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TRANSMISSION OF ELECTRONIC EFFECTS IN *trans*-HYDRIDO(ARENETHIOLATO)BIS(TRIPHENYLPHOSPHINE)PLATINUM(II) COMPLEXES

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SUMMARY

A series of *para*-substituted benzenethiols have been shown to react with $Pt(Ph_3P)_3$ or $Pt(Ph_3P)_4$ to form *trans*-$[PtH(SC_6H_4Y)(Ph_3P)_2]$ where $Y=NO_2$, Br, Cl, F, H, CH_3, CH_3O, or NH_2. Good correlations have been obtained when ν(Pt–H) or J(Pt–H) is plotted against the Hammett substituent parameter, σ_p. These linear correlations are discussed in terms of electron density changes at platinum due to the mesomeric and inductive effects of the *para*-substituent. The electronic spectra of this series of complexes have been examined in benzene and are characterized by a charge transfer band which has been assigned to an L → M electron transfer process.

INTRODUCTION

Reactions of the platinum(0) complex, $Pt(Ph_3P)_4$ with a variety of simple covalent molecules have been investigated in several laboratories and have been well documented in recent review articles[1,2]. The coordinatively unsaturated species, $Pt(Ph_3P)_2$ which is closely related to $Pt(Ph_3P)_4$ has been reported to react with benzenethiol to form *trans*-$[PtH(SPh)(Ph_3P)_2]$[3]. It has also recently been reported that this particular complex may also be obtained from the reaction of benzenethiol with $Pt(Ph_3P)_3$[4]. As part of a general interest pertaining to substituent effects in transition metal complexes[5,6], we have prepared a series of complexes of the type, *trans*-$[PtH(SC_6H_4Y)(Ph_3P)_2]$ where $YC_6H_4S^-$ is a *para*-substituted benzenethiolato ligand and $Y=NO_2$, Br, Cl, F, H, CH_3, CH_3O, or NH_2, in order to ascertain whether or not the inductive and mesomeric effects of the substituent, Y, manifest themselves in the gross physical and chemical properties of these particular complexes. Initial experiments have involved a detailed examination of the infrared, electronic, and nuclear magnetic resonance (NMR) spectral properties of these complexes. The results of these particular experiments are herein reported.

RESULTS AND DISCUSSION

The complexes, *trans*-$[PtH(SC_6H_4Y)(Ph_3P)_2]$ may be readily prepared by allowing $Pt(Ph_3P)_3$ or $Pt(Ph_3P)_4$ to react with the appropriate benzenethiol in ben-

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zene at room temperature according to eqn. (1) where $n=3$ or 4.

$$Pt(Ph_3P)_n + HSC_6H_4Y \rightarrow trans\text{-}[PtH(SC_6H_4Y)(Ph_3P)_2] + (n-2)\ Ph_3P \quad (1)$$

(*a*). *Infrared spectra*

The ν(Pt–H) vibration in the infrared spectra of complexes of the type, *trans*-$[PtHX(Et_3P)_2]$ is sensitive to the nature of the anionic ligand, X[7], where $X = NO_3^-$, Cl^-, Br^-, I^-, SCN^-, CN^-, a substituted acetato[8], or a substituted benzoato ligand[8]. Similar results have also been reported for a series of complexes, *trans*-$[PtH(L)(Ph_3P)_2]$ where L=thiobenzoato or thioacetato[9]. Consequently, it was expected that the ν(Pt–H) vibration in the infrared spectra of the complexes prepared in this investigation would be sensitive to the nature of the substituent, Y. The pertinent infrared data are presented in Table 1 and confirm this expectation. A simple least-squares plot of ν(Pt–H) (which should parallel the Pt–H force constant), measured in chloroform *versus* the Hammett substituent parameter, σ_p, is shown in Fig. 1. The linearity of this plot indicates that there is a definite correlation between ν(Pt–H) and the inductive and mesomeric effects of the substituent, Y. This linear correlation is also valid in benzene (Table 1). The ν(Pt–H) vibration shifts to higher frequency as the electron withdrawing ability of Y increases and to lower frequency as the substituent becomes more electron releasing. Hence, the changes in ν(Pt–H) simply reflect the change in electron density at platinum as the substituent, Y, is varied. Removal of electron density at the platinum increases the Pt–H bond strength while an increase in electron density at platinum reduces the Pt–H bond strength. These changes in ν(Pt–H) are analogous to the changes in ν(C≡O) which are observed when CO is *trans* to $YC_6H_4S^-$ in the complexes, *trans*-$[IrHCl(SC_6H_4Y)(CO)(Ph_3P)_2$[5].

TABLE 1

ν(Pt–H) FREQUENCIES (cm^{-1}) FOR THE COMPLEXES, *trans*-$[PtH(SC_6H_4Y)(Ph_3P)_2]$

Complex	*Solvent*	*ν(Pt–H) (cm^{-1})*
$PtH(SC_6H_4NO_2)(Ph_3P)_2$	$CHCl_3$	2143
	C_6H_6	2130
$PtH(SC_6H_4Br)(Ph_3P)_2$	$CHCl_3$	2132
	C_6H_6	2120
$PtH(SC_6H_4Cl)(Ph_3P)_2$	$CHCl_3$	2133
	C_6H_6	2120
$PtH(SC_6H_4F)(Ph_3P)_2$	CHC_3	2132
	C_6H_6	2118
$PtH(SC_6H_5)(Ph_3P)_2$	$CHCl_3$	2127
	C_6H_6	2117
$PtH(SC_6H_4CH_3)(Ph_3P)_2$	$CHCl_3$	2128
	C_6H_6	2113
$PtH(SC_6H_4OCH_3)(Ph_3P)_2$	$CHCl_3$	2122
	C_6H_6	2117
$PtH(SC_6H_4NH_2)(Ph_3P)_2$	$CHCl_3$	2126
	C_6H_6	2112

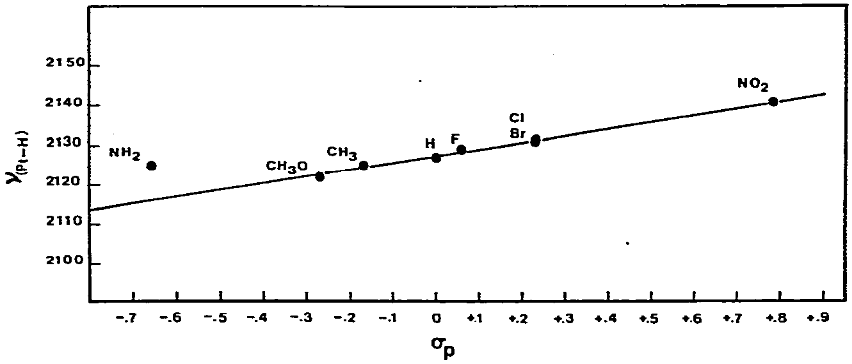

Fig. 1. Hammett plot of ν(Pt–H) *vs.* σ_p.

(*b*). *Electronic spectra*

The electronic spectral data obtained in benzene are given in Table 2. The spectra of all the complexes are characterized by an intense absorption band between ca. 26.3 and 29.2 kK which is absent in the spectrum of the corresponding "free" (uncoordinated) $YC_6H_4S^-$ ligand. The position of this absorption band is fairly sensitive to the nature of the substituent, Y, but there appears to be no simple correlation between the energy of the transition giving rise to this absorption band and the Hammett substituent parameter, σ_p.

This band may be readily assigned to a ligand-to-metal (L→M) electron transfer by taking into account the intensity of the band ($\varepsilon \approx 3 \times 10^3\ M^{-1} \cdot cm^{-1}$), the absence of a corresponding band in the spectra of the $YC_6H_4S^-$ ligands, and the hypsochromic shift of the absorption maximum as the *para*-substituent, Y, becomes more electron-withdrawing (see Table 2). The electronic origin of this band most probably involves the promotion of an electron from a filled *p*-orbital localized on sulfur to the vacant $d_{x^2-y^2}$ orbital localized on platinum[10]. It may be noted that an additional intense band was observed in the spectrum of *trans*-[$PtH(SC_6H_4NO_2)(Ph_3P)_2$] at 22.4 kK. This particular band has been assigned to an internal ligand

TABLE 2

ELECTRONIC SPECTRAL DATA IN BENZENE

Complex	λ (*Å*)	$\tilde{\nu}$ (*K*)	ε ($M^{-1} \cdot cm^{-1}$)	*Transition*
$PtH(SC_6H_4NO_2)(Ph_3P)_2$	4496	22420	19320	L→L
	3425	29200	3270	L→M
$PtH(SC_6H_4Br)(Ph_3P)_2$	3695	27060	3560	L→M
$PtH(SC_6H_4Cl)(Ph_3P)_2$	3697	27050	3560	L→M
$PtH(SC_6H_4F)(Ph_3P)_2$	3698	27040	2960	L→M
$PtH(SC_6H_5)(Ph_3P)_2$	3795	26350	3250	L→M
$PtH(SC_6H_4CH_3)(Ph_3P)_2$	3796	26340	3120	L→M
$PtH(SC_6H_4OCH_3)(Ph_3P)_2$	3799	26320	3040	L→M
$PtH(SC_6H_4NH_2)(Ph_3P)_2$	3800[a]	26320[a]	2400	L→M

[a] Shoulder.

(L→L) transition since "free" $O_2NC_6H_4S^-$ exhibits an absorption band at 23.5 kK ($\varepsilon = 15.0 \times 10^3\ M^{-1}\cdot cm^{-1}$) and the corresponding thiol, $O_2NC_6H_4SH$ absorbs at 31.5 kK ($\varepsilon = 12.0 \times 10^3\ M^{-1}\cdot cm^{-1}$)[11].

(c). ^1H *NMR*

The expected high-field NMR spectrum for hydrogen bonded to platinum in a complex of the type, *trans*-$[PtH(SC_6H_4Y)(Ph_3P)_2]$ should consist of a "triplet of triplets" because of coupling between hydrogen and the ^{31}P nuclei (spin $\frac{1}{2}$) as well as coupling with the ^{195}Pt nuclei (spin $\frac{1}{2}$, natural abundance of 33.7%)[7]. At the normal operating temperature of the 100 MHz NMR spectrometer, the spectrum of *trans*-$[PtH(SC_6H_4NO_2)(Ph_3P)_2]$ in $CDCl_3$ exhibited the expected "triplet of triplets" centered at ca. 20 ppm [J(P–H) 12.9 Hz, J(Pt–H) 1006 Hz] upfield from TMS whereas the spectra of *trans*-$[PtH(SC_6H_4Y)(Ph_3P)_2]$ (where Y = F, Cl, Br, H, CH_3, CH_3O or NH_2) only exhibited a triplet centered at ca. 20 ppm upfield from TMS [J(Pt–H) ≈ 1000 Hz]. These observations suggest that the rapid intermolecular exchange process given by eqn. (2) is occurring at 37° for this latter group of complexes[4].

$$trans\text{-}[PtH(SC_6H_4Y)(Ph_3P)_2] \rightarrow PtH(SC_6H_4Y)(Ph_3P) + Ph_3P \qquad (2)$$

Lowering the temperature to −30° slows this exchange sufficiently so that both types of spin–spin coupling may be observed and the spectra are resolved into a well defined "triplet of triplets". The NMR data recorded at −30° in $CDCl_3$ are presented in Table 3. Typical spectra represented by *trans*-$[PtH(SC_6H_4CH_3)(Ph_3P)_2]$ are presented in Fig. 2. Recently, phosphine exchange has also been reported for some trialkylphosphine complexes of platinum(0)[12]. The slow exchange process indicated for the *p*-nitrobenzenethiolato complex mentioned above may be taken as a reflection of the substantial electron withdrawing ability of the nitro substituent which is expected to increase the effective nuclear charge at platinum with a concomittant increase in Pt–P bond strength.

TABLE 3

NMR DATA FOR THE COMPLEXES, *trans*-$[PtH(SC_6H_4Y)(Ph_3P)_2]^a$

Complex	*τ(Pt–H) (ppm)*	*J(Pt–H) (Hz)*	*J(P–H) (Hz)*
$PtH(SC_6H_4NO_2)(Ph_3P)_2$	19.86	1006	12.9
$PtH(SC_6H_4Br)(Ph_3P)_2$	19.93	981	13.4
$PtH(SC_6H_4Cl)(Ph_3P)_2$	19.96	980	13.4
$PtH(SC_6H_4F)(Ph_3P)_2$	19.99	973	13.6
$PtH(SC_6H_5)(Ph_3P)_2$	19.87	969	13.4
$PtH(SC_6H_4CH_3)(Ph_3P)_2$	19.92	962	13.8
$PtH(SC_6H_4OCH_3)(Ph_3P)_2$	19.99	959	13.8
$PtH(SC_6H_4NH_2)(Ph_3P)_2$	19.98	954	13.8

[a] Measured in $CDCl_3$ at −30° with TMS as internal reference.

It was initially anticipated that the high-field chemical shift of the hydrogen bonded to platinum would reflect any change in electron density at the metal as a result of the inductive and mesomeric effects of the *para*-substituent associated with

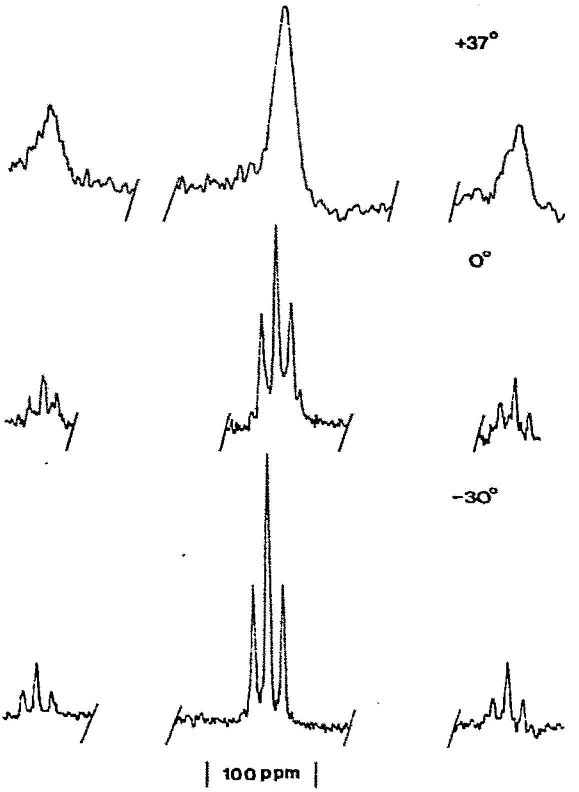

Fig. 2. High-field ^{1}H NMR spectrum of *trans*-[PtH(SC$_6$H$_4$CH$_3$)(Ph$_3$P)$_2$] at various temperatures.

the YC$_6$H$_4$S$^-$ moiety. The data presented in Table 3 clearly indicate that the chemical shift of the hydride ligand bonded to Pt is insensitive to the nature of the substituent, Y. The behaviour of τ(Pt–H) in these arenethiolato complexes differs from that reported for the complexes, *trans*-[PtH(L)(Et$_3$P)$_2$][8]. Also, the P–H coupling constants are unaffected by a change in substituent. On the other hand, the Pt–H coupling constants are significantly sensitive to substituent changes. A plot of J(Pt–H) *versus* the Hammett substituent parameter, σ_p, is shown in Fig. 3. The linearity of this plot indicates that there is a definite correlation between these two quantities. A similar linear plot of J(Pt–H) *versus* σ_p may be obtained for the benzoato complexes, *trans*-[PtH(O$_2$C-C$_6$H$_4$Y)(Et$_3$P)$_2$, using the data of Atkins *et al.*[8] and is included in Fig. 3.

The factors governing the magnitude of the Pt–H coupling constant have been discussed[13]. Since coupling constants are strongly dependent upon electronic effects for a given pair of nuclei, it is possible to simply relate the change in the magnitude of J(Pt–H) to a change in electron density at the platinum atom. Hence, an increase in electron density at platinum will reduce its effective nuclear charge which in turn manifests itself by lowering the Pt–H coupling constant. Conversely, the platinum–hydrogen coupling constant will increase with decreasing electron density at the metal atom. It then appears that J(Pt–H) is a sensitive indicator of a change in electron density at platinum in the complexes, *trans*-[PtH(SC$_6$H$_4$Y)-

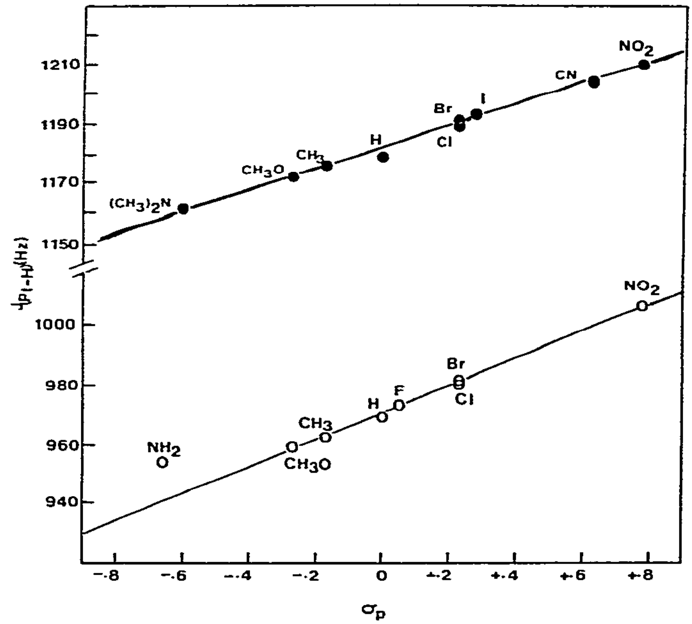

Fig. 3. Plot of J(Pt–H) *vs.* σ_p; ○, *trans*-$[PtH(SC_6H_4Y)(Ph_3P)_2]$; ●, *trans*-$[PtH(O_2CC_6H_4Y)(Et_3P)_2]$.

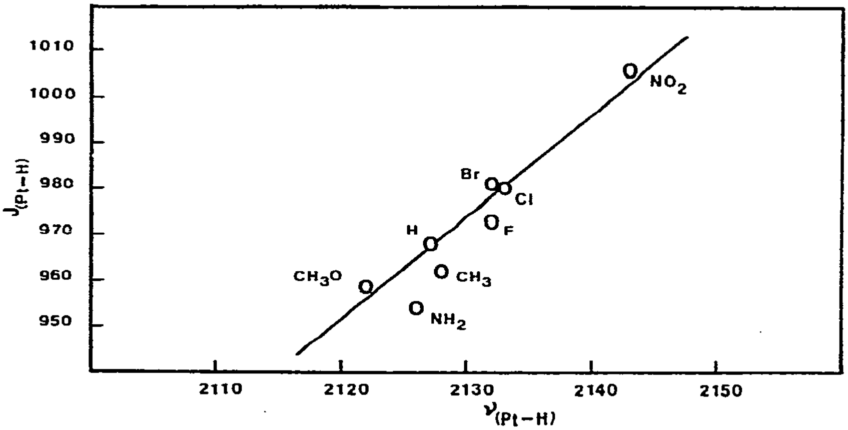

Fig. 4. Plot of J(Pt–H) *vs.* ν(Pt–H).

$(Ph_3P)_2]$. Electron withdrawing substituents increase the effective nuclear charge at platinum and *vice versa* for electron releasing substituents. This behaviour is entirely consistent with the observed shifts of ν(Pt–H) in the infrared spectra. In fact, a linear relationship exists between these two measured quantities (see Fig. 4). The variations in J(Pt–H) may also be interpreted as providing a measure of the amount of 6s orbital participation from platinum in the platinum–hydrogen bond[8]. Similar results relating methyl ^{13}C–H coupling constants to the electronic nature of a substituent in a series of substituted toluenes, tert-butylbenzenes, N,N-dimethylanilines, and anisoles[14] have been reported and discussed.

It is interesting to point out that for the series of complexes, *trans*-[$PtHX(Et_3P)_2$] where X=Cl, Br, I, NO_2, NO_3, SCN, or CN, both J(Pt–H) and τ(Pt–H) show a marked dependence on the nature of X[7,15]. However, there appears to be no simple correlation between the nature of the ligand, X, and J(Pt–H) or τ(Pt–H).

In conclusion, the spectral data presented herein confirm the *trans*-configuration assigned to $PtH(SC_6H_4Y)(Ph_3P)_2$. The experiments also demonstrate that *para*-substituted benzenethiolato ligands are capable of changing the electron density at platinum to such an extent that this may be detected by simple spectroscopic measurements.

EXPERIMENTAL

Materials

Triphenylphosphine was purchased from Eastman Organic Chemicals, Inc., and was recrystallized from ethanol. The substituted benzenethiols were commercially available and were used as received. The complexes, $Pt(Ph_3P)_3$ and $Pt(Ph_3P)_4$ were prepared according to a standard literature procedure[16].

trans-Hydrido(arenethiolato)bis(triphenylphosphine)platinum(II)

The following general procedure was used to prepare these complexes. Tetrakis(triphenylphosphine)platinum(0) (0.50 g) or tris(triphenylphosphine)platinum(0) (0.50 g) was dissolved in oxygen-free benzene (15 ml). To this solution was added an excess of the appropriate arenethiol (0.5 g or 0.5 ml) and the resulting solution was stirred at room temperature for about 30 min. The solution was then quickly filtered into 50–80 ml of petroleum ether (b.p. 35–60°) or n-pentane to precipitate the desired complex which was collected by filtration, washed with petroleum ether or n-pentane, and dried *in vacuo* over boiling benzene for 24 h. Yields were in the range, 65–85%. Analytical data are presented in Table 4. Attempts were made to purify the complexes by crystallization, but in all cases decomposition occurred. Many of the complexes were analyzed in duplicate with no significant improvement in the difference between the observed and calculated values.

TABLE 4

ANALYTICAL DATA FOR THE COMPLEXES, *trans*-[$PtH(SC_6H_4Y)(Ph_3P)_2$]

Complex	*Found (%)*		*Calcd. (%)*		*M.p. (°C)*
	C	*H*	*C*	*H*	
$PtH(SC_6H_4NO_2)(Ph_3P)_2$	56.97	4.09	57.61	3.54	146–148
$PtH(SC_6H_4Br)(Ph_3P)_2$	55.53	4.09	55.47	3.85	136–137
$PtH(SC_6H_4Cl)(Ph_3P)_2$	58.94	4.56	58.33	4.05	135–137
$PtH(SC_6H_4F)(Ph_3P)_2$	60.24	4.53	59.46	4.13	129–131
$PtH(SC_6H_5)(Ph_3P)_2$	60.71	4.63	60.75	4.34	132–134
$PtH(SC_6H_4CH_3)(Ph_3P)_2$	60.95	4.89	61.71	4.15	105–107
$PtH(SC_6H_4OCH_3)(Ph_3P)_2$	60.62	4.70	60.06	4.45	124–126
$PtH(SC_6H_4NH_2)(Ph_3P)_2$	60.06	4.60	59.67	4.38	113–115

Physical measurements

Infrared spectra were recorded on a Beckman IR-12 spectrophotometer; the ν(Pt–H) frequencies are reliable to ±2 cm^{-1}. Preliminary electronic spectra were recorded on a Bausch and Lomb 505 spectrometer. The spectral data presented in Table 2 were obtained on a Cary-14 spectrophotometer using 1.00 cm rectangular quartz cells. Beer's Law was obeyed for all the spectra. ^{1}H NMR spectra were recorded on a Varian HA100 spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as internal reference.

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