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## Cationic Carbonyl and Related Complexes of Pentachlorophenylnickel(II)

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The solution of *trans*-C<sub>6</sub>Cl<sub>5</sub>Ni(PPhMe<sub>2</sub>)<sub>2</sub>OClO<sub>3</sub>, prepared in situ from *trans*-C<sub>6</sub>Cl<sub>5</sub>Ni(PPhMe<sub>2</sub>)<sub>2</sub>Cl and silver perchlorate in benzene, reacts under an atmosphere of carbon monoxide to give a cationic carbonylnickel(II) complex, *trans*-[C<sub>6</sub>Cl<sub>5</sub>Ni(PPhMe<sub>2</sub>)<sub>2</sub>CO]<sup>+</sup>ClO<sub>4</sub><sup>-</sup>, which has been characterized by microanalysis, infrared and electronic spectroscopies, and derivatization to *trans*-C<sub>6</sub>Cl<sub>5</sub>Ni(PPhMe<sub>2</sub>)<sub>2</sub>COOR.

### Introduction

A sharp point of contrast between divalent Ni, Pd, and Pt is that while platinum forms stable cationic carbonyl complexes of type [M(PR<sub>3</sub>)<sub>2</sub>(CO)X]<sup>+</sup>, palladium forms relatively fewer and nickel forms none. Church and May<sup>1</sup> found that displacement of halide from M(PR<sub>3</sub>)<sub>2</sub>X<sub>2</sub> by carbon monoxide in the presence of sodium perchlorate proceeded only with complexes of platinum and not with complexes of palladium or nickel. Clark and Dixon<sup>2</sup> reported that the reaction mixture obtained from Ni(PR<sub>3</sub>)<sub>2</sub>X<sub>2</sub>, carbon monoxide, and boron trifluoride contains unstable [Ni(PR<sub>3</sub>)<sub>2</sub>(CO)X]<sup>+</sup>. The difficulty in preparation of such cationic carbonyl complexes of nickel(II) may be ascribed to either or both of two factors: (a) the low energy and contraction of the 3d orbitals in cationic nickel(II), which causes π bonding with carbon monoxide to become unfavorable; and (b) the kinetic instability, such as observed for *trans*-[Pd(PEt<sub>3</sub>)<sub>2</sub>(CO)Cl]<sup>+</sup>BF<sub>4</sub><sup>-</sup>, which readily loses<sup>2b</sup> carbon monoxide on standing to give the chloride-bridged palladium complex, [Pd<sub>2</sub>Cl<sub>2</sub>(PEt<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>[BF<sub>4</sub>]<sub>2</sub><sup>-</sup>. The recent successful synthesis<sup>3,4</sup> of stable cationic nickel complexes of type *trans*-[C<sub>6</sub>Cl<sub>5</sub>Ni(PR<sub>3</sub>)<sub>2</sub>L]<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (where L was N or P donors) prompted us to study the synthesis of analogous carbonyl (=L) complexes, which, if formed, would be expected to be kinetically stable because the pentachlorophenyl group cannot function as a bridging group.

### Results and Discussion

**Preparation of Complexes.** The chloride ligand in *trans*-C<sub>6</sub>Cl<sub>5</sub>Ni(PR<sub>3</sub>)<sub>2</sub>Cl (PR<sub>3</sub> = PPhMe<sub>2</sub> (**1a**), PPh<sub>2</sub>Me (**1b**)) is labile and the complexes react readily with silver perchlorate in benzene resulting in the precipitation of silver chloride.<sup>3,4</sup> Other chloro(organo)nickel complexes such as *trans*-C<sub>6</sub>Cl<sub>5</sub>Ni(PPh<sub>3</sub>)<sub>2</sub>Cl or *trans*-o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Ni(PPhMe<sub>2</sub>)<sub>2</sub>Cl decompose during a similar reaction.<sup>5</sup> Addition of *n*-hexane to the filtrate obtained from **1b** causes a slow deposition of crystals of the perchloratonickel complex, *trans*-C<sub>6</sub>Cl<sub>5</sub>Ni(PPh<sub>2</sub>Me)<sub>2</sub>OClO<sub>3</sub> (**2b**), as its benzene solvate. The latter can be converted to the unsolvated complex by heating. An analogous procedure directed to the isolation of a complex from **1a** results in a sticky brown material and no pure perchlorato complex, **2a**, has been isolated as yet, probably due to its highly hygroscopic nature. However, treatment of the solution under air or moisture causes the formation of crystals of the aquonickel complex, *trans*-[C<sub>6</sub>Cl<sub>5</sub>Ni(PPhMe<sub>2</sub>)<sub>2</sub>OH<sub>2</sub>]<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (**3a**). Analogous perchloratopalladium(II)<sup>6</sup> and -platinum(II)<sup>7</sup> and cationic aquoplatinum(II)<sup>7</sup> complexes have recently been reported.

The perchloratonickel complex, **2a**, prepared in situ in benzene, reacts with carbon monoxide at ca. 5 °C to give a light yellow precipitate of the cationic carbonylnickel complex *trans*-[C<sub>6</sub>Cl<sub>5</sub>Ni(PPhMe<sub>2</sub>)<sub>2</sub>CO]<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (**4a**). In this reaction removal of the carbon monoxide atmosphere from the reaction vessel causes the precipitate to dissolve, giving the original orange-brown solution. The complex **4a** isolated is stable in a sealed tube but is very sensitive toward moisture to give the

aquonickel complex **3a**. This property is in contrast to that of the cationic carbonylplatinum complex, *trans*-[PtCl(CO)(PEt<sub>3</sub>)<sub>2</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup>, which reacts with water at the carbonyl ligand under reflux to give carbon dioxide and *trans*-PtHCl(PEt<sub>3</sub>)<sub>2</sub>.<sup>8</sup> Another cationic carbonylnickel complex, **4b**, seems to be obtained as the benzene solvate from **2b** in a similar manner as for **4a**, but it is very unstable and easily decomposes to the perchloratonickel complex, **2b**, on standing. In these decompositions of the carbonylnickels the carbonyl ligand is substituted by oxygen-containing ligands, which are also very labile as will be shown below. The complex **4a** is one of very few well-identified carbonylnickel(II) derivatives so far reported and appears to represent a new type among nickel complexes, the others being largely confined to compounds<sup>9</sup> of the type (η<sup>3</sup>-allyl)Ni(CO)X and (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ni(CO)X. Some pentacoordinated nickel(II) complexes of carbon monoxide have been reported.<sup>10</sup>

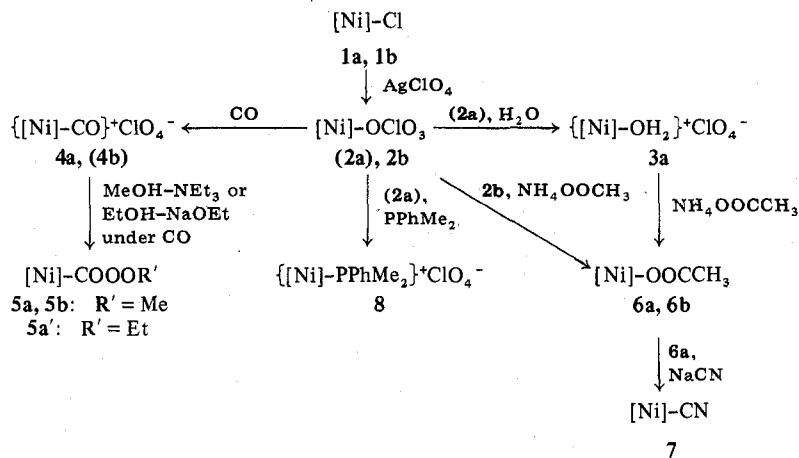
The remarkable reaction of alkoxide ion in attacking the carbonyl carbon of cationic metal carbonyl complexes has been described for iridium,<sup>11</sup> manganese,<sup>12</sup> rhodium,<sup>13</sup> platinum,<sup>8,14</sup> and palladium<sup>15</sup> central metals with a number of different surrounding ligands. The carbonylnickel complex **4a** also reacts with methanol under an atmosphere of carbon monoxide in the presence of triethylamine to give the air-stable methoxycarbonylnickel complex, **5a**.<sup>16</sup> Ethoxycarbonylnickel, **5a'**, can be obtained from **4a** in a similar manner but using sodium ethoxide instead of triethylamine, reflecting the lower acidity of ethanol (pK<sub>a</sub> = 17) than methanol (pK<sub>a</sub> = 16). The reaction of perchloratonickel **2b** with carbon monoxide in methanol in the presence of triethylamine gives another methoxycarbonylnickel complex, **5b**. It is not clear at present whether these reactions involve the nucleophilic attack of alcohol (or alkoxide ion) on the coordinated carbonyl carbon atom<sup>17</sup> or the insertion of a free carbon monoxide into nickel-alkoxide bond which is formed at an earlier stage.<sup>18</sup> Alkoxy carbonylnickel complexes of type NiCl(COOR)(PPh<sub>3</sub>)<sub>2</sub> have recently been obtained<sup>19</sup> by oxidative addition of alkyl chloroformates to Ni(PPh<sub>3</sub>)<sub>4</sub> or Ni(C<sub>2</sub>H<sub>4</sub>)(PPh<sub>3</sub>)<sub>3</sub> and are reported to be very air sensitive.

The aquonickel **3a** and perchloratonickel **2b** complexes react with ammonium acetate to give the corresponding acetoxy-nickel derivatives, **6a** and **6b**. The acetoxy ligand in **6a** can be substituted by cyanide ion to give the complex **7**. A cationic complex, *trans*-[C<sub>6</sub>Cl<sub>5</sub>Ni(PPhMe<sub>2</sub>)<sub>3</sub>]<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (**8**), is also prepared from **1a**, silver perchlorate, and dimethyl(phenyl)phosphine in acetone.

The above reactions are summarized in Scheme I.

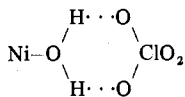
**Ir, <sup>1</sup>H NMR, and Electronic Spectra.** The ir spectra of all the complexes show characteristic bands due to the tertiary phosphine and pentachlorophenyl groups. A perchlorato group has been known<sup>20</sup> to show some characteristic absorption patterns in the Cl-O stretching region depending on the interaction mode. The one band absorption in the carbonylnickel complex **4a** and trisdimethyl(phenyl)phosphine complex **8** is typical of free perchlorate (T<sub>d</sub>) anion, but several absorption

Scheme I



[Ni] = *trans*-C<sub>6</sub>Cl<sub>5</sub>Ni(PR<sub>3</sub>)<sub>2</sub>; PR<sub>3</sub> = PPhMe<sub>2</sub> (a), PPh<sub>2</sub>Me (b); complexes in parentheses are not isolated in pure form

bands observed for perchloratonickel complex **2b**, as well as aquonickel complex **3a**, are indicative of perchlorato group distortion from *T<sub>d</sub>* symmetry due probably to any interaction with nickel species. However, we defer further assignment of the interaction mode for **2b** because the solution spectra in this region are very different from the solid state spectra and ill formed with many shoulders. The presence of perchlorato interaction in the aquonickel complex **3a** is also clear from conductivity measurements in dichloromethane; concentrated solutions of **3a** show much lower conductivity values, as shown in the experimental section, than those observed for analogous cationic pentachlorophenylnickel complexes.<sup>3,4</sup> The interaction mode of the perchlorate anion in **3a** is considered to be one involving hydrogen bonding such as



because in the <sup>1</sup>H NMR spectra the chemical shift and the peak shape of the OH<sub>2</sub> proton resonance vary significantly with concentration (see the Experimental Section).

In the ir spectra of cationic carbonylnickel complexes **4a** and **4b**, a very intense band is observed at 2100 cm<sup>-1</sup>, which is almost consistent with, or slightly lower than, the frequencies observed for several cationic carbonylplatinum<sup>2,7,8,21</sup> or -palladium<sup>2</sup> but is considerably higher than those observed for a number of zerovalent carbonylnickel<sup>22</sup> and divalent carbonylnickel<sup>10</sup> complexes. The higher frequency is consistent with the lesser π-bonding capability of cationic divalent nickel compared with that of zerovalent or neutral divalent nickel. The ir spectra of methoxycarbonyl complex **5a** show strong bands at 1621 and 1020 cm<sup>-1</sup> characteristic of the methoxycarbonyl group<sup>19</sup> and those of **5b** at 1622 and 1046 cm<sup>-1</sup>, while the spectra of the acetoxynickel complexes **6a** and **6b** show strong bands near 1610 and 1320 cm<sup>-1</sup>.

The <sup>1</sup>H NMR spectra of all the nickel complexes so far measured in the present study show a triplet (1:2:1) of bands due to the phosphine methyl protons and are consistent with *trans* square-planar configurations of the complexes.<sup>23</sup> The spectral pattern of complex **5a** is unchanged even at -60 °C, and no evidence was obtained for the presence or absence of free rotation around the nickel-methoxycarbonyl bond, although we expect its presence.

The electronic spectra of some arylnickel complexes of type *trans*-RNi(PR<sub>3</sub>)<sub>2</sub>X have been discussed by Miller et al.<sup>24</sup> The transition observed in the visible region is predominantly *d<sub>xy</sub>-d<sub>x<sup>2</sup>-y<sup>2</sup></sub>* and is thought to be one of the useful tools for the identification of complex formation. In Table I are listed the values of λ<sub>max</sub> for the transition observed for some penta-

Table I. Electronic Spectral Data for *trans*-C<sub>6</sub>Cl<sub>5</sub>Ni(PPhMe<sub>2</sub>)<sub>2</sub>X and *trans*-[C<sub>6</sub>Cl<sub>5</sub>Ni(PPhMe<sub>2</sub>)<sub>2</sub>L]<sup>+</sup>ClO<sub>4</sub><sup>-</sup> in Dichloromethane

X or L	λ <sub>max</sub> , nm (ε) <sup>a</sup>	X or L	λ <sub>max</sub> , nm (ε)
COOMe	340 (sh)	NCS <sup>c</sup>	396 (488)
C≡N	356 (829)	OOCCH <sub>3</sub>	412 (585)
C=O <sup>b</sup>	363 (sh)	Cl	420 (518)
P(OMe) <sub>3</sub> <sup>c</sup>	365 (837)	OH <sub>2</sub>	424 (475)
PPhMe <sub>2</sub>	383 (500)	Br <sup>c</sup>	427 (488)
NCMe <sup>c</sup>	383 (736)	I <sup>c</sup>	441 (476)
3,5-lutidine <sup>d</sup>	384 (650)		

<sup>a</sup> The spectra exhibited very intense bands in the ultraviolet region tailing toward the visible region. The total ε values are shown here. <sup>b</sup> Measured for Nujol mull. <sup>c</sup> Prepared in ref 4. <sup>d</sup> Prepared in ref 3.

chlorophenylnickel derivatives of types *trans*-C<sub>6</sub>Cl<sub>5</sub>Ni-(PPhMe<sub>2</sub>)<sub>2</sub>X and *trans*-[C<sub>6</sub>Cl<sub>5</sub>Ni(PPhMe<sub>2</sub>)<sub>2</sub>L]<sup>+</sup>ClO<sub>4</sub><sup>-</sup>. Although the total range of energy of this transition is seen to be quite small, the variation in the λ<sub>max</sub> with changes in coordinating atom of the ligand X or L follows a well-known spectrochemical series:<sup>25</sup> C > P > N > O ≈ Cl > Br > I. The cationic carbonylnickel **4a** and the methoxycarbonylnickel **5a** complexes apparently show the transition in the region expected for a C ligand and the aquonickel **3a** and the acetoxynickel **6a** complexes in the region for an O ligand in spite of the differences in the complex type, i.e., cationic or neutral.

At the end of revision of this article we found a report by Uson, Fornies, and Martinez who obtained analogous cationic carbonyl complexes of palladium(II).<sup>26</sup>

## Experimental Section

It is often cited that concentrated solutions of silver perchlorate in dry benzene are shock sensitive and that organometallic perchlorates, especially those containing distorted perchlorato group from *T<sub>d</sub>* symmetry, are treacherous. Before we reached the results shown in the herein, we performed the reactions several times in scales of less than 0.2 mmol and checked the thermal properties with the sample used for the measurement of melting point by heating further until any decomposition occurred. No complex in this work was explosive below ca. 240 °C, where most complexes decomposed to gray or black solid. However, we recommend that those chemists who trace our work should work only on a small scale as shown below.

Both *trans*-C<sub>6</sub>Cl<sub>5</sub>Ni(PPhMe<sub>2</sub>)<sub>2</sub>Cl (**1a**) and *trans*-C<sub>6</sub>Cl<sub>5</sub>Ni-(PPh<sub>2</sub>Me)<sub>2</sub>Cl (**1b**) were prepared as described previously.<sup>3</sup> Ir spectra were recorded on a Hitachi 225 spectrophotometer over the range 4000–500 cm<sup>-1</sup> using Nujol mulls spread over a cesium iodide plate. <sup>1</sup>H NMR spectra were recorded on a JEOL Model JNM-PS-100 spectrometer operating at 100 MHz. Chemical shifts were measured relative to TMS as an internal standard. Electronic spectra were measured on a Hitachi Two-Wavelength Double Beam Spectrophotometer Model 356.

**Attempts to Isolate Perchloratonickel Complexes; Preparation of the Aquo Complex  $trans-[C_6Cl_5Ni(PPhMe_2)_2(OH_2)]^+ClO_4^-$  (3a) and the Perchloratonickel Complex  $trans-C_6Cl_5Ni(PPh_2Me)_2OClO_3$  (2b).** A solution of **1a** (0.310 g, 0.50 mmol) in 10 ml of dry benzene was added under nitrogen atmosphere to a solution of silver perchlorate (0.113 g, 0.55 mmol), which had been dried over  $P_2O_5$ , in 20 ml of dry benzene. The silver chloride precipitate was removed by filtration to give an orange-brown solution. Addition of *n*-hexane did not cause any crystal formation and the solvents were removed under reduced pressure. The resultant sticky brown material was successfully crystallized from undried benzene-*n*-hexane or diethyl ether-*n*-hexane under air to give the cationic aquonickel complex **3a**: yield 71%; mp 129–133 °C. Anal. Calcd for  $NiC_{22}H_{24}O_5P_2Cl_6$ : C, 37.65; H, 3.45; Cl, 30.31. Found: C, 37.79; H, 3.37; Cl, 30.15. This complex was obtained more conveniently using moist acetone as the reaction solvent followed by recrystallization from diethyl ether-*n*-hexane. The ir spectrum showed bands due to  $OH_2$  at 3260 (m, br) and 1625 (vw, br)  $cm^{-1}$  and bands due to  $ClO_4^-$  at 1143, 1100, and 1036  $cm^{-1}$ . The  $^1H$  NMR spectrum showed resonances at  $\tau$  8.40 (t) ( $J_P = 8$  Hz) (P-CH<sub>3</sub>) and 7.31 (broad singlet) ( $OH_2$ ) (5%  $CH_2Cl_2$  solution) and at  $\tau$  8.38 (t) (P-CH<sub>3</sub>) and 8.09 (s) ( $OH_2$ ) (1% solution). The molar conductivities of  $1.0 \times 10^{-3}$ ,  $10^{-4}$ ,  $10^{-5}$ , and  $10^{-6}$  M solutions in dichloromethane at 25 °C were 2.4, 6.8, 20.0, and 46.0  $\Omega^{-1} cm^2 M^{-1}$ , respectively.

A solution of **1b** (1.488 g, 2.00 mmol) in 20 ml of benzene was treated with silver perchlorate in a similar manner as above, and 40 ml of *n*-hexane was added to the orange-brown filtrate. The mixture, when kept at room temperature, slowly deposited crystals of the perchloratonickel complex **2b** as its 1.5 mol benzene solvate, yield 67% (Anal. Calcd for  $NiC_{41}H_{35}O_4P_2Cl_6$ : C, 53.23; H, 3.81. Found: C, 53.65; H, 3.81), which were heated at 115 °C for several hours to give the unsolvated complex **2b**, mp 202–204 °C. Anal. Calcd for  $NiC_{32}H_{26}O_4P_2Cl_6$ : C, 47.57; H, 3.24; Cl, 26.33. Found: C, 47.72; H, 3.32; Cl, 26.38. The ir spectrum showed bands due to  $OClO_3$  group at 1170, 1153, and 1019  $cm^{-1}$ . One more band at 1103  $cm^{-1}$  is attributable by its medium intensity to the pentachlorophenyl group. The  $^1H$  NMR spectrum ( $CH_2Cl_2$  solution) showed the P-CH<sub>3</sub> resonance at  $\tau$  7.81 (t) ( $J_P = 7$  Hz).

**Preparation of Cationic Carbonyl Complexes,  $trans-[C_6Cl_5Ni(PR_3)_2CO]^+ClO_4^-$ :  $PR_3 = PPhMe_2$  (4a),  $PPh_2Me$  (4b).** A solution of **2a**, prepared in situ from **1a** (4.00 mmol) and silver perchlorate (4.10 mmol) in 80 ml of benzene, was stirred at 5 °C under an atmosphere of carbon monoxide for ca. 1 h to give a light yellow precipitate. On removing the carbon monoxide atmosphere, the precipitate dissolved to give the original orange-brown solution. Therefore, the precipitate was separated under an atmosphere of carbon monoxide, or very quickly under air, to give the cationic carbonyl complex **4a** in a yield of 83% (mp 138–140 °C), which was stored in sealed tubes. Anal. Calcd for  $NiC_{23}H_{22}O_5P_2Cl_6$ : C, 38.81; H, 3.12. Found: C, 38.42; H, 3.05. The ir spectrum showed the characteristic  $\nu(CO)$  band at 2100 (s)  $cm^{-1}$  and  $\nu(ClO_4^-)$  band at 1090 (vs)  $cm^{-1}$ . The spectrum of a sample exposed to air for a few days was identical with that of a mixture of the carbonyl complex **4a** and the aquo complex **3a**. Due to the instability in solution, the  $^1H$  NMR spectrum was not measured, and the electronic spectrum was measured in a Nujol mull.

In a similar manner as above, another cationic carbonyl complex **4b** seemed to be obtained from **2b**, because the ir spectrum of the fresh product showed the  $\nu(CO)$  band at 2100  $cm^{-1}$  and the  $\nu(ClO_4^-)$  band at 1100  $cm^{-1}$  with shoulders. However, the elemental analyses were not reproducible and not in close agreement with theory, probably because the product was indefinitely benzene solvated and thermally unstable. On heating at 115 °C it changed to perchloratonickel complex **2b**.

**Preparation of Alkoxy carbonylnickel Complexes,  $trans-C_6Cl_5Ni(PR_3)_2COOR'$ :  $PR_3 = PPhMe_2$  ( $R' = Me$ ) (5a),  $PPhMe_2$  ( $R' = Et$ ) (5a'),  $PPh_2Me$  ( $R' = Me$ ) (5b).** The cationic carbonyl complex **4a** (2.292 g, 3.22 mmol), freshly prepared as above, was suspended in 60 ml of dry methanol at 0 °C under an atmosphere of carbon monoxide. Addition of a few drops of triethylamine gave at once a clear solution and subsequently precipitation of light yellow crystals of the methoxycarbonyl complex **5a**, yield 72%. An analytical sample was recrystallized from methanol and/or *n*-hexane under CO, mp 144–146 °C. Anal. Calcd for  $NiC_{24}H_{25}O_2P_2Cl_5$ : C, 44.80; H, 3.92; Cl, 27.55. Found: C, 44.88; H, 3.96; Cl, 27.59. The ir spectrum showed characteristic bands due to the COOMe group at 1612 (vs)

and 1020 (vs)  $cm^{-1}$ , and the  $^1H$  NMR spectrum ( $CH_2Cl_2$  solution) showed resonances at  $\tau$  8.51 (t) ( $J_P = 8$  Hz) (P-CH<sub>3</sub>) and 6.87 (s) (O-CH<sub>3</sub>).

The ethoxycarbonyl complex **5a'** was prepared in a similar manner as above but using NaOEt instead of triethylamine in ethanol and was purified by recrystallization from *n*-hexane under CO: yield 45%, mp 117 °C. Anal. Calcd for  $NiC_{25}H_{27}O_2P_2Cl_5$ : C, 45.68; H, 4.14; Cl, 26.96. Found: C, 45.84; H, 4.19; Cl, 26.91. The ir spectrum showed characteristic bands due to the COOEt group at 1607 (vs) and 1030 (vs)  $cm^{-1}$  and the  $^1H$  NMR spectrum ( $CH_2Cl_2$  solution) showed resonances at  $\tau$  8.51 (t) ( $J_P = 8$  Hz) (P-CH<sub>3</sub>), 9.11 (t) (C-CH<sub>3</sub>), and 6.43 (q) (O-CH<sub>2</sub>).

The perchloratonickel complex **2b** (0.808 g, 1.0 mmol) was dissolved in 30 ml of dry methanol at 0 °C under an atmosphere of carbon monoxide. Triethylamine (0.5 ml) was added and the solution was stirred for 2 h to give a precipitate of another methoxycarbonyl complex **5b**, yield 65%. The product was recrystallized from  $CH_2Cl_2$ -*n*-hexane to obtain an analytical sample, mp 144–146 °C. Anal. Calcd for  $NiC_{34}H_{29}O_2P_2Cl_5$ : C, 53.21; H, 3.81; Cl, 23.10. Found: C, 53.13; H, 3.96; Cl, 23.23. The ir spectrum showed the bands due to the COOMe group at 1622 (vs) and 1046 (vs)  $cm^{-1}$  and the  $^1H$  NMR spectrum ( $CH_2Cl_2$  solution) showed resonances at  $\tau$  8.05 (t) ( $J_P = 8$  Hz) (P-CH<sub>3</sub>) and 7.19 (s) (O-CH<sub>3</sub>).

**Preparation of Acetoxynickel Complexes,  $trans-C_6Cl_5Ni(PR_3)_2OOCCH_3$ :  $PR_3 = PPhMe_2$  (6a),  $PPh_2Me$  (6b).** A mixture of the aquo complex **3a** (0.281 g, 0.40 mmol) and ammonium acetate (0.2 g, a large excess) in 10 ml of methanol was stirred at room temperature to give an orange-yellow solution. Water (10 ml) was added, and the precipitate was recrystallized from *n*-hexane to give the acetoxynickel complex **6a**, yield 75%. This complex has been reported previously.<sup>4</sup>

To a mixture of the perchloratonickel complex **2b** (0.30 mmol) and ammonium acetate (an excess) in 10 ml of methanol was added 20 ml of water, and the sticky precipitate was crystallized from *n*-hexane to give the acetoxynickel complex **6b**: yield 50%; mp 145–147 °C. Anal. Calcd for  $NiC_{34}H_{29}O_2P_2Cl_5$ : C, 53.21; H, 3.81; Cl, 23.10. Found: C, 53.24; H, 3.60; Cl, 22.95. The ir spectrum showed characteristic bands due to the OOCCH<sub>3</sub> group at 1613 (vs) and 1320 (vs)  $cm^{-1}$ , and the  $^1H$  NMR spectrum ( $CH_2Cl_2$  solution) showed the resonances at  $\tau$  7.97 (t) ( $J_P = 8$  Hz) (P-CH<sub>3</sub>) and 8.90 (s) (C-CH<sub>3</sub>).

**Preparation of  $trans-C_6Cl_5Ni(PPhMe_2)_2CN$  (7).** A mixture of acetoxynickel complex **6a** (0.257 g, 0.40 mmol) and sodium cyanide (0.10 g, an excess) in 10 ml of acetone was boiled for 10 min. After evaporation of the acetone under reduced pressure, water was added, and the insoluble portion was recrystallized from  $CH_2Cl_2$ -*n*-hexane to give pale yellow crystals of **7**: yield 75%; mp 196–198 °C. Anal. Calcd for  $NiC_{23}H_{22}NP_2Cl_5$ : C, 45.25; H, 3.63; N, 2.29. Found: C, 45.30; H, 3.58; N, 2.46. The ir spectrum showed the characteristic  $\nu(C\equiv N)$  band at 2110 (w)  $cm^{-1}$ , and the  $^1H$  NMR spectrum ( $CH_2Cl_2$  solution) showed the P-CH<sub>3</sub> resonance at  $\tau$  8.30 (t) ( $J_P = 8$  Hz).

**Preparation of  $trans-[C_6Cl_5Ni(PPhMe_2)_2]^+ClO_4^-$  (8).** To a solution of **3a**, prepared in situ from **1a** (0.50 mmol) in 20 ml of acetone, was added 0.2 ml (an excess) of dimethyl(phenyl)phosphine under a nitrogen atmosphere. The solvent was removed under reduced pressure and the residual sticky material was crystallized from ethanol to give orange-yellow crystals of **8**: yield 67%; mp 174–176 °C. Anal. Calcd for  $NiC_{30}H_{33}O_4P_3Cl_6$ : C, 43.84; H, 4.05. Found: C, 43.82; H, 4.32. The  $^1H$  NMR spectrum ( $CDCl_3$  solution) showed the P-CH<sub>3</sub> proton resonances at  $\tau$  8.66 (t) ( $J_P = 7$  Hz) and 8.90 (d) ( $J_P = 8$  Hz).

**Registry No.** **1a**, 15526-04-2; **1b**, 26025-08-1; **2a**, 59982-55-7; **2b**, 59982-56-8; **3a**, 58355-47-8; **4a**, 59982-58-0; **4b**, 59982-60-4; **5a**, 59982-61-5; **5a'**, 59982-62-6; **5b**, 59982-63-7; **6a**, 58281-19-9; **6b**, 59982-64-8; **7**, 59991-83-2; **8**, 59982-66-0.

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## The Kinetics of Olefin-Olefin Substitution Reactions in a Series of Platinum(II) Complexes

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The kinetics of substitution of styrene by 1-pentene in a series of *trans*-PtCl<sub>2</sub>(Ol)(An) complexes where An is a para-substituted aniline were studied in chloroform by stopped-flow methods. The second-order rate constants for substitution at 25 °C were found to be greater than 3000 M<sup>-1</sup> s<sup>-1</sup>. The presence of small quantities of ethanol in the chloroform decreases the rates of the direct second-order substitution pathway and increases the apparent solvent-assisted pathway. The reactions in the reverse direction were complicated by the fast reaction with excess styrene to produce *trans*-dichlorobis(styrene)platinum. A kinetic trans effect was observed in the reactions in both directions, the rates of olefin substitution decreasing as a function of the para substituent on the aniline in the order Cl > H > CH<sub>3</sub> > OCH<sub>3</sub>.

### Introduction

The kinetics of ligand substitution reactions in square-planar platinum(II) complexes have been extensively studied.<sup>2-7</sup> Nearly all of the substitution kinetics have been found to obey a two-term rate law describing two simultaneous reaction pathways. The  $k_1$  term is the second-order rate constant for



$$\text{rate} = [k_1(\text{Y}) + k_s](\text{Pt}-\text{X}) \quad (2)$$

the direct bimolecular substitution of the leaving ligand (X) by the incoming ligand (Y). This path is generally believed to go through a five-coordinate, approximately trigonal-bipyramidal transition state, with the entering ligand (Y), the leaving ligand (X), and the trans ligand (T) in the trigonal plane. The  $k_s$  term represents a solvent assisted path, the rate of which is independent of the concentration of the entering ligand (Y). This path presumably involves the displacement of the leaving ligand by a solvent molecule in the rate-determining step by bimolecular substitution. The solvent molecule is then rapidly displaced by the incoming ligand to give the product complex.

The reactions are invariably carried out in a large excess of incoming ligand (Y) so that the data may be treated in a

first-order fashion to obtain the observed pseudo-first-order rate constant, eq 3. A plot of  $k_{\text{obsd}}$  vs. the concentration of

$$k_{\text{obsd}} = k_1(\text{Y}) + k_s \quad (3)$$

Y gives  $k_1$  as the slope and  $k_s$  as the intercept.

In solvents which are capable of coordinating strongly to the metal the  $k_s$  term is usually found to make a significant contribution to the rate of reaction, sometimes dominating the direct path. In weakly coordinating solvents the solvent path makes little contribution, often indistinguishable from zero.

In 1936 Anderson first reported the substitution reactions of olefins in Zeise's salt and related compounds.<sup>8</sup> These reactions have been widely used in the preparation of platinum-olefin compounds and the reactions are known to be fast. However, very little quantitative work has been done on the rates of olefin substitution in platinum(II) complexes.<sup>9-11</sup>

In this work the rates of olefin-olefin substitution were studied by stopped-flow methods in a series of square-planar platinum(II) complexes of the type *trans*-PtCl<sub>2</sub>(Ol)(An), where Ol is styrene or 1-pentene and An is a para-substituted aniline, eq 4.

Anilines were chosen as the trans ligands not only because of their ready availability but also because the para substituents markedly change the base strength of the primary amine group coordinated to the metal and it was anticipated that such a change in the  $\sigma$  donor properties of the amine should affect