

isolated. Elemental analyses on several preparations were not reproducible even though other zerovalent phosphine complexes of nickel or palladium<sup>23</sup> give stable adducts with CS<sub>2</sub>.

A suspension of Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub> in dry benzene was refluxed with excess benzoyl cyanide to give the yellow-orange square-planar diamagnetic complex *trans*-[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>Ni(CN)<sub>2</sub>·2C<sub>6</sub>H<sub>6</sub> (mp 143–145 °C;  $\nu(\text{CN})$  2145 cm<sup>-1</sup>) in 81% yield. This complex was further characterized by NMR and elemental analyses. When the reaction was run in toluene or anisole, toluene and anisole solvates were formed. This reaction occurred much more slowly than the analogous reaction with benzoyl chloride. The large difference in reactivity between benzoyl chloride and cyanide can be attributed to the relative strengths of the carbon-carbon and carbon-chlorine bonds in these two compounds.

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**Registry No.** (Ph<sub>2</sub>PH)<sub>3</sub>NiI<sub>2</sub>, 16102-67-3; (Ph<sub>2</sub>PH)<sub>3</sub>NiBr<sub>2</sub>, 38199-79-0; (Ph<sub>2</sub>PH)<sub>3</sub>NiCl<sub>2</sub>, 38199-78-9; Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>](CN)<sub>2</sub>, 62059-29-4; Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>3</sub>(NCS)<sub>2</sub>, 62066-86-8; Ni[P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>4</sub>, 14221-00-2; Ni[P(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sub>4</sub>, 14839-39-5; Ni[P(OCH<sub>3</sub>)<sub>3</sub>]<sub>4</sub>, 14881-35-7; Ni[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)]<sub>4</sub>, 62066-87-9; Ni[C<sub>6</sub>H<sub>5</sub>-P(OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub>, 62066-88-0; Ni[P(OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>4</sub>, 62066-89-1; Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub>, 31410-77-2; Ni[DP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub>, 62066-90-4; Ni[DP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>3</sub>I<sub>2</sub>, 62066-91-5; Ni[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>NCS)<sub>2</sub>, 62066-92-6; *trans*-[HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>(CN)<sub>2</sub>, 62066-85-7; HClI<sub>3</sub>, 75-47-8; CH<sub>3</sub>I, 74-88-4; CH<sub>2</sub>I<sub>2</sub>, 75-11-6; cyclohexyl iodide, 626-62-0; iodo-benzene, 591-50-4; 2-iodoethylbenzene, 103-63-9; HCBBr<sub>3</sub>, 75-25-2; *d*-bromocamphor, 25619-71-0; 2-bromo-2-phenylacetophenone,

1484-50-0; bromobenzene, 108-86-1; crotyl bromide, 4784-77-4; C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Br, 100-39-0; benzoyl chloride, 98-88-4; C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Cl, 100-44-7; *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl, 104-82-5; P(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, 122-52-1; I<sub>2</sub>, 7553-56-2; CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>I, 27636-85-7; ICH<sub>2</sub>COOH, 64-69-7.

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## Equilibrium Energetics of Cis-Trans Isomerization for a Series of Palladium(II) Isocyanate-Phosphine Complexes. Study of Phosphine Electronic Effects. 2<sup>1</sup>

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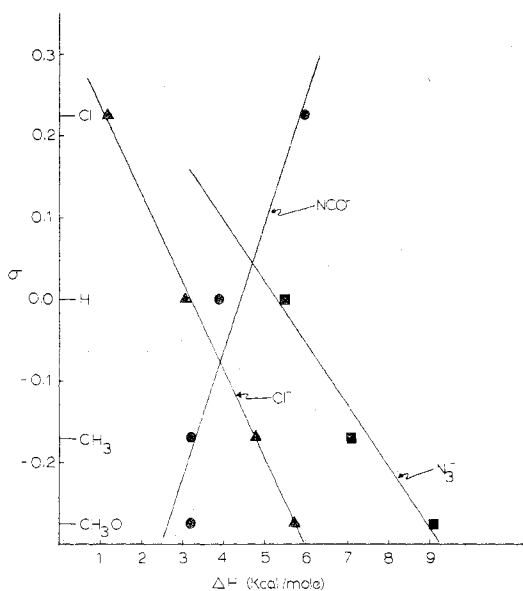
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Equilibrium thermodynamics for the cis-trans isomerization of the para-substituted phosphine complexes [(4-ZC<sub>6</sub>H<sub>4</sub>)<sub>n</sub>P(CH<sub>3</sub>)<sub>3-n</sub>]<sub>2</sub>Pd(NCO)<sub>2</sub> ( $n = 1$ ; Z = Cl, H, CH<sub>3</sub>, CH<sub>3</sub>O;  $n = 2$ , Z = Cl, H, CH<sub>3</sub>) have been determined in several solvents by variable-temperature proton NMR spectroscopy. The cis isomer is generally thermodynamically more stable than the trans isomer, and the nature of the solvent greatly influences the relative isomer population, the cis isomer being favored by polar solvents. The complexes all contain N-bonded isocyanate under all conditions studied both in the solid state and in solution. All complexes are cis in the solid state except [(4-ZC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>PCH<sub>3</sub>]<sub>2</sub>Pd(NCO)<sub>2</sub>, Z = CH<sub>3</sub> and Cl, which are trans. The isomerization process is not entropy controlled and probably occurs via a solvent-association mechanism. Linear correlations of both  $\Delta H$  and  $\Delta S$  with Hammett  $\sigma$  constants of Z are found. The enthalpy and entropy of the reaction *cis*-[ArP(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Pd(NCO)<sub>2</sub>  $\rightleftharpoons$  *trans*-[ArP(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Pd(NCO)<sub>2</sub> both decrease as the basicity of the phosphine increases. This is opposite to the increase in enthalpy and entropy with increasing basicity observed for the (Ar<sub>2</sub>PCH<sub>3</sub>)<sub>2</sub>Pd(NCO)<sub>2</sub> complexes and all of the analogous azide and chloride complexes. Reasons for this reversal in behavior are suggested. The rates of isomerization of the isocyanate complexes are considerably slower than those of the corresponding chloride and azide complexes. Phosphine exchange in the isocyanate complexes is much slower than for the corresponding cyanide, azide, and chloride complexes.

## Introduction

Several studies of the cis-trans isomerization of square-planar palladium(II) complexes of the type (R<sub>3</sub>P)<sub>2</sub>PdX<sub>2</sub> have recently been reported.<sup>1-7,10</sup> It has been demonstrated in these studies that the rate of the isomerization process, the mechanism, and the relative isomer population are all in-

fluenced by the size and basicity of the phosphine, the nature of the anionic ligand, and the nature of the solvent.<sup>4-7,10</sup> The relative magnitudes of the various contributing terms to  $\Delta H$  and  $\Delta S$  have been discussed<sup>1,4,10</sup> and it has been established that the enthalpy and entropy of solvation are the most important factors influencing the isomer population.<sup>1,4,10</sup>



**Figure 1.** Plots of  $\Delta H$  vs. Hammett  $\sigma$  constants for the complexes  $[(4-ZC_6H_4)P(CH_3)_2]_2PdX_2$  in  $CDCl_3$ :  $\bullet$ ,  $X^- = NCO^-$ ;  $\blacktriangle$ ,  $X^- = Cl^-$ ;  $\blacksquare$ ,  $X^- = N_3^-$ .

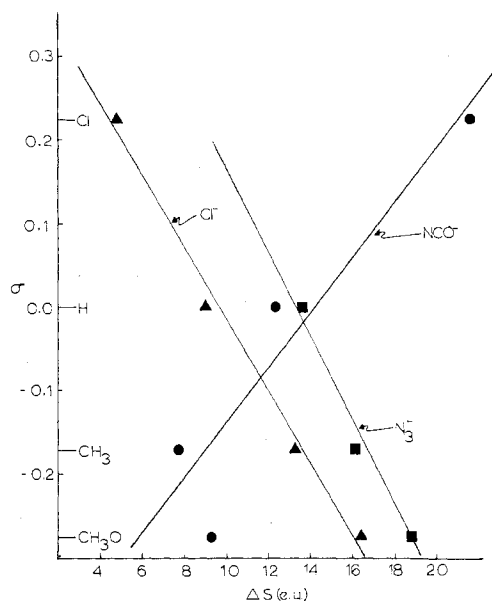
Consequently, by utilizing suitably polar anions it should be possible to change the isomer population from wholly trans to wholly cis by changing the solvent. We have recently shown that the complexes  $(R_3P)_2Pd(CN)_2$  are wholly trans<sup>8</sup> in all solvents in which they are soluble. On the other hand, the complexes  $(R_3P)_2PdX_2$ ,  $X = Cl, N_3$ , and tetrazolate, are equilibrium mixtures of cis and trans isomers in solution.<sup>5,9,10</sup> The dipole moments of the compounds  $CH_3X$  are as follows:  $X = CN$ ,  $\mu = 3.92$  D;<sup>11</sup>  $X = NCG$ ,  $\mu = 2.81$  D;<sup>12</sup>  $X = N_3$ ,  $\mu = 2.17$  D;<sup>13</sup>  $X = Cl$ ,  $\mu = 1.87$  D.<sup>14</sup> We anticipated from purely  $\sigma$ -bonding considerations that the Pd-X bond dipoles would lie in this same order. This suggested to us that the  $(R_3P)_2Pd(NCO)_2$  complexes might be highly susceptible to solvent control of isomer population. For this reason we have prepared a number of complexes of the type  $(R_3P)_2Pd(NCO)_2$  and investigated their solution behavior. The phosphines were chosen so as to vary electronic effects with concomitant minimal variation in steric effects.

### Experimental Section

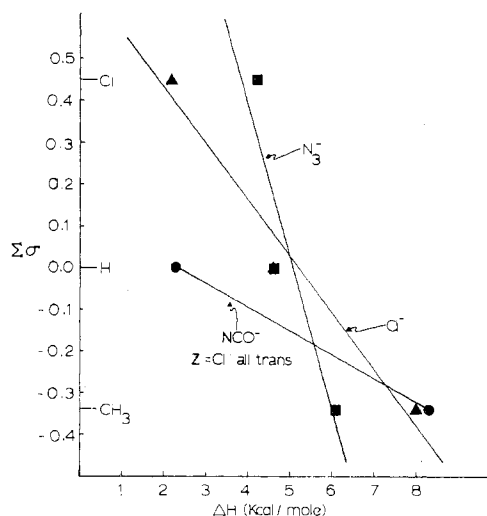
Chemicals were reagent grade and used as received or purified by standard procedures when necessary. All solvents, when necessary, were dried by standard procedures and stored over Linde 4-Å molecular sieves for at least 2 days prior to use. All reactions involving phosphines were conducted in a prepurified nitrogen atmosphere. All physical measurements were obtained as previously described.<sup>1,9</sup> The complexes were prepared by metathesis reactions of the chloride complexes<sup>9</sup> with  $AgNCO$ <sup>15</sup> in acetone in the dark. All isocyanate complexes were handled in the dark as much as possible because they are all photosensitive. Upon exposure to light they all turn black without deposition of palladium metal. Most form colorless crystals as well as the black material upon exposure to light. The nature of this photodecomposition has not been investigated. Equilibrium thermodynamics were determined as previously described.<sup>4-6,9,10</sup>

### Results

The infrared data presented in Table I establish that each of these complexes contains N-bound isocyanate<sup>16</sup> and that all the complexes are cis in the solid state except for  $[(4-ZC_6H_4)_2PCH_3]_2Pd(NCO)_2$ ,  $Z = CH_3$  and  $Cl$ , which are trans. Upon dissolution in polar solvents (see Table II for specific solvents), all of the complexes are wholly cis in solution as shown by the 1:1 doublet  $^1H$  NMR resonances<sup>17</sup> for the  $PCH_3$  protons. Conductance titrations on  $5 \times 10^{-3}$  M solutions of the complex  $[(4-ClC_6H_4)_2PMe]_2Pd(NCO)_2$  with the respective phosphine to a 2:1 molar ratio of phosphine to complex were



**Figure 2.** Plots of  $\Delta S$  vs. Hammett  $\sigma$  constants for the complexes  $[(4-ZC_6H_4)P(CH_3)_2]_2PdX_2$  in  $CDCl_3$ :  $\bullet$ ,  $X^- = NCO^-$ ;  $\blacktriangle$ ,  $X^- = Cl^-$ ;  $\blacksquare$ ,  $X^- = N_3^-$ .



**Figure 3.** Plots of  $\Delta H$  vs. Hammett  $\sigma$  constants for the complexes  $[(4-ZC_6H_4)_2PCH_3]_2PdX_2$  in  $CDCl_3$ :  $\bullet$ ,  $X^- = NCO^-$ ;  $\blacktriangle$ ,  $X^- = Cl^-$ ;  $\blacksquare$ ,  $X^- = N_3^-$ .

performed in nitromethane and chloroform. In both cases the conductances were in the same range as those of the ligand alone in these solvents suggesting that none of these complexes ionize in any of the solvents in which NMR data were obtained.<sup>1,4-10</sup> Dissolution of the complexes in several solvents produces equilibrium mixtures of the cis and trans isomers (see Table II for data). In each of these cases an increase in temperature caused an increase in the trans isomer population at the expense of the cis isomer population. Consequently, the cis isomers are in general thermodynamically more stable than the corresponding trans isomers as has also been found for most other complexes<sup>4-7,10</sup> of the type  $(R_3P)_2PdX_2$  except perhaps<sup>8</sup>  $(R_3P)_2Pd(CN)_2$ . No other species are present in any of these solutions. The thermodynamic data presented in Table II were obtained from linear regression analysis of  $\ln K$  vs.  $1/T$  plots of the variable-temperature  $^1H$  NMR data and the linear relationships have confidence limits of greater than 95%. In general, the isomerization of the isocyanate complexes is not entropy controlled as  $T\Delta S$  is in general not greater than  $\Delta H$ .

Table I. <sup>1</sup>H NMR and Infrared Data for the Complexes [(4-ZC<sub>6</sub>H<sub>4</sub>)<sub>n</sub>P(CH<sub>3</sub>)<sub>3-n</sub>]<sub>2</sub>Pd(NCO)<sub>2</sub>

Z	n	$\delta(\text{CH}_3)$ (J) <sup>a</sup>		$\nu(\text{CN})^b$	$\nu(\text{CO})^b$	$\nu(\text{NCO})^b$	$\nu(\text{MN})^b$
		Cis	Trans				
CH <sub>3</sub> O <sup>c</sup>	1	1.63 (10.8)	1.69 (6)	2210	1330	533	326
CH <sub>3</sub> <sup>d</sup>	1	1.57 (10.6)	1.63 (7)	2228	1324	608	377
				2150		606	354
H	1	1.68 (11)	1.73 (7)	2196	1335	622	415
				2190		610	315
Cl	1	1.75 (12)	1.83 (7)	2215	1333	645	363
				2170		611	354
CH <sub>3</sub> <sup>e</sup>	2	1.89 (11)	1.98 (7)	2204	1344	625	378
				2190		637	352
H	2	1.77 (10)	2.00 (7.2)	2220	1338	605	350
				2220		637	371
Cl	2		1.96 (7.2)	2210	1343	597	362

<sup>a</sup>  $\delta$  in ppm relative to internal TMS in CDCl<sub>3</sub>;  $J = {}^2J_{\text{PH}} + {}^4J_{\text{PH}}$  in Hz. <sup>b</sup> Infrared frequencies in cm<sup>-1</sup> for Nujol mulls. <sup>c</sup>  $\delta(\text{CH}_3\text{O}) = 3.83$ . <sup>d</sup>  $\delta(\text{CH}_3) = 2.37$ . <sup>e</sup>  $\delta(\text{CH}_3) = 2.35$ .

Table II. Equilibrium Thermodynamics for the Reactions

*cis*-[(4-ZC<sub>6</sub>H<sub>4</sub>)<sub>n</sub>P(CH<sub>3</sub>)<sub>3-n</sub>]<sub>2</sub>Pd(NCO)<sub>2</sub> ⇌  
*trans*-[(4-ZC<sub>6</sub>H<sub>4</sub>)<sub>n</sub>P(CH<sub>3</sub>)<sub>3-n</sub>]<sub>2</sub>Pd(NCO)<sub>2</sub>

Z	n	Solvent	$\Delta S$ , eu	$\Delta H$ , kcal/mol	$\Delta G_{305}$ , kcal/mol
Cl <sup>a</sup>	1	CDCl <sub>3</sub>	21.6 ± 1	6.0 ± 0.1	-0.6 ± 0.1
Cl	2	CDCl <sub>3</sub>	All trans	All trans	All trans
H <sup>b</sup>	1	CDCl <sub>3</sub>	12.3	3.9	0.2
H	1	CD <sub>3</sub> NO <sub>2</sub>	1.1	0.6	0.2
H	1	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	5.2	1.2	-0.4
H	2	CDCl <sub>3</sub>	11.8	2.3	-1.3
H	2	1,2-Cl <sub>2</sub> C <sub>2</sub> H <sub>4</sub>	9.1	3.0	0.2
H	2	<i>sym</i> -C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub>	15.1	4.8	0.1
H	2	<i>cis</i> -C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	19.4	5.7	-0.2
CH <sub>3</sub> <sup>c</sup>	1	CDCl <sub>3</sub>	7.7	3.2	0.8
CH <sub>3</sub>	2	CDCl <sub>3</sub>	26.1	8.3	0.4
CH <sub>3</sub>	2	<i>sym</i> -C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub>	15.1	4.8	0.2
CH <sub>3</sub> O <sup>d</sup>	1	CDCl <sub>3</sub>	9.3	3.2	0.4
CH <sub>3</sub> O	1	1,1,2-Cl <sub>3</sub> C <sub>2</sub> H <sub>3</sub>	11.1	5.1	1.8
CH <sub>3</sub> O	1	<i>cis</i> -C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	3.6	2.3	1.6

<sup>a</sup> This complex is greater than 95% *cis* in (CD<sub>3</sub>)<sub>2</sub>CO, CD<sub>3</sub>CN, and CD<sub>3</sub>NO<sub>2</sub>. <sup>b</sup> This complex is greater than 95% *cis* in *sym*-C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> and C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>. <sup>c</sup> This complex is greater than 95% *cis* in 1,2-Cl<sub>2</sub>C<sub>2</sub>H<sub>4</sub>, *sym*-C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>, 1,1,2-C<sub>2</sub>H<sub>3</sub>Cl<sub>3</sub>, and CD<sub>3</sub>NO<sub>2</sub>. <sup>d</sup> This complex is greater than 95% *cis* in C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>.

## Discussion

Both  $\Delta H$  and  $\Delta S$  are linearly related to the Hammett  $\sigma$  constants<sup>18</sup> for each homologous series as illustrated in Figures 1-4. The data<sup>1</sup> for the analogous chloride and azide complexes are also presented in Figures 1-4 for comparison. From the data in these figures, it can be seen that for the reaction *cis*-(R<sub>3</sub>P)<sub>2</sub>Pd(NCO)<sub>2</sub> ⇌ *trans*-(R<sub>3</sub>P)<sub>2</sub>Pd(NCO)<sub>2</sub>  $\Delta H$  and  $\Delta S$  both increase with increasing phosphine basicity for the (Ar<sub>2</sub>PCH<sub>3</sub>)<sub>2</sub>Pd(NCO)<sub>2</sub> complexes and for all of the chloride and azide complexes. In contrast,  $\Delta H$  and  $\Delta S$  both decrease with increasing phosphine basicity for the [ArP(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Pd(NCO)<sub>2</sub> complexes. We have previously shown<sup>1,4,10</sup> that  $\Delta H$  of solvation and  $\Delta S$  of solvation are the major contributors to  $\Delta H$  and  $\Delta S$  of isomerization and that the *cis* isomers are more polar than the *trans* so that solvent is released upon going from the *cis* isomer to the *trans* isomer. With this in mind, the phosphine electronic effects manifested for the (Ar<sub>2</sub>PC-H<sub>3</sub>)<sub>2</sub>Pd(NCO)<sub>2</sub> complexes and for all of the chloride and azide complexes can be rationalized by either  $\sigma$ -bonding or  $\pi$ -bonding arguments.<sup>19</sup> If solvent is also released from the *cis* isomer on forming the *trans* isomer for the [ArP(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Pd(NCO)<sub>2</sub> complexes, the phosphine electronic effects for these complexes cannot be rationalized by  $\sigma$ -bonding arguments. These effects can be rationalized by invoking palladium-phosphorus  $\pi$  bonding and/or palladium-isocyanate  $\pi$  bonding.<sup>20</sup> However, the current opinion<sup>21</sup> of most authors

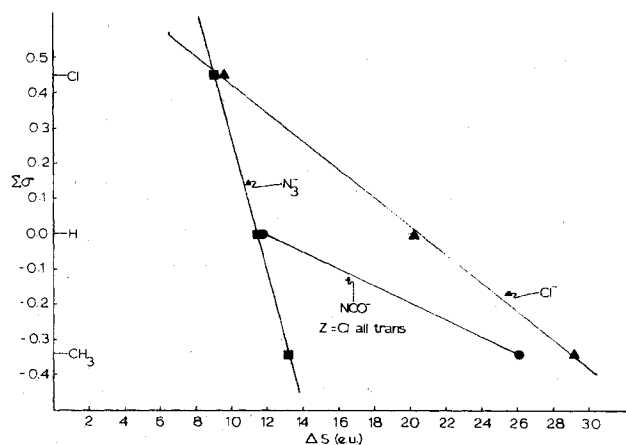


Figure 4. Plots of  $\Delta S$  vs. Hammett  $\sigma$  constants for the complexes [(4-ZC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>PCH<sub>3</sub>]<sub>2</sub>PdX<sub>2</sub> in CDCl<sub>3</sub>: ●, X<sup>-</sup> = NCO<sup>-</sup>; ▲, X<sup>-</sup> = Cl<sup>-</sup>; ■, X<sup>-</sup> = N<sub>3</sub><sup>-</sup>.

is that no phosphorus-palladium  $\pi$  bonding is present in molecules of this sort, or at the very most if it does exist, it is very weak, too weak to explain these results.

There should be two major contributions to both  $\Delta H$  and  $\Delta S$ . For  $\Delta H$  these are solvation effects ( $\Delta H_{\text{sol}}$ ) and changes in internal bond strengths ( $\Delta H_{\text{bond}}$ ). For  $\Delta S$  these are solvation effects ( $\Delta S_{\text{sol}}$ ) and changes in internal degrees of freedom ( $\Delta S_{\text{free}}$ ). Thus

$$\Delta H = \Delta H_{\text{sol}} + \Delta H_{\text{bond}} \quad (1)$$

$$\Delta S = \Delta S_{\text{sol}} + \Delta S_{\text{free}} \quad (2)$$

Since there is a good trend between  $\Delta H$  and  $\Delta S$ , as shown by the data in Figure 5, it seems that  $\Delta H_{\text{sol}}$  and  $\Delta S_{\text{sol}}$  are once again the most important contributors to  $\Delta H$  and  $\Delta S$ , respectively. They are, however, not the only important terms or  $\Delta H$  and  $\Delta S$  would be linearly related. In addition, we see from the data in Table II and Figures 1-4 that  $\Delta H_{\text{bond}}$  must be fairly large because the complex [(4-ClC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>PCH<sub>3</sub>]<sub>2</sub>Pd(NCO)<sub>2</sub> is wholly *trans* in CDCl<sub>3</sub> while the complex of a more basic phosphine [(4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>PCH<sub>3</sub>]<sub>2</sub>Pd(NCO)<sub>2</sub> is 65% *cis* in this same solvent. Thus, phosphine electronic effects (these two complexes should have identical steric requirements) are sufficient to almost completely alter the geometry. Solvent effects are similarly large as changing the solvent from CDCl<sub>3</sub>,  $\mu = 1.01$  D,<sup>14</sup> to 1,2-dichloroethane,  $\mu = 1.19$  D,<sup>14</sup> changes  $K_{\text{eq}} = [\text{trans}]/[\text{cis}]$  from 8.5 to 0.72 for [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PCH<sub>3</sub>]<sub>2</sub>Pd(NCO)<sub>2</sub>, a factor greater than an order of magnitude in  $K_{\text{eq}}$ . Similarly, on going from CDCl<sub>3</sub>,  $\mu = 1.01$  D,<sup>14</sup> to 1,1,2-trichloroethane,  $\mu = 1.22$  D,<sup>14</sup>  $K_{\text{eq}}$  changes from 0.52 to

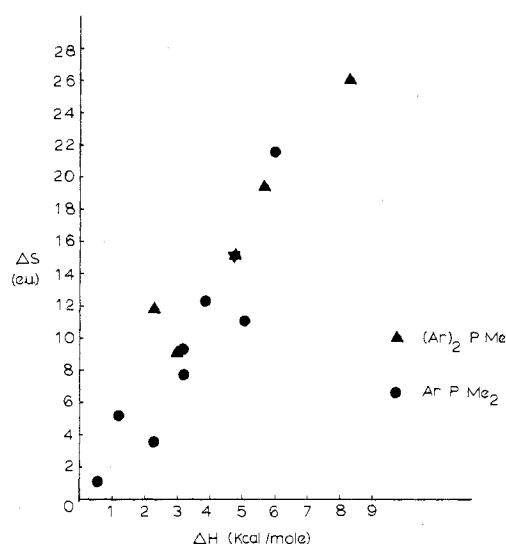


Figure 5. Plot of  $\Delta H$  vs.  $\Delta S$  for the compounds  $(R_3P)_2Pd(NCO)_2$  in all solvents investigated.

0.06 for  $[(4-CH_3OC_6H_4)P(CH_3)_2]_2Pd(NCO)_2$ . Using the values for the lowest energy electronic transition which is generally assigned as  $\nu(^1E_g \leftarrow ^1A_{1g})$  ( $\mu m^{-1}$ ) for  $PdX_4^{2-}$  as a measure of the relative anion-palladium bond strengths one finds the following order:  $Cl^-$  (1.67)<sup>22</sup> <  $N_3^-$  (2.40)<sup>23</sup> <  $NCO^-$  (3.38)<sup>24</sup> <  $CN^-$  (4.16).<sup>25</sup> This same order has been found for the trans influence of these ligands in platinum(II) compounds as determined by NMR coupling constants,<sup>26</sup> and it appears that the relative trans influence of these ligands is the same for square-planar complexes of palladium(II) and platinum(II).<sup>26</sup> Consequently, if anion bonding effects were controlling geometry via the trans influence,<sup>26</sup> the complexes should show a decreasing population of the trans isomers in this same sequence for the same phosphines in the same solvent.<sup>19</sup> Experimentally, for  $[(C_6H_5)_2PCH_3]_2PdX_2$  in  $CDCl_3$  the values for  $K_{eq} = [trans]/[cis]$  at 305 K are as follows:  $X = Cl$ ,<sup>1</sup> 11.9;  $X = N_3$ ,<sup>1</sup> 0.05;  $X = NCO$ , 8.7;  $X = CN$ ,<sup>8</sup> >19. Similarly, for  $[(C_6H_5)P(CH_3)_2]_2PdX_2$  in  $CDCl_3$  the  $K_{eq}$ 's at 305 K are as follows:  $X = Cl$ ,<sup>1</sup> 0.55;  $X = N_3$ ,<sup>1</sup> 0.11;  $X = NCO$ , 0.74;  $X = CN$ ,<sup>8</sup> >19. Clearly then, in neither of these two sequences do the isomer populations follow the expected sequence of anion bonding or trans influence effects.

The data presented in Figures 1 and 3 provide comparisons of anion and phosphine electronic effects. There should be two major contributions to  $\Delta H_{bond}$  and these are  $\Delta H_{steric}$  and  $\Delta H_{electronic}$ . Thus  $\Delta H_{bond} = \Delta H_{steric} + \Delta H_{electronic}$ . These two terms should work in opposition to one another. As steric effects increase, the bonds should be weakened, and as the bonds are strengthened and shortened, steric effects should become more pronounced. By comparing the slopes of the correlations between  $\Delta H$  and Hammett  $\sigma$  constants (reflecting phosphine basicity) we see for the  $(Ar_2PCH_3)_2PdX_2$  complexes (Figure 3) that the phosphine electronic effects vary in the following order:  $X^- = NCO^- > X^- = Cl^- > X^- = N_3^-$ . This is precisely what would be expected on the basis of the steric effects of the anion. Since the azide ion is linear but the  $Pd-N_3$  angle<sup>27</sup> is about  $125^\circ$ , the conical area that this anion will occupy in solution will be larger than the area occupied by chloride which will in turn be larger than the area occupied by the linear<sup>24</sup>  $NCO^-$  ion. The steric effects in the  $[ArP(CH_3)_2]_2PdX_2$  series should be less than those in the  $(Ar_2PCH_3)_2PdX_2$  series and this is evident from the data in Figures 1 and 3. The phosphine electronic effects follow the same trends for both  $[ArP(CH_3)_2]_2PdX_2$  and  $(Ar_2PCH_3)_2PdX_2$ ,  $X^- = Cl^-$ ,  $N_3^-$ , but opposite trends for  $X^- = NCO^-$ . It seems that electronic effects are more important

than steric effects for the  $[ArP(CH_3)_2]_2PdX_2$  complexes such that for these complexes the contributions to  $\Delta H_{eq}$  decrease in the order  $\Delta H_{sol} > \Delta H_{electronic} > \Delta H_{steric}$ . Since  $\pi$  bonding should be more sensitive to steric effects than  $\sigma$  bonding, these data are consistent with but do not necessarily demonstrate the existence of  $\pi$  bonding between palladium and phosphorus and/or palladium and anion.<sup>20</sup> These data also suggest that for compounds of this sort containing anions as polar as isocyanate there is appreciable solvation of both the cis and trans isomers.

The rates of the isomerization processes vary greatly. The time required for phosphine exchange or for equilibrium to be reached follows the order of cyanides<sup>8</sup> (instantaneously) < chlorides<sup>4</sup> (seconds) < azides<sup>1</sup> (minutes) < isocyanates (hours) < tetrazolates<sup>5</sup> (hours). The  $P-CH_3$  doublet for the isocyanate complexes collapses to a singlet in the  $^1H$  NMR spectra in the presence of excess ligand (1:4 = complex:ligand in  $CD_3NO_2$ ) indicating that phosphine exchange with excess phosphine does occur. The rate of exchange is dependent upon the concentration of excess phosphine and a larger excess is necessary to cause exchange in the isocyanate complexes than for the azide, chloride, or cyanide complexes (in that order). Exchange is also more rapid when  $(CH_3O)_3P$  is used as the catalyzing ligand than when either  $Ar_2PCH_3$  or  $ArP(CH_3)_2$  is utilized as the catalyzing ligand. In addition, mixed-ligand<sup>17</sup> complexes  $PdLL'(NCO)_2$  are present in these solutions. Thus, phosphine exchange and isomerization both proceed through pentacoordinate transition states.<sup>7</sup> The relative rates of phosphine exchange and isomerization are related to the activation energies which for example for the unidirectional isomerization of cis to trans should be related to the energy difference between the cis isomer and the pentacoordinate transition states. The relative rates could then be rationalized either on the basis of the relative stabilities of the cis isomers or on the basis of the relative stabilities of the pentacoordinate transition states.

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**Registry No.** *cis*- $[(4-CH_3OC_6H_4)P(CH_3)_2]_2Pd(NCO)_2$ , 58237-42-6; *trans*- $[(4-CH_3OC_6H_4)P(CH_3)_2]_2Pd(NCO)_2$ , 62210-65-5; *cis*- $[(4-CH_3C_6H_4)P(CH_3)_2]_2Pd(NCO)_2$ , 58179-10-5; *trans*- $[(4-CH_3C_6H_4)P(CH_3)_2]_2Pd(NCO)_2$ , 62210-66-6; *cis*- $[(C_6H_5)P(CH_3)_2]_2Pd(NCO)_2$ , 58179-08-1; *trans*- $[(C_6H_5)P(CH_3)_2]_2Pd(NCO)_2$ , 62210-67-7; *cis*- $[(4-ClC_6H_4)P(CH_3)_2]_2Pd(NCO)_2$ , 58179-11-6; *trans*- $[(4-ClC_6H_4)P(CH_3)_2]_2Pd(NCO)_2$ , 62210-68-8; *cis*- $[(4-CH_3C_6H_4)_2P(CH_3)]_2Pd(NCO)_2$ , 58179-12-7; *trans*- $[(4-CH_3C_6H_4)_2P(CH_3)]_2Pd(NCO)_2$ , 62210-69-9; *cis*- $[(C_6H_5)_2P(CH_3)]_2Pd(NCO)_2$ , 58179-09-2; *trans*- $[(C_6H_5)_2P(CH_3)]_2Pd(NCO)_2$ , 62210-70-2; *trans*- $[(4-ClC_6H_4)_2P(CH_3)]_2Pd(NCO)_2$ , 62210-71-3.

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## Complexes of the Platinum Metals. 9.<sup>1</sup> Chemistry of the Species $[M(OCOCF_3)_2CO(PPh_3)_2]$ and $[MH(OCOCF_3)CO(PPh_3)_2]$ (M = Ru or Os)

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The complexes  $[M(OCOCF_3)_2(CO)(PPh_3)_2]$  (M = Ru or Os) and their alcoholysis products  $[MH(OCOCF_3)(CO)(PPh_3)_2]$  react with carbon monoxide to yield the dicarbonyls  $[M(OCOCF_3)_2(CO)_2(PPh_3)_2]$  and  $[MH(OCOCF_3)(CO)_2(PPh_3)_2]$ , respectively. The hydrides  $[MH(OCOCF_3)(CO)(PPh_3)_2]$  add triphenylphosphine to form the species  $[MH(OCOCF_3)(CO)(PPh_3)_3]$ . Acetylacetonone (acac H) and hexafluoroacetylacetonone (facfac H) react with  $[M(OCOCF_3)_2(CO)(PPh_3)_2]$  in boiling alcohol to form  $\beta$ -diketone complexes  $[M(acac)(OCOCF_3)(CO)(PPh_3)_2]$  and  $[M(facfac)(OCOCF_3)(CO)(PPh_3)_2]$ , respectively; in the presence of potassium hydroxide, acetylacetonone affords the hydrides  $[MH(acac)(CO)(PPh_3)_2]$ . The complexes  $[M(OCOCF_3)_2(CO)(PPh_3)_2]$  also react with sodium acetate in methanol and ethanol to yield the products  $[M(OCOCH_3)_2(CO)(PPh_3)_2]$  and  $[MH(OCOCH_3)(CO)(PPh_3)_2]$ , respectively. Sodium nitrate in methanol affords the mixed nitrate/trifluoroacetato complexes  $[M(NO_3)(OCOCF_3)(CO)(PPh_3)_2]$  and sulfur dioxide in methanol yields the mixed methylsulfonato/trifluoroacetato species  $[M(SO_3CH_3)(OCOCF_3)(CO)(PPh_3)_2]$ . The course of these reactions and the structure and stereochemistry of the products are discussed.

### Introduction

We have recently reported<sup>2</sup> the synthesis and characterization of a wide range of perfluorocarboxylato complexes of the platinum group metals, and have shown<sup>3</sup> that the bis-(trifluoroacetato) derivatives  $[M(OCOCF_3)_2(CO)(PPh_3)_2]$  (M = Ru, Os) are homogeneous catalysts for the dehydrogenation of simple primary, secondary, and cyclic alcohols. The catalytic reaction involves alcoholysis to yield alkoxides  $[M(OCHR'R')(OCOCF_3)(CO)(PPh_3)_2]$  which subsequently undergo  $\beta$ -elimination to form an aldehyde (R = H) or ketone (R  $\neq$  H) and the isolable hydride intermediates  $[MH(OCOCF_3)(CO)(PPh_3)_2]$ .<sup>3</sup>

In this paper we report further studies on the chemical reactivity of the catalysts  $[M(OCOCF_3)_2(CO)(PPh_3)_2]$  and the hydride intermediates  $[MH(OCOCF_3)(CO)(PPh_3)_2]$ . The reactions described were designed to yield information concerning other possible catalytic reactions, and to highlight the unusual reactivity of the monodentate carboxylate ligands in these complexes. Products isolated have been characterized by analytical and spectroscopic methods and, where possible, their stereochemistry has been assigned.

Several of the new complexes reported display stereochemical nonrigidity, in particular the intramolecular exchange of mono- and bidentate carboxylate and/or nitrate ligands.

### Experimental Section

The complexes  $[M(OCOCF_3)_2(CO)(PPh_3)_2]$  were prepared as previously described.<sup>2</sup> Reactions were performed under nitrogen, but, unless otherwise indicated, the products were manipulated in air. Systems involving the hydrides  $[MH(OCOCF_3)(CO)(PPh_3)_2]$  were handled under strictly anaerobic conditions. Unless otherwise indicated, washings were performed using  $2 \times 2.5$  cm<sup>3</sup> of each solvent specified.

Analyses, by the microanalytical laboratory of the University College London, and melting points, taken in sealed tubes under nitrogen, are given in Table I. Infrared spectra of solid samples were obtained as Nujol mulls using a Perkin-Elmer 457 grating spectrometer. Proton and <sup>31</sup>P NMR spectra were recorded at 90 and 36.43 MHz, respectively, using a Bruker HFX90 spectrometer. The <sup>31</sup>P

NMR spectra were calibrated against external H<sub>3</sub>PO<sub>4</sub> and values are quoted as the difference in ppm from this reference; shifts to high frequency are positive. Spectroscopic data are recorded in Tables II (infrared and <sup>1</sup>H NMR) and III (<sup>31</sup>P NMR).

**Carbonylhydrido(trifluoroacetato)bis(triphenylphosphine)ruthenium(II)**,  $[RuH(OCOCF_3)CO(PPh_3)_2]$ . Carbonylbis(trifluoroacetato)bis(triphenylphosphine)ruthenium (0.2 g) was heated under reflux in ethanol (5.0 cm<sup>3</sup>) to give initially a bright yellow solution. This rapidly turned lime-green, and a pale yellow, crystalline solid began to precipitate. After 15 min the mixture was cooled, the *yellow crystals* were filtered off under nitrogen, washed successively with degassed methanol, water, and methanol, then dried in vacuo (yield 78%).

**Carbonylhydrido(trifluoroacetato)bis(triphenylphosphine)osmium(II)**,  $[OsH(OCOCF_3)CO(PPh_3)_2]$ . Carbonylbis(trifluoroacetato)bis(triphenylphosphine)osmium (0.2 g) was heated under reflux in ethanol (5.0 cm<sup>3</sup>) for 20 min. During this time the initial complex dissolved to give a pale pink solution, from which *yellow crystals* rapidly precipitated. The mixture was allowed to cool, then the crystals were filtered off under nitrogen, washed successively with degassed methanol, water, and methanol, and dried in vacuo (yield 76%).

**Carbonylhydrido(trifluoroacetato)tris(triphenylphosphine)ruthenium(II)**,  $[RuH(OCOCF_3)CO(PPh_3)_3]$ . Carbonylbis(trifluoroacetato)bis(triphenylphosphine)ruthenium (0.2 g) was added to a boiling solution of triphenylphosphine (0.2 g) in ethanol (10.0 cm<sup>3</sup>), and the mixture was heated under reflux for 20 min. The yellow coloration rapidly faded, and after 15 min *creamy-white crystals* began to precipitate. After 20 min the mixture was allowed to cool; then the crystals were filtered off, washed successively in methanol, water, and methanol, and dried in vacuo (yield 93%).

A similar procedure, employing carbonylbis(trifluoroacetato)bis(triphenylphosphine)osmium (0.2 g), gave creamy white crystals of **carbonylhydrido(trifluoroacetato)tris(triphenylphosphine)osmium(II)**,  $[OsH(OCOCF_3)CO(PPh_3)_3]$  (yield 88%).

**Dicarbonylbis(trifluoroacetato)bis(triphenylphosphine)ruthenium(II)**,  $[Ru(OCOCF_3)_2(CO)_2(PPh_3)_2]$ . Carbon monoxide was bubbled through a boiling solution of carbonylbis(trifluoroacetato)bis(triphenylphosphine)ruthenium (0.2 g) in benzene (10.0 cm<sup>3</sup>) to give an initial yellow coloration. Boiling was continued for 30 min, during which time the solution became colorless; the benzene was then removed by evaporation under reduced pressure. The resultant oil was crystallized from dichloromethane/methanol as *white crystals* which