Articles

## Synthesis of Carbonyl–Olefin Complexes of Platinum(II), PtX<sub>2</sub>(CO)(olefin), and the Catalytic Hydrochlorination of Olefins

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The mixed olefin-carbonyl complexes of platinum(II),  $PtX_2(CO)(C_6H_{10})$ , X = Cl, Br, have been prepared by the reaction of  $PtX_2(CO)_2$  with cyclohexene or, better, from  $Pt_2Cl_4(CO)_2$  and the olefin. Spectroscopic evidence has been gathered for the existence in solution of the mixed olefin-carbonyl species of platinum(II) with cyclopentene, ethylene, and propylene. Spectroscopic data are in agreement with the cis geometry of the complexes. The olefin ligand is promptly displaced by carbon monoxide. The chloro-carbonyl complex  $PtCl_2(CO)(C_6H_{10})$  reacts with dry HCl to yield cyclohexyl chloride and  $Pt_2Cl_4(CO)_2$ . The mixed carbonyl-cyclohexene complex, or  $PtCl_2(CO)_2$  or  $Pt_2Cl_4(CO)_2$  were found to be effective catalyst precursors for the hydrochlorination with dry HCl of a number of symmetrical (cyclohexene, norbornene), terminal (1-decene, propylene, styrene), and internal olefins (cis-2-decene, trans-2-decene, trans-5-decene), in hydrocarbon or chlorinated solvents. Hydrochlorination of cyclohexene- $1,3,3-d_3$  gives the syn addition product, no anti product being observed, in contrast with the results of the hydrochlorination of the same substrate in glacial acetic acid with anhydrous hydrogen chloride. With terminal olefins, Markovnikov hydrochlorination was observed.

### Introduction

The competitive coordination of CO and olefins to transition-metal centers is an interesting subject, in connection with a number of catalytic processes involving both reagents, such as the hydroformylation reaction,<sup>1</sup> the functionalization of olefins with carbon monoxide,<sup>2</sup> and the telomerization of CO and ethylene.<sup>3</sup> In an earlier paper,<sup>4</sup> some of us have studied the displacement of coordinated CO from AuCl(CO) by norbornene and found that the olefin complex is slightly favored. Halo complexes of platinum(II) of the type  $PtX_2L_2$  are good candidates for studying the competition between CO and olefin within the same metal center due to the presence of two coordination sites for neutral ligands L. Another important aspect is the modification of the reactivity induced by coordination. In this connection, earlier work<sup>5</sup> had indicated that the  $\sigma$ -component is predominant in the Pt-CO system and in related ones containing palladium(II)<sup>6</sup> or gold(I);<sup>7</sup> moreover, a recent spectroscopic investigation on  $[PtCl_3(C_2H_4)]^-$  has reinterpreted the Pt-olefin bond in terms of a predominant  $\sigma$ -component.<sup>8</sup> Thus, a change of reactivity with respect to the uncoordinated species is expected upon coordination of CO and/or olefin to platinum(II) and several examples of platinum(II) complexes are known with coordinated CO or olefin acting as a reactive site for nucleophiles.<sup>9</sup> In this paper the mixed carbonyl-olefin complexes of platinum(II), PtX<sub>2</sub>(CO) olefin, X = Cl, Br, are reported, together with the stoichiometric reaction of one of the complexes (X = Cl; olefin)cyclohexene) with dry hydrogen chloride. As an extension of this study, the addition of HCl to some olefins under anhydrous conditions, catalyzed by platinum(II) is also reported.

#### **Experimental Section**

Analytical Instrumentation. The IR spectra were recorded with Perkin-Elmer 283 or 783 spectrophotometers: each spectrum in the carbonyl stretching region was calibrated with CO. The <sup>1</sup>H NMR spectra were recorded with Varian 60, XL-100, or Germini 200 instruments, the chemical shifts being expressed as  $\delta$  (ppm) from TMS. The <sup>13</sup>C NMR spectra were recorded at 75.-5 MHz on a Varian XVR 300 or on a Gemini 200 spectrometer, the chemical shifts being expressed as  $\delta$  (ppm) from TMS. The <sup>if J</sup>Pt

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Table I. IR Data for cis-PtX<sub>2</sub>(CO)(olefin) (X = Cl, Br) and for the Corresponding Uncomplexed Olefins

compd	ν <sub>CO</sub> , cm <sup>-1</sup>	ν <sub>C</sub> C, cm <sup>-1</sup>	$\nu_{\rm Pt-X}, {\rm ~cm^{-1}}$	solvent
$PtCl_2(CO)(C_6H_{10})$	2116 (2108)	1495°	340, 320 <sup>b</sup>	CH <sub>2</sub> Cl <sub>2</sub> (toluene)
$PtBr_2(CO)(C_6H_{10})$	2108 (2099)	1493ª	231, 212°	CH <sub>2</sub> Cl <sub>2</sub> (toluene)
$PtCl_2(CO)(C_5H_8)$	2118	1470ª	not measured	sym- C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>
$PtCl_{2}(CO)(C_{3}H_{6})$	2125	1520		CDČl <sub>3</sub>
$PtCl_{2}(CO)(C_{2}H_{4})$	2125	1436		CDCl <sub>3</sub>
$C_{e}H_{10}$		1650		toluene
C <sub>5</sub> H <sub>8</sub>		1615		CH <sub>2</sub> Cl <sub>2</sub>
$C_{3}H_{5}$		1650		CDCl <sub>3</sub>
$C_2H_4$		1623ď		neat, gas
				phase

<sup>o</sup>PCTFE mull, CaF<sub>2</sub> disk. <sup>b</sup>PCTFE mull, polyethylene disks. "Nujol mull, polyethylene disks. "Raman active vibration, gas phase, from Smith, W. L.; Mills, I. M. J. Chem. Phys. 1964, 40, 2095.

NMR spectra were recorded at 64.374 MHz on a Varian XVR 300 spectrometer. The gas-mass analyses were performed on a VG 7070 or on a Hewlett-Packard 5970 spectrometer connected to a DANI 3800 gas chromatograph. The gas chromatographic analyses were carried out with a Dani 3200 gas chromatograph, or Varian 6000 or 3400 instruments.

General Procedure. Unless otherwise stated, all the operations were carried out under an atmosphere of prepurified dinitrogen. Solvents were dried by conventional methods prior to use. CO (Rivoira, Chivasso, Torino, Italy), C<sub>2</sub>H<sub>4</sub> (Matheson), C<sub>3</sub>H<sub>6</sub> (Matheson), and HBr (Matheson) were used as received. Hydrogen chloride was prepared by dropping concentrated H<sub>2</sub>SO<sub>4</sub> on solid NH4Cl. Cyclohexene and cyclopentene were distilled from sodium sand. The compound cis-PtCl<sub>2</sub>(CO)<sub>2</sub> was prepared by two different routes: (a) by carbonylation of a platinum(IV) chloride in SOCl<sub>2</sub> as medium<sup>10,11</sup> or (b) by treatment of  $trans-PtI_2(CO)_2$ with a chlorinating agent, preferably  $SO_2Cl_2$ , followed by recrystallization from toluene.<sup>12</sup> The dimer  $Pt_2Cl_4(CO)_2$  was prepared as reported in the literature.<sup>5</sup> The ethylene dimer complex  $PtCl_4(C_2H_4)_2$  was prepared according to the literature<sup>13</sup> with a slight modification: an aqueous hydrochloric acid solution of  $H_2PtCl_4$  (containing 12.8 mmol of Pt) was degassed and then saturated with ethylene. After stirring for a week at room temperature, the yellow solution was concentrated to dryness. The residue was dissolved in toluene and recrystallized at about -78 °C (50% yield). The dimer  $Pt_2Cl_4(C_6H_{10})_2$  was prepared according to the literature.<sup>14</sup>

Preparation of cis-Dichloro( $\eta^2$ -cyclohexene)carbonylplatinum(II),  $PtCl_2(CO)(C_6H_{10})$ . (a) From  $PtCl_2(CO)_2$  and Cyclohexene in CH<sub>2</sub>Cl<sub>2</sub>. Cyclohexene (59.2 mmol) was added to a solution of cis-PtCl<sub>2</sub>(CO)<sub>2</sub> (3.11 g, 9.65 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL). The solution was stirred at room temperature and repeatedly degassed. After 5 h, an IR spectrum of the solution showed that the bands due to the original chloro-carbonyl complex were no longer present and a new strong band was observed at 2116 cm<sup>-1</sup>. The solution was evaporated to a small volume and n-heptane (50 mL) was then added. The colorless complex precipitated out: it was filtered and dried under vacuum (2.94 g, 81% yield) IR (Nujol mull, KBr disks): 3025 mw, 2102 vs, 2056 w, 1495 mw, 1435 m, 1413 m, 1260 w, 1159 w, 1000 m, and 865 m cm<sup>-1</sup>; (polychlorotrifluoroethylene, polyethylene disks) 340 m and 320 m cm<sup>-1</sup>; see also Table I. See Tables II and III for the <sup>1</sup>H and <sup>13</sup>C NMR spectra, respectively. The compound shows a  $^{195}$ Pt NMR resonance at 3284 ppm upfield with respect to aqueous H<sub>2</sub>PtCl<sub>6</sub>, in CD<sub>2</sub>Cl<sub>2</sub> as solvent, at 22 °C; under similar conditions, cis-PtCl<sub>2</sub>(CO)<sub>2</sub> has a <sup>196</sup>Pt NMR peak at 3949 ppm. Anal. Calcd for C<sub>7</sub>H<sub>10</sub>Cl<sub>2</sub>OPt: C, 22.4; H, 2.7. Found: C, 21.7; H, 2.5.

(b) From Pt<sub>2</sub>Cl<sub>4</sub>(CO)<sub>2</sub> and Cyclohexene in sym-C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>. Cyclohexene (49.4 mmol) was added to a suspension of  $Pt_2Cl_4(CO)_2$ (0.583 g, 0.99 mmol) in sym-C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> (10 mL). An IR spectrum of the solution measured after a few minutes showed the band at 2116 cm<sup>-1</sup> only, due to the carbonyl stretching vibration of the carbonyl-olefin complex. By addition of n-heptane (10 mL), the colorless product precipitated out. It was filtered and dried under reduced pressure (0.235 g, 22% yield). Anal. Calcd for the formula  $PtCl_2(C_6H_{10})(CO) \cdot C_2H_2Cl_4, C_9H_{12}OCl_6Pt: C, 19.9; H, 2.2.$  Found: C, 19.8; H, 2.3.

In an experiment specially designed for the identification of the probable intermediate  $trans-PtCl_2(CO)(C_6H_{10})$ , the same reaction was carried out in toluene with an insufficient amount of olefin (T = -26 °C, molar ratio Pt/C<sub>6</sub>H<sub>10</sub> = 1.35) and monitored at that temperature by IR spectroscopy: only cis-PtCl<sub>2</sub>- $(CO)(C_6H_{10})$  was detected (at the temperature of the experiment, the solubility of the dimer was too low for its carbonyl band to be observed).

Preparation of cis-Dibromo( $\eta^2$ -cyclohexene)carbonylplatinum(II),  $PtBr_2(CO)(C_6H_{10})$ . A solution of cis- $PtBr_2(CO)_2$ (0.299 g, 0.73 mmol) in sym-C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> (5 mL) was reacted with cyclohexene (49.4 mmol). The solution was stirred for some hours at room temperature and periodically degassed until a colorless microcrystalline product precipitated out. It was filtered and dried under reduced pressure (0.051 g, 15% yield). IR (Nujol, CaF<sub>2</sub> disks): 3020 s, 2097 vs, 2050 w, 1493 m, 1432 m, 1412 m, cm<sup>-1</sup>; (Nujol, polyethylene disks) 231 and 212 cm<sup>-1</sup>.  $\nu_{CO}$  (sym-C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> or CH<sub>2</sub>Cl<sub>2</sub> solution): 2108 cm<sup>-1</sup> (see Table I). For the <sup>13</sup>C NMR spectrum, see Table III. Anal. Calcd for C<sub>7</sub>H<sub>10</sub>Br<sub>2</sub>OPt: C, 18.1; H, 2.2. Found: C, 17.9; H, 2.0.

IR and NMR Evidence for the Formation of PtCl<sub>2</sub>-(CO)(olefin) (olefin = Cyclopentene, Propylene, Ethylene). (a) Cyclopentene. The addition of cyclopentene (22.7 mmol) to a solution of cis-PtCl<sub>2</sub>(CO)<sub>2</sub> (0.100 g, 0.31 mmol) in sym-C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> (10 mL) caused gas evolution and the disappearance of the IR carbonyl bands of the starting metal complex: a new band in the CO stretching region appeared at 2118 cm<sup>-1</sup>, attributable to  $PtCl_2(CO)(C_5H_8)$ . No appreciable variation of the IR spectrum was observed by saturating the solution with CO at atmospheric pressure, unless the excess of olefin was removed. Then, cis- $PtCl_2(CO)_2$  was formed again, ( $\nu_{CO}$ , 2176 and 2136 cm<sup>-1</sup>). For IR and <sup>1</sup>H NMR spectra of the cyclopentene-carbonyl complex, see Tables I and II, respectively.

(b) Propylene. A suspension of Pt<sub>2</sub>Cl<sub>4</sub>(CO)<sub>2</sub> (286 mg, 0.49 mmol) in CDCl<sub>3</sub> (3 mL) was saturated with propylene. A yellow-orange solution was obtained, with IR bands at 2125, 1650 (uncomplexed olefin), and 1520  $cm^{-1}$ . The excess olefin was removed under reduced pressure and the solution was saturated with dinitrogen: the IR spectrum still showed bands at 2125 and 1520 cm<sup>-1</sup> attributed to the olefin-carbonyl complex. This solution was used for measuring the <sup>1</sup>H and <sup>13</sup>C NMR spectra (Tables II and III, respectively). For the IR spectra, see Table I.

(c) Ethylene. (1) The dimer  $Pt_2Cl_4(CO)_2$  (200 mg, 0.34 mmol,  $\nu_{\rm CO}$  2136 cm<sup>-1</sup>) was suspended in CDCl<sub>3</sub> (3 mL). The suspension was saturated with ethylene at room temperature. An IR spectrum showed bands at 2125 and 1436 cm<sup>-1</sup>, attributed to PtCl<sub>2</sub>(C-O)(C<sub>2</sub>H<sub>4</sub>). An <sup>1</sup>H NMR spectrum was recorded, after degassing and saturating the solution with  $N_2$  (see Table II).

(2) The dimer  $Pt_2Cl_4(C_2H_4)_2$  (0.866 g, 1.47 mmol) was suspended in CDCl<sub>3</sub> (5 mL). The supernatant solution was colored but its IR spectrum did not show any band attributable to C=C stretching of the coordinated olefin. The reactor was degassed and an amount of CO (60 mL, T = 18 °C, P = 1 atm, 2.5 mmol), lower than the stoichiometric one, was introduced with a syringe. The mixture was stirred at room temperature for 4 h. An IR spectrum of the yellow-orange solution showed bands at 2176 m w cm<sup>-1</sup> due to *cis*-PtCl<sub>2</sub>(CO)<sub>2</sub>, produced according to reaction 2, and at 2125 vs and 1436 m cm<sup>-1</sup>, attributable to PtCl<sub>2</sub>(CO)(C<sub>2</sub>H<sub>4</sub>) (for the IR data, see Table I). The intensity of the bands at 2125 and 1436 cm<sup>-1</sup> did not decrease by reducing the partial pressure of CO. The <sup>13</sup>C NMR data of the soluble carbonyl-olefin complex are given in Table III.

$$Pt_2Cl_4(C_2H_4)_2 + 2CO \rightleftharpoons 2PtCl_2(CO)(C_2H_4)$$
(1)

$$PtCl_2(CO)(C_2H_4) + CO \rightleftharpoons PtCl_2(CO)_2 + C_2H_4$$
(2)

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Table II.	<sup>1</sup> H NMR Data f	or <i>cis</i> -PtX	2 (CO)(olefin)	and for the	e Corresponding	; Olefins

compd	olefinic prot	tons <sup>a</sup> δ, ppm; <sup>δ</sup> assignment; <sup>e</sup> ( <sup>2</sup> J	(J <sub>H-H</sub> , Hz) (J <sub>H-H</sub> , Hz)	other protons <sup>a</sup> $\delta$ , ppm; <sup>b</sup> assignment <sup>c</sup> ( <sup>2</sup> J <sub>Pt-H</sub> , Hz)	solvent
	5.76 m [H <sup>1</sup> ]	4.94 d [H <sup>3</sup> ] (17)	4.83 d [H <sup>2</sup> ] (10)	1.63 d [CH <sub>3</sub> ]	CDCl <sub>3</sub>
$PtCl_{2}(CO)(C_{3}H_{6}) \\ C_{6}H_{10}^{d} \\ PtCl_{2}(CO)(C_{6}H_{10})^{e} \\ C_{2}H_{4} \\ PtCl_{2}(CO)(C_{6}H_{10}) \\ PtCl_{2}(CO)(C_{6}H_{10})^{e} \\ PtCl_{$	6.0 m [H <sup>1</sup> ] 5.7 m 5.9 m (72) 5.40 s	5.00 d [H <sup>3</sup> ] (70) (7.5)	4.9 d [H <sup>2</sup> ] (54) (15)	2.2 d [CH <sub>3</sub> ] (52) 1.9 m; 1.53 m 2.8 m; 1.7 m	$CDCl_3$ $CD_2Cl_2$ $CD_2Cl_2$ $CDCl_3$ $CDCl_3$
$\begin{array}{c} PtCl_2(CO)(C_2H_4)\\ C_5H_8\\ PtCl_2(CO)(C_5H_8) \end{array}$	5.18 t (58) 5.72 s <sup>f</sup> 6.41 t (75)			2.31 t; 1.84 m 2.83 t; 1.70 m	CDCl <sub>3</sub> CDCl <sub>3</sub> CDCl <sub>3</sub>

<sup>a</sup> Multiplicity: s = singlet; d = doublet; t = triplet; m = multiplet. <sup>b</sup> In CDCl<sub>3</sub> with TMS as internal standard. <sup>c</sup> In brackets. <sup>d</sup> In C<sub>6</sub>D<sub>6</sub>.<sup>e</sup> In CD<sub>2</sub>Cl<sub>2</sub>. <sup>f</sup>Apparent singlet.

Table III.	<sup>13</sup> C NMR Data	for cis-PtX <sub>2</sub> (CO)(olefin)	and for the Correspondin	g Uncomplexed Olefins
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compd	olefinic carbon nuclei: $\delta$ , ppm, <sup>a</sup> assignments <sup>b</sup> ( <sup>1</sup> J <sub>Pt-C</sub> , Hz)	other carbon nuclei: $\delta$ , ppm, <sup>a</sup> assignments <sup>b</sup> ( $J_{Pt-C}$ , Hz)	solvent
	114.8 [C <sup>1</sup> ]; 132.9 [C <sup>2</sup> ]	18.5 [C <sup>3</sup> ]	CDCl <sub>3</sub>
$H^{2}$ CH <sub>3</sub> PtCl <sub>2</sub> (CO)(C <sub>3</sub> H <sub>6</sub> )	77.8 $[C^1]$ (123); 108.6 $[C^2]$ (99)	23.4 [C <sup>3</sup> ] 150.8 [CO] (1640)	$CDCl_3$
$\begin{array}{c} C_2H_4\\ PtCl_2(CO)(C_2H_4) \end{array}$	123° 82.7 (98) <sup>d</sup>	150.8 [CO] (1585)	cyclohexane CDCl <sub>3</sub>
$\beta \overset{\alpha}{\underset{\beta}{\longrightarrow}} \overset{\star}{\overset{\star}{\star}}$	127°	25 [C∝]° 23 [C <sup>β</sup> ]°	cyclohexane
$\mathbf{a}$ PtCl <sub>2</sub> (CO)(C <sub>6</sub> H <sub>10</sub> )	105.9 [C*] (104.3)	29.50 [C <sup>*</sup> ] 21.50 [C <sup>*</sup> ] 153.3 [CO] (1730)	$\mathrm{CD_2Cl_2}/\mathrm{CH_2Cl_2}$
$PtBr_2(CO)(C_6H_{10})$	106.5 [C*] (93.6)	29.7 [C <sup>o</sup> ] 21.3 [C <sup>f</sup> ] 154.0 [CO] (1712)	$\rm CD_2 Cl_2/CH_2 Cl_2$

<sup>a</sup> The <sup>13</sup>C chemical shifts were measured, in the case of  $CD_2Cl_2$  solutions, relative to the internal solvent resonance and are given in ppm downfield from TMS by using the following relation:  $\delta_{TMS} = (\delta CH_2Cl_2 - 54)$  ppm. <sup>b</sup> In brackets. <sup>c</sup>From Dorman, D. E.; Jautelat, M.; Roberts, J. D. J. Org. Chem. 1971, 36, 2757.  $\delta$  measured with respect to  $CS_2$  and converted by using the relation  $\delta(CS_2) = \delta(TMS) + 193$ . <sup>d</sup> Another weak signal is present at  $\delta$  83.9 ( $J_{Pt-C} = 132$ ) ppm probably due to  $Pt_2Cl_4(C_2H_4)_2$ .

**Reaction of** cis**-PtCl<sub>2</sub>(CO)(C**<sub>6</sub>H<sub>10</sub>) **with CO.** A solution of PtCl<sub>2</sub>(CO)(C<sub>6</sub>H<sub>10</sub>) (0.050 g, 0.13 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL), prepared under dinitrogen, was saturated with CO at 1 atm and stirred for about 30 min at room temperature. An IR spectrum of the solution showed the presence of only cis-PtCl<sub>2</sub>(CO)<sub>2</sub> ( $\nu_{CO}$  2177 and 2136 cm<sup>-1</sup>).

Reaction of  $Pt_2Cl_4(C_2H_4)_2$  with CO (Monitored by Gas Volumetry). A thin-wall sealed ampule containing 0.278 g (0.47 mmol) of  $Pt_2Cl_4(C_2H_4)_2$  was placed under CO in a reactor containing toluene (20 mL) presaturated with CO. The reactor was connected to a gas volumetric apparatus thermostated at  $25.5 \pm$ 0.1 °C. The ampule was broken and the CO absorption measured. After about 1 h, the gas absorption was over and a gas chromatographic analysis<sup>15</sup> of the gas phase showed the presence of ethylene. After appropriate correction, the absorbed CO was calculated to be 89% of the value expected for eq 3.

$$Pt_2Cl_4(C_2H_4)_2 + 4CO \rightarrow 2PtCl_2(CO)_2 + 2C_2H_4$$
(3)

**Reaction of Pt<sub>2</sub>Cl<sub>4</sub>(C<sub>6</sub>H<sub>10</sub>)<sub>2</sub> with CO.** A pale yellow solution of Pt<sub>2</sub>Cl<sub>4</sub>(C<sub>6</sub>H<sub>10</sub>)<sub>2</sub> (0.075 g, 0.11 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) originally under dinitrogen, was saturated with CO. The solution became colorless, and within a few minutes, the conversion to *cis*-PtCl<sub>2</sub>(CO)<sub>2</sub>, through the transient formation of PtCl<sub>2</sub>(CO)(C<sub>6</sub>H<sub>10</sub>), was nearly quantitative, as shown by the IR spectrum.

**Reaction of PtCl<sub>2</sub>(CO)(C<sub>6</sub>H<sub>10</sub>) with HCl in Toluene.** A solution of PtCl<sub>2</sub>(CO)(C<sub>6</sub>H<sub>10</sub>) (0.208 g, 0.55 mmol) in toluene (5 mL) was saturated with dry HCl. An IR spectrum of the solution measured after 1 h of stirring at room temperature, showed a new band in the carbonyl stretching region at 2129 cm<sup>-1</sup> attributable to Pt<sub>2</sub>Cl<sub>4</sub>(CO)<sub>2</sub>. In addition, new bands at 2860 cm, 1260 s, and 1218 w cm<sup>-1</sup> were observed and were assigned to chlorocyclohexane

by comparison with the IR spectrum of a toluene solution of an authentic sample.<sup>16</sup> After 8 h, the IR band due to the carbonyl-olefin complex was absent, whereas the absorptions due to cyclohexyl chloride had increased in intensity.

Hydrochlorination of Cyclohexene in the Presence of  $PtCl_2(C_6H_{10})(CO)$  (or *cis*- $PtCl_2(CO)_2$ , or  $Pt_2Cl_4(CO)_2$ ). In a three-necked reactor, toluene (30 mL), cyclohexene (29.6 mmol, a 0.90 M solution), and a thin-wall sealed ampule containing  $PtCl_2(CO)(C_6H_{10})$  (0.050 g, 0.13 mmol) were introduced. The system was thermostatted at  $24.0 \pm 0.1$  °C and saturated with dry HCl. The solution was gently stirred to avoid premature breaking of the thin walled ampule. The solution was monitored by IR spectroscopy.<sup>17,18</sup> After 120 h, the IR spectrum of the solution showed the typical cyclohexene bands with practically unchanged intensity. The ampule was then broken and the following IR data were obtained 120 h after breaking the ampule: cyclohexene concentration about 0.29 M; cyclohexyl chloride concentration about 0.61 M, corresponding to a cyclohexyl chloride/Pt molar ratio of about 140. After 172 h from the ampule breaking, no cyclohexene bands were observed. In another experiment, a three-necked reactor was filled with toluene (25 mL), cyclohexene (9.87 mmol; a 0.38 M solution), and a thin-wall sealed ampule containing cis-PtCl<sub>2</sub>(CO)<sub>2</sub> (0.172 g, 0.53 mmol). The system was thermostatted at  $28.7 \pm 0.1$  °C and then saturated with dry HCl. After 80 h, the IR spectrum of the solution showed the typical cyclohexene bands with substantially unchanged in-

<sup>(15)</sup> Chromosorb column 102; 2 m.

<sup>(16)</sup> A spurious contribution to the 1260-cm<sup>-1</sup> band comes from silicone grease. (17) The cyclohexene band at 1138 cm<sup>-1</sup>  $(n = 31.5 \text{ M}^{-1} \text{ cm}^{-1})$  and the

<sup>(17)</sup> The cyclohexene band at  $1138 \text{ cm}^{-1}$  ( $n = 31.5 \text{ M}^{-1} \text{ cm}^{-1}$ ) and the cyclohexyl chloride band at  $1218 \text{ cm}^{-1}$  ( $n = 47.5 \text{ M}^{-1} \text{ cm}^{-1}$ ) were used to monitor the reaction.

<sup>(18)</sup> To avoid opening the reactor, IR samples from the solution were withdrawn by syringe through a silicone rubber plug.

Table IV. Conversion of Propylene to 2-Chloropropane in  $CDCl_3$ , T = 22 °C, with  $Pt_2Cl_4(CO)_2$  as Catalyst Precursor

time, h	conversion, molar ratio C <sub>3</sub> H <sub>7</sub> Cl/Pt
21	10
70	40
90	60
120	80

tensity. On the other hand, after 40 h from the ampule breakage, the conversion of cyclohexene to cyclohexyl chloride was nearly complete. Mass spectrometry showed that cyclohexyl chloride was the only chlorinated product present in the reaction mixture. Analogous results were obtained with Pt<sub>2</sub>Cl<sub>4</sub>(CO)<sub>2</sub>. On the contrary, a similar experiment carried out with PdCl<sub>2</sub> at 29 °C did not result in the production of  $C_6H_{11}Cl$  at any appreciable rate.

Hydrochlorination of Propylene Catalyzed by Pt<sub>2</sub>Cl<sub>4</sub>(CO)<sub>22</sub> Monitored by IR and <sup>1</sup>H NMR Spectra. In a reactor of approximate capacity of 150 mL, Pt<sub>2</sub>Cl<sub>4</sub>(CO)<sub>2</sub> (0.070 g, 0.12 mmol) was introduced together with CDCl<sub>3</sub> (3 mL) and 2,6-dichlorobenzaldehyde<sup>19</sup> (0.335 g, 1.91 mmol), to be used as internal standard for the <sup>1</sup>H NMR quantitative determinations. The mixture was saturated with propylene (P = 1 atm, T = 22 °C). An IR spectrum of the solution showed bands at 2125 cm<sup>-1</sup> ( $\nu_{CO}$ of  $PtCl_2(CO)(C_3H_6)$ ) and at 1645 cm<sup>-1</sup> ( $\nu_{C=C}$  of the uncomplexed olefin). The <sup>1</sup>H NMR spectrum showed broad signals at about  $\delta$  1.7 ppm, with a shoulder at about  $\delta$  2.1 ppm (CH<sub>3</sub> of uncomplexed and coordinated olefin, respectively); the resonance at about 4.9 (H2, H3, see Table II for the numbering scheme) and at about  $\delta$  5.9 ppm (H1) are attributed to the coalescence of uncomplexed and coordinated olefin signals. The solution was cooled at about -80 °C and dry HCl was introduced (P = 1 atm); the temperature was then allowed to rise and, after 21 h of stirring at 22 °C, the reactor was finally vented and the IR and <sup>1</sup>H NMR spectra of the solution were measured. The IR band at 2125 cm<sup>-1</sup> was unchanged in intensity, while the intensity of the band at 1645 cm<sup>-1</sup> had decreased. Two new bands, attributable to 2-chloropropane (by comparison with an authentic sample), were observed at 1375 w and 1260 s cm<sup>-1</sup>. The reaction was followed by IR and <sup>1</sup>H NMR spectra for some days (see Table IV). The sample withdrawn for the spectroscopic analysis was reintroduced into the reactor and the reaction conditions maintained as described above. The amount of 2-chloropropane produced was measured from the <sup>1</sup>H NMR integrated area of the methine septuplet of  $C_3H_7Cl$  with respect to the singlet due to the internal standard (2,6-dichlorobenzaldehyde).

In a preliminary test, carried out by the same procedure, the interaction between propylene and dry HCl in CDCl<sub>3</sub> (3 mL) was studied in the absence of  $Pt_2Cl_4(CO)_2$  and no addition product was formed. In contrast the presence of  $Pt_2Cl_4(CO)_2$  (1.2 mmol), in 3 mL of CDCl<sub>3</sub>, saturated at room temperature with propylene at ca. 1 atm (see above), gave 2.4 mmol of 2-chloropropane in 20 h. To verify that Pt(II) complexes do not catalyze 1-chloropropane isomerization, 1-chloropropane (0.25 mL, 3.5 mmol) and Pt<sub>2</sub>- $Cl_4(CO)_2$  were introduced (T = 20 °C) in a Schlenk tube together with  $\text{CDCl}_3$  (2 mL). No isomerization occurred over 50 h as shown by <sup>1</sup>H NMR spectra, not even in the presence of dry HCl (P about 1 atm).

Hydrochlorination of Cyclohexene-1,3,3- $d_3$  in the Presence of a Stoichiometric Amount of cis-PtCl<sub>2</sub>(CO)<sub>2</sub>. Degassed deuteriochloroform (0.8 mL), cis-PtCl<sub>2</sub>(CO)<sub>2</sub> (54 mg, 0.17 mmol) and cyclohexene-1,3,3- $d_3$  (16 mg, 0.19 mmol) were placed in a NMR tube. The solution was saturated with HCl at about -78 °C, and the tube was then spinned for 12 h at room temperature until all the olefin had reacted. NMR analysis showed that syn addition of HCl occurred to give 1. The proton attached to the chlorine-bearing carbon gave a doublet signal with J = 9 Hz and the remainder of the NMR spectrum was in accord with the data reported in the literature.<sup>20</sup> The ratio of 1/2 was 42/58, and none

Table V. Hydrochlorination of Norbornene Catalyzed by cis-PtCl<sub>2</sub>(CO)<sub>2</sub><sup>a</sup>

reacn time, min	norbornene, %	exo-2-chloro- bicyclo[2.2.1]heptane, %
25	57	43
40	38	62
55	18	82
70	7	93
85	5	95
100	1	99

<sup>a</sup> The product distribution was determined by GC with an OV-101 column. NMR and MS of exo-2-chlorobicyclo[2.2.1]heptane was identical in all respects with the authentic material.

of the anti addition product was formed (eq 4). When the experiment was repeated without the platinum complex, no reaction occurred after 12 h.



Hydrochlorination of Other Olefins in the Presence of cis-PtCl<sub>2</sub>(CO)<sub>2</sub> as the Catalyst Precursor. Reaction of 1-Decene with HCl. Gaseous HCl was bubbled through a benzene (6 mL) solution containing 1-decene (0.294 g, 2.10 mmol) and cis-PtCl<sub>2</sub>(CO)<sub>2</sub> (0.031 g, 0.10 mmol). After 192 h, GC analysis indicated a 66/34 molar ratio of product/reactant. The reaction mixture was passed through a short silica gel column, the filtrate was concentrated to remove benzene, and the resulting oil was subjected to short-path distillation, affording 0.226 g (61%) of chlorodecanes and 0.074 g (25%) of 1-decene. The proportion of 2-chlorodecanes to isomeric chlorodecanes was 83/17 (NMR determination). When the above experiment was repeated for 104 h in the absence of cis-PtCl<sub>2</sub>(CO)<sub>2</sub>, the ratio of 1-decene/2chlorodecane was 99/1.

Addition of HCl to cis-2-Decene. A mixture of cis-2-decene (0.087 g, 0.62 mmol) and cis-PtCl<sub>2</sub>(CO)<sub>2</sub> (0.010 g, 0.031 mmol) in benzene (2.0 mL) was stirred in a Schlenk tube under HCl, for 192 h at room temperature. The proportion of chlorodecanes to 1-decene was 91/9 (GC analysis). After removal of solvent, the resulting oil was subjected to silica gel chromatography, affording 2-chlorodecane and 3-chlorodecane in a 46/54 ratio (total yield 90%). A control experiment, i.e. without the platinum catalyst. gave 2-decene and chlorodecanes in a ratio of 89/11 after reaction for 260 h.

Addition of HCl to trans-2-Decene. Use of trans-2-decene instead of cis-2-decene as reactant resulted in the formation of chlorodecanes in 90% isolated yield, the ratio of 2-chlorodecanes/3-chlorodecanes being 42/58. The control experiment, i.e., without cis-PtCl<sub>2</sub>(CO)<sub>2</sub>, run for 192 h at room temperature, gave trans-2-decene/chlorinated products in a ratio of 89/11.

Reaction of trans-5-Decene with HCl. In a three-necked flask containing a reflux condenser, a stopper, and a gas inlet tube was placed benzene (6.0 mL), trans-5-decene (0.30 g, 2.14 mmol), and cis-PtCl<sub>2</sub>(CO)<sub>2</sub> (5.0 mg, 0.016 mmol). Hydrogen chloride was bubbled through the stirred solution for 92 h giving 5-chlorodecane/trans-5-decene in a 59/41 molar ratio. The ratio was 79/21 after 192 h. Workup as described above afforded pure 5-chlorodecane in 76% yield.

Reaction of Styrene with HCl. A mixture of styrene (0.34 g, 3.3 mmol) and cis-PtCl<sub>2</sub>(CO)<sub>2</sub> (5.0 mg, 0.016 mmol) in toluene (5 mL) was stirred under HCl for 24 h (Schlenk tube). Analysis by gas chromatography showed that 1-chloro-1-phenylethane and styrene were present in a molar ratio of 89/11. Workup by flash chromatography on silica gel afforded 0.352 g (77% yield) of the pure product (identification by comparison of NMR and MS with an authentic sample). Repetition of the experiment in the absence of the platinum catalyst afforded 1-chloro-1-phenylethane in a 55/45 ratio (to styrene).

Addition of HCl to Norbornene. A mixture of norbornene (0.070 g, 0.74 mmol) and cis-PtCl<sub>2</sub>(CO)<sub>2</sub> (0.012 g, 0.37 mmol) in

<sup>(19)</sup> A blank experiment showed that 2,6-dichlorobenzaldehyde was

<sup>(19)</sup> A biant experiment showed that 2,6 did hor oben 2aiden, de was unaffected under the experimental conditions.
(20) (a) Fahey, R. C.; Monahan, M. W. J. Chem. Soc., Chem. Commun.
1967, 936. (b) Fahey, R. C.; Monahan, M. W.; McPhersons, C. A. J. Am. Chem. Soc. 1970, 92, 2810. (c) Fahey, R. C.; Monahan, M. W.; McPhersons, C. A. J. Am. Chem. Soc. 1970, 92, 2816. (d) Fahey, R. C.; Monahan, M. W.; McPhersons, C. A. J. Am. Chem. Soc. 1970, 92, 2816. (d) Fahey, R. C.; Monahan, M. W.; McPhersons, C. A. J. Am. Chem. Soc. 1970, 92, 2816. (d) Fahey, R. C.; Monahan, M. W.; McPhersons, C. A. J. Am. Chem. Soc. 1970, 92, 2816. (d) Fahey, R. C.; Monahan, M. W.; McPhersons, C. A. J. Am. Chem. Soc. 1970, 92, 2816. (d) Fahey, R. C.; Monahan, M. W.; McPhersons, C. A. J. Am. Chem. Soc. 1970, 92, 2816. (d) Fahey, R. C.; Monahan, M. W.; McPhersons, C. A. J. Am. Chem. Soc. 1970, 92, 2816. (d) Fahey, R. C.; Monahan, M. W.; McPhersons, C. A. J. Am. Chem. Soc. 1970, 92, 2816. (d) Fahey, R. C.; Monahan, M. W.; McPhersons, C. A. J. Am. Chem. Soc. 1970, 92, 2816. (d) Fahey, R. C.; Monahan, M. W.; McPhersons, C. A. J. Am. Chem. Soc. 1970, 92, 2816. (d) Fahey, R. C.; Monahan, M. W.; McPhersons, C. A. J. Am. Chem. Soc. 1970, 92, 2816. (d) Fahey, R. C.; Monahan, M. W.; McPhersons, C. A. J. Am. Chem. Soc. 1970, 92, 2816. (d) Fahey, R. C.; Monahan, M. W.; McPhersons, C. A. J. Am. Chem. Soc. 1970, 92, 2816. (d) Fahey, R. C.; Monahan, M. W.; McPhersons, C. A. J. Am. Chem. Soc. 1971, 92, 9445. [d] Fahey, R. C.; Monahan, M. W.; McPhersons, C. A. J. Am. Chem. Soc. 1971, 92, 9445. [d] Fahey, R. C.; Monahan, M. W.; McPhersons, C. A. J. Am. Chem. Soc. 1971, 92, 9445. [d] Fahey, R. C.; Monahan, M. W.; McPhersons, C. A. J. Am. Chem. Soc. 1971, 92, 945. [d] Fahey, R. C.; Monahan, M. W.; McPhersons, C. A. J. Am. Chem. Soc. 1971, 92, 945. [d] Fahey, R. C.; Monahan, M. W.; McPhersons, C. A. J. Am. Chem. Soc. 1971, 92, 945. [d] Fahey, R. C.; Monahan, M. W.; McPhersons, C. A. J. Am. Chem. Soc. 1971, 94, 94, 94, 94, 94, 94, 94, 94, 94 Monahan, M. W.; McPhersons, C. A. J. Am. Chem. Soc. 1971, 93, 2445.

43

40

57

60

<sup>a</sup>See footnote of Table V.

115

130

toluene (2.5 mL) was stirred under HCl (Schlenk tube). The reaction mixture was monitored by GC and the results are presented in Table V. Workup after 85-100 min gave exo-2chlorobicyclo[2.2.1]heptane in 74% yield. In Table VI are listed the results for the uncatalyzed addition of HCl to norbornene in toluene (Schlenk tube).

### **Results and Discussion**

The formation of mixed carbonyl-olefin complexes of platinum(II) has been mentioned in the literature as early as 1870. Schützenberger<sup>21</sup> reported the formation of an ethylene-carbonyl complex by reacting the  $Pt_2Cl_4(CO)_2$ dimer with ethylene; however, the exact nature of this compound was not established and the present paper gives a contribution to the understanding of this early literature report. Also, Chalk<sup>22</sup> reported the formation in solution of carbonyl-olefin complexes (olefin = 1-hexene, 1-octene, styrene) by bubbling CO through solutions containing  $Pt_2Cl_4(olefin)_2$ ; the characterization was based on the presence of a carbonyl stretching vibration at about 2110 cm<sup>-1</sup>, accompanied by a second band at 2170 cm<sup>-1</sup>, presumably due to some cis-PtCl<sub>2</sub>(CO)<sub>2</sub> present in equilibrium (vide infra).<sup>23</sup> The results of the present paper definitely establish the existence of the mixed carbonyl-olefin complexes of platinum(II), and some of them were isolated and/or characterized by the usual spectroscopic techniques. (see Tables I-III). The cis-PtX<sub>2</sub>(olefin)(CO) complexes were prepared according to eq 5-7.24

cis-PtX<sub>2</sub>(CO)<sub>2</sub> + olefin  $\Rightarrow$  cis-PtX<sub>2</sub>(CO)(olefin) + CO

X = Cl, Br, olefin = cyclohexene;

X = Cl, olefin = cyclopentene

(5)

 $Pt_2Cl_4(CO)_2 + 2 \text{ olefin} \rightarrow 2cis-PtCl_2(CO)(\text{olefin})$ (6)

olefin = cyclohexene, ethylene, propylene

$$Pt_2Cl_4(C_2H_4)_2 + 2CO \rightarrow 2cis - PtCl_2(CO)(C_2H_4) \quad (7)$$

The mixed complexes are usually unstable in the presence of CO, equilibrium (5) being shifted to the left at room temperature and at atmospheric pressure of CO. Thus, when cis-PtX<sub>2</sub>(CO)<sub>2</sub> was used as starting material, good yields of the mixed complex were obtained by using an excess of the olefin and by removing CO; this method is therefore best applied to liquid olefins, such as cyclohexene and cyclopentene. With gaseous olefins (ethylene, propylene) the formation of the  $PtCl_2(CO)$  (olefin) complexes is best carried out according to eq 6, starting from the dimeric carbonyl complex  $Pt_2Cl_4(CO)_2$ . In the absence of CO, the mixed complexes appear to be stable; this is true, for a limited period of time, even for the products containing ethylene and propylene, i.e. gaseous olefins at room temperature. Decomposition of these products to form the dimers  $Pt_2Cl_4(olefin)_2$  or  $Pt_2Cl_4(CO)_2$  would clearly require dissociation of coordinated CO or olefin, which apparently is a relatively high-energy pathway. The dichloro- and dibromocarbonyl cyclohexene platinum(II) complexes,  $PtCl_2(CO)(C_6H_{10})$  and  $PtBr_2(CO)(C_6H_{10})$ , were isolated as cream-colored microcrystalline solids, sensitive to moisture, but indefinitely stable in the solid state under an inert atmosphere. The other complexes were characterized in solution by IR and NMR spectroscopy. The IR data are collected in Table I. The presence of a unique CO stretching vibration suggests the presence of only one geometrical isomer; the presence of two IR bands in the region of the Pt-X stretching vibrations allows the assignment of the cis geometry to the complex. Therefore the formation of the cis isomer from reaction 5 is to be expected. However, starting from the centrosymmetric chloride-bridged dimers<sup>25</sup>  $Pt_2Cl_4(CO)_2$  or  $Pt_2Cl_4(C_2H_4)_2$  (eqs 6 and 7), the kinetically controlled product should be the trans isomer, in view of the greater trans effect of both CO and olefin with respect to the chloride ligand. Nevertheless, only the cis isomer was always observed, by IR monitoring of the reacting solution, even when the reaction (6) was carried out at low temperature (about -26 °C) with a substoichiometric amount of cyclohexene, i.e., under conditions appropriately chosen to minimize isomerization processes. These results can be compared with others reported in the literature. The reactions between  $Pt_2X_4(PR_3)_2$  and olefins (olefin = ethylene, propylene, 1-heptene), have been extensively studied<sup>26</sup> and the trans isomers have been detected. They are in equilibrium with the dimeric precursor, and the free olefin (eq 8), and  $Pt_2X_4(PR_3)_2 + 2 \text{ olefin} \approx 2trans-PtX_2(PR_3)(\text{olefin})$  (8)

rapidly exchange the coordinated olefin and are converted to the cis isomer at room temperature at a rate that allows monitoring the reaction by the usual spectroscopic techniques. Further comparison can be made with the reactions between  $Pt_2X_4(CO)_2$  (X = Cl, Br, I) and CO (eq 9).

$$Pt_{2}X_{4}(CO)_{2} + 2CO \approx 2trans - PtX_{2}(CO)_{2}$$
(9)

In this case too, the trans isomers were observed and even isolated.<sup>5,27</sup> The chloro- and bromo trans complexes rapidly isomerize at room temperature to the more stable cis species (see eq 10), whereas the iodo complex, trans-

tra

$$ns-PtX_2(CO)_2 \rightleftharpoons cis-PtX_2(CO)_2$$
 (10)

$$X = Cl, Br$$

 $PtI_2(CO)_2$ , is more stable than the cis isomer. We believe that although their direct experimental observation failed, the trans-PtCl<sub>2</sub>(CO)(olefin) products are intermediates of both reactions 6 and 7, being converted to the more stable cis isomer by an even easier kinetic pathway than in the case of the dicarbonyl platinum(II) complexes. Again similar to the dicarbonyl systems, the cis-PtCl<sub>2</sub>(CO)(olefin) complexes would require a relatively high activation energy

<sup>(21) (</sup>a) Schützenberger, P. Bull. Soc. Chim. Fr. 1870, 14, 97. (b) Schützenberger, P. Compt. Rend. 1870, 70, 1287. (c) Schützenberger, P. Zentralblatt 1870, 438. (22) Chalk, A. J. Tetrahedron Lett. 1964, 2627.

<sup>(23)</sup> The dicarbonyl derivative cis-PtCl<sub>2</sub>(CO)<sub>2</sub> of  $C_{20}$  symmetry has two IR-active carbonyl stretching vibrations (A1 + E) at 2170 and 2126 cm<sup>-1</sup> in toluene (Belli Dell'Amico, D.; Calderazzo, F.; Dell'Amico, G. Gazz. Chim. Ital. 1977, 107, 101).

<sup>(24)</sup> No iodo-carbonyl complexes of platinum(II) could be obtained: attempts to form such compounds by reactions of type 5 or 6, X = I, failed

<sup>(25)</sup> The structure of  $Pt_2Cl_4(CO)_2$  is assumed to be the same as that established for Pt<sub>2</sub>I<sub>4</sub>(CO)<sub>2</sub>; in the case of compounds with general formula Pt<sub>2</sub>Cl<sub>4</sub>(olefin)<sub>2</sub>, the structure of the derivatives of cyclopentene and heptene are known (Bordner, J.; Wertz, D. W. Inorg. Chem. 1974, 13, 1639)

<sup>(26)</sup> Cross, R. J.; Davidson, M. F. J. Chem. Soc., Dalton Trans. 1987, 139, and references therein.

<sup>(27)</sup> Belli Dell'Amico, D.; Calderazzo, F.; Veracini, C. A.; Zandonă, N. Inorg. Chem. 1984, 23, 3030; 4781.

to be converted to the  $Pt_2X_4L_2$  (L = CO or olefin) complexes by a dissociation process, which explains their relative stability both in solution and in the solid state.

<sup>1</sup>H and <sup>13</sup>C NMR Data. The data of the mixed carbonyl-olefin complexes are presented in Tables II and III. It is worth pointing out that the NMR spectra of the complexes were measured for samples obtained in the absence of free olefin or carbon monoxide, in order to avoid erratic chemical shift values due to fast (on the NMR time scale) exchange between coordinated and dissolved ligand.<sup>28</sup> The dynamics of the exchange between the free and coordinated olefin have been qualitatively studied in the case of cyclohexene and propylene via <sup>1</sup>H NMR measurements at different temperatures. Usually, the platinum(II)-olefin complexes show a rapid exchange<sup>29</sup> in solution between free and coordinated olefin.

In the case of the cyclohexene complex, the exchange is slow on the NMR time scale. The NMR spectra of solutions containing  $PtCl_2(CO)(cyclohexene)$  and free cyclohexene in  $CD_2Cl_2$  at room temperature or in  $C_6D_6$  in the range 20-60 °C show the distinct signals of the two compounds. On the contrary, the system  $PtCl_2(CO)$  (propylene)/propylene in CDCl<sub>3</sub>, from room temperature to about -15 °C, appears to undergo a rapid exchange as the signals due to the olefinic protons coalesce (at about -15 °C the methyl signals of the free and coordinated olefin begin to separate, although they remain broad). The <sup>1</sup>H NMR spectra of the complexes show a small shift to lower field (except in the case of the ethylene complex) of the olefinic hydrogens upon coordination to the metal. As far as the platinum(II) complexes are concerned, the literature, usually but not always, reports<sup>29</sup> proton shifts to higher fields. As far as the <sup>13</sup>C NMR data are concerned, the olefinic carbon nuclei of the complexes gave resonances at higher fields than the free olefins (see Table III). The  $\Delta \delta$  ( $\delta$  free olefin –  $\delta$  complex) value is considered to be a measure of the  $\sigma$ - and  $\pi$ -contribution to the olefin-metal bond<sup>29-31</sup> while the  ${}^{1}J_{Pt-C}$  value is regarded as being a measure of the metal-olefin  $\sigma$ -interaction.<sup>32</sup> The  $J_{1^{38}Pt}{}^{13}C$ value for the mixed ethylene-carbonyl complex is intermediate between those reported<sup>31b</sup> for the anionic [Pt- $Cl_3(C_2H_4)$ <sup>-</sup> derivative (194 Hz) and for the cationic complex  $[Pt(Me)(PMe_2Ph)_2(C_2H_4)]^+$  (50 Hz). In the case of the halo-carbonyl derivatives it has been found<sup>5</sup> that the  $J_{199}$  Pt<sup>13</sup>C values decrease in the sequence Pt<sub>2</sub>X<sub>4</sub>(CO)<sub>2</sub> >  $[PtX_3(CO)]^- > cis-PtX_2(CO)_2 \ge trans-PtX_2(CO)_2$ , thus suggesting that the main factor involved in determining the coupling constant is the number of halide ligands per platinum. The ethylene complexes appear to follow the same trend, which may be taken as indicating a stronger  $\sigma$ -component to the Pt-ethylene bond in the sequence  $[PtCl_3(C_2H_4)]^- > PtX_2(CO)(C_2H_4)$ . It is further to be considered that the  $J_{186Pt-13C}$  value decreases on going from the chloro to the bromo derivative of the cyclohexene complexes  $PtX_2(CO)(C_6H_{10})$ ; this is also in agreement with what has been found earlier in several families of halo

carbonyl complexes<sup>5</sup> of platinum(II). Use can therefore be made of the same type of arguments, i.e. that the Ptolefin  $\sigma$ -bond becomes weaker in the sequence Cl > Br. In the case of a nonsymmetrical olefin, i.e. propylene (Table III), the  $\Delta\delta$  and  ${}^{1}J_{\text{Pt-c}}$  values of the unsubstituted olefin carbon atom (C1), are greater than those of the substituted carbon atom (C2) (see numbering scheme of Table III). That seems to usually be the case<sup>31a,32</sup> when the substituent is an electron-releasing or an aromatic group. In support of this are the results of some structural studies<sup>33</sup> on platinum(II) complexes with olefins of the type RCH=CH<sub>2</sub> (R = alkyl or aryl), showing that the unsubstituted olefin carbon atom is usually closer to the metal. Steric hindrance may be responsible for these findings.

Reactions of  $PtCl_2(CO)(C_6H_{10})$  with HCl. We reasoned that an examination of the behavior of the mixed carbonyl-olefin complex PtCl<sub>2</sub>(CO)C<sub>6</sub>H<sub>10</sub> with dry hydrogen chloride in an organic sovlent could be of interest in connection with the general problem of reactivity change induced by metal coordination. The carbonyl-cyclohexene platinum(II) derivative was chosen as a model compound to test the general features of this system in comparison with the literature data concerning the hydrochlorination of cyclohexene to cyclohexyl chloride.<sup>20,34</sup> Addition of HCl to coordinated cyclohexene was regarded, in fact, to be the most likely reaction pattern, although others could not be excluded in principle (olefinic substitution, oxidative addition). In toluene as solvent, the platinum(II) carbonyl olefin complex is almost quantitatively converted to the dimeric chloro carbonyl while coordinated cyclohexene is converted to cyclohexyl chloride (eq 11).

$$2PtCl_2(CO)(C_6H_{10}) + 2HCl \rightarrow Pt_2Cl_4(CO)_2 + 2C_6H_{11}Cl$$
(11)

In view of the conflicting reports<sup>20,34</sup> in the literature concerning the hydrochlorination of cyclohexene, comparative experiments were carried out in order to verify whether the platinum complex was involved in the observed formation of cyclohexyl chloride. As a matter of fact, the possibility existed that cyclohexene could have been expelled from the coordination sphere of the metal followed by the addition of HCl to uncoordinated cyclohexene (eqs 12 and 13). However, contrary to an earlier

$$PtCl_2(CO)(C_6H_{10}) \rightarrow \frac{1}{2}Pt_2Cl_4(CO)_2 + C_6H_{10}$$
 (12)

$$C_6H_{10} + HCl \rightarrow C_6H_{11}Cl$$
(13)

report,<sup>34</sup> we found that the hydrochlorination of cyclohexene does not substantially proceed at room temperature in toluene. Thus, as it had already been shown that the addition of cyclohexene to the platinum dimer (see the Experimental Section) occurs rapidly, the requirements were met for the platinum(II)-catalyzed hydrochlorination of cyclohexene (eq 14).

$$PtCl_{2}(CO)(C_{6}H_{10}) + HCl \rightarrow \frac{1}{2}Pt_{2}Cl_{4}(CO)_{2} + C_{6}H_{11}Cl$$
(14a)

$${}^{1/2}Pt_{2}Cl_{4}(CO)_{2} + C_{6}H_{10} \rightarrow PtCl_{2}(CO)(C_{6}H_{10}) (14b)$$

$$C_6H_{10} + HCl \xrightarrow{(10)} C_6H_{11}Cl$$
(14)

Catalytic Hydrochlorination of Olefins. Hydrochlorination of cyclohexene occurs at room temperature in the presence of  $PtCl_2(CO)(C_6H_{10})$  as catalyst precursor.

<sup>(28)</sup> It has recently been shown (ref 7) that the <sup>13</sup>C NMR spectra of about 90% <sup>13</sup>C-enriched solutions containing both AuCl(CO) and Au-Br(CO), measured under a carbon monoxide atmosphere, give separate resonances at about -50 °C; at room temperature the resonances collapse to a single one due to fast exchange of coordinated and dissolved CO.

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At 24 °C, in toluene as solvent, about 140 mol of C<sub>6</sub>H<sub>11</sub>Cl was produced per mole of platinum in 120 h. Under the same conditions, in the absence of the platinum complex, cyclohexene and HCl gave no significant reaction. Similar results were obtained by using  $Pt_2Cl_4(CO)_2$  or cis-PtCl<sub>2</sub>- $(CO)_2$  as catalyst precursors. In order to ascertain the stereochemistry of the reaction, cyclohexene- $1,3,3-d_3$  was hydrochlorinated in the presence of cis-PtCl<sub>2</sub>(CO)<sub>2</sub>. This reaction was run with a stoichiometric amount of the platinum complex in order to increase the rate and thus minimize deuterium scrambling over long times. At room temperature, all the olefin had substantially reacted; the solution contained the products shown in eq 4. It is worth noting that these results again differ considerably from those obtained in glacial acetic acid as solvent<sup>20b,c</sup> in the hydrochlorination of the same deuterated substrate, the main difference being that no anti product 3 was observed in the platinum-catalyzed reaction. The prevailing for-



mation of the syn adduct suggests that addition of the HCl components occurs on the same side of the carbon-carbon double bond coordinated to platinum. Platinum-catalyzed hydrochlorination was also verified with 1-decene, cis-2decene, trans-2-decene, trans-5-decene, styrene, and norbornene. In all cases, an increase of the reaction rate was observed with platinum(II): the increase was high (cyclohexene, 1-decene) or moderate (propylene, cis-2-decene, trans-2-decene, styrene, norbornene). For example, styrene and norbornene (Tables V and VI) undergo HCl addition without  $PtCl_2(CO)_2$ , but the reaction is promoted by the metal complex. In the case of nonsymmetrical olefins, such as propylene, 1-decene, and styrene, the product of hydrochlorination arising from the chlorine addition to the less-substituted carbon atom (Markovnikov rule) was found, namely, 2-chloropropane, 2-chlorodecane and 1-(chlorophenyl)ethane, respectively, as if protonation of the unsaturated carbon atom, leading to the more stable carbocation, were the primary attack.

In conclusion, this paper has shown that soluble platinum(II) carbonyl derivatives are able to promote the hydrochlorination of several olefins. The reaction is regioselective in the case of terminal olefins giving the Markovnikov product. While the addition of HBr or HI to olefins are well known to occur at room temperature, HCl usually requires higher temperatures<sup>35</sup> or the presence of a catalyst, generally a Lewis acid, such as  $AlCl_3$  or FeCl<sub>3</sub>.<sup>36,37</sup>

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# Synthesis and Reactivity of $(\eta^5-C_5H_5)Os(N)(CH_2SiMe_3)_2$ , the First Cyclopentadienyl–Nitrido Transition-Metal Complex

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The first cyclopentadienyl-nitrido complexes of a transition metal were prepared by the reactions between  $[NBu^{n}_{4}][Os(N)Cl_{2}(CH_{2}SiMe_{3})_{2}] \text{ and either } NaC_{5}H_{5} \text{ or } LiC_{5}Me_{5}. \text{ The complexes } (\eta^{5}-C_{5}H_{5})Os(N)(CH_{2}SiMe_{3})_{2}$ and  $(\eta^5-C_5Me_5)Os(N)(CH_2SiMe_3)_2$  were characterized by spectroscopic techniques and elemental analysis. They are soluble in organic solvents, volatile, and stable to air and water. The nitrogen atom in  $(\eta^5$ - $C_5H_5$ )Os(N)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> is a "soft" Lewis base. It binds reversibly to BF<sub>3</sub> in solution, forming a 1:1 adduct. With silver(I) salts, a 2:1 adduct is formed. The silver-bridged complex  $[[(\eta^5-C_5H_5)Os(CH_2SiMe_3)_2]_2(\mu-C_5H_5)Os(CH_2SiMe_3)Os(CH_2SiMe_3)_2]_2(\mu-C_5H_5)Os(CH_2SiMe_3)Os(CH_2S$ with silver(1) sails, a 2:1 adduct is formed. The silver-bridged complex  $[[(\eta^5-C_5H_5)Os(CH_2SiMe_3)_2]_2[\mu^5-NAgN)]$ NAgN) $[BF_4]$  was isolated in good yield from the reaction between  $(\eta^5-C_5H_5)Os(N)(CH_2SiMe_3)_2$  and AgBF<sub>4</sub> and was structurally characterized. Crystal data for Os<sub>2</sub>AgSi<sub>4</sub>F<sub>4</sub>N<sub>2</sub>C<sub>26</sub>BH<sub>54</sub> are a = 15.348 (3) Å, b = 18.272(3) Å, c = 14.114 (2) Å,  $\beta = 91.76$  (1)°, V = 3956 (2) Å<sup>3</sup>,  $\rho = 1.817$  g/cm<sup>3</sup>,  $\mu = 70.56$  cm<sup>-1</sup>, space group =  $P2_1/c$  ( $C^5_{2h}$ ), and Z = 4. Final agreement factors are R = 0.065 and  $R_w = 0.078$ . The nitrido complex is displaced from silver by PPh<sub>3</sub> but not by Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>. Alkylation of the nitrogen atom in ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Os(N)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> and CH<sub>3</sub>OSO<sub>2</sub>CF<sub>3</sub> produced an alkylimido complex, [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Os(NMe)-(CH<sub>2</sub>SiMe<sub>2</sub>).]USO<sub>2</sub>CF<sub>1</sub>  $(CH_2SiMe_3)_2$ [OSO<sub>2</sub>CF<sub>3</sub>].

### Introduction

Cyclopentadienylmetal compounds are known for all of the transition metals. The ligand is versatile and can coordinate through one carbon atom to form a simple  $\sigma$ bond to the metal, through three carbon atoms to form an allyl-type metal complex ( $\eta^3$  coordination), or with all five carbon atoms ( $\eta^5$  coordination). The  $\sigma$ -donor and  $\pi$ -acceptor abilities of the ligand stabilize transition-metal complexes in low oxidation states. Complexes containing both carbonyl and cyclopentadienyl ligands have been studied for many years.<sup>1</sup>

The cyclopentadienyl ligand is also compatible with metals in higher oxidation states. Many cyclopentadienyl

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