are indebted to Dr. T. Shingu and Miss M. Okawa for measurements on a Varian A-60 spectrometer.

---

(13) R. Cramer, *J. Amer. Chem. Soc.*, **86**, 217 (1964).

Contribution from the Departments of Chemistry,
Norfolk State College, Norfolk, Virginia 23504,
and Indiana University,[1] Bloomington, Indiana 47401

Studies in Boron Hydrides. VIII. Substituent Effects in Boron Hydrides. Pentaborane(9) and Phenylboronic Acid

By Allen R. Siedle* and George M. Bodner

Received February 28, 1972

We have become interested in using nuclear magnetic resonance techniques to study the magnitude and nature of substituent effects in various boron hydride derivatives. Boron-11 nmr spectroscopy, long recognized for its utility in obtaining structural information,[2] has received far less use as a method for examining substituent effects. Beachell and Beistel[3] observed a linear correlation between the boron-11 nmr chemical shifts in a series of para-substituted phenylboronic acids relative to phenylboronic acid and the Hammett σ value of the substituent. Onak and coworkers[4] studied the boron-11 nmr spectra of methyl- and halogen-substituted pentaboranes and accounted for the observed chemical shifts in terms of six parameters for the CH_3, Cl, and Br groups. These parameters are singular owing to the geometry of the pentaborane(9) molecule and may not be readily compared with substituent parameters employed in the treatment of more conventional derivatives, *e.g.*, benzene. Furthermore, no separation of the effects of CH_3, Cl, or Br into resonance and inductive effects was made by these workers. We have reexamined extant boron-11 nmr chemical shift data for these systems and attempted to rationalize these shifts in terms of familiar substituent effects which have proved to be so useful in organic chemistry.

Experimental Section

The treatment which we have adopted is based upon the substituent constants derived by Swain and Lupton.[5] The change in the chemical shift of the nucleus of interest in the substituted derivative relative to that of the unsubstituted derivative, $\int_{H}^{X}$, is factored into inductive (or field) and resonance effects as shown in eq 1, where F and R are the field and resonance constants of

$$\int_{H}^{X} = fF + rR \qquad (1)$$

---

* To whom correspondence may be addressed at Indiana University.

(1) Contribution No. 2120.

(2) G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969.

(3) H. C. Beachell and D. W. Beistel, *Inorg. Chem.*, **3**, 1028 (1964).

(4) P. M. Tucker, T. Onak, and J. B. Leach, *ibid.*, **9**, 1430 (1970).

(5) C. G. Swain and A. C. Lupton, Jr., *J. Amer. Chem. Soc.*, **90**, 4328 (1968).