# Competition between Carbon Monoxide and Alkenes in Chloro Complexes of Platinum(II)

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Alkenes (cyclohexene; 1-octene) and dienes (cyclooctadiene, COD; norbornadiene, NBD) react with *cis*-PtCl$_2$(CO)$_2$, leading, respectively, to partial and complete displacement of coordinated carbon monoxide. Equilibrium constants at 21 °C in 1,2-dichloroethane are $(2.4 \pm 0.5) \times 10^{-3}$ and $(2.8 \pm 0.4) \times 10^{-2}$ for cyclohexene and 1-octene, respectively. Thermodynamic data correspond to $\Delta H°$ (kJ mol$^{-}$) and $\Delta S°$ (J mol$^{-1}$ K$^{-1}$) = 30 ± 4 and 51 ± 15 for cyclohexene and 36 ± 2 and 95 ± 8 for 1-octene.
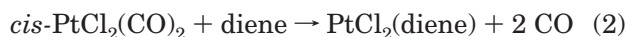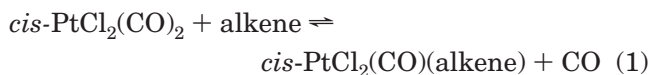
## Introduction

Carbon monoxide and alkenes in combination are used in organic syntheses of industrial relevance promoted by transition metals, such as hydroformylation and related reactions[1] and CO/olefin co-polymerization.[2] In this connection, the study of the competitive coordination of CO and alkene is important in order to clarify the role of the metal center and to rationalize the observed trends of catalytic efficiency. Some late transition metals (Ni, Pd), with their appropriate ligand environment, catalyze the alternating copolymerization of alkenes and CO.[2] On the other hand, it is well established that olefin polymerization, as catalyzed by both early[3] and late transition metals,[4] can be negatively affected by CO. As a matter of fact, carbon monoxide has often been used to quench the polymerization process,[5] the preferred coordination of CO being presumably responsible for this behavior. The nature of the metal−olefin bond is a subject of great interest,[6] particularly in comparison with the competitive metal−CO interaction. For early transition metals, quantitative studies show that alkenes are unable to displace coordinated carbon monoxide.[7] However, alkenes containing electron-withdrawing substituents (tetracyanoethylene, fumaronitrile) give complete displacement of carbon monoxide from VCp$_2$(CO).[7d]

The relative affinity of alkenes and CO for late transition metal cations with electronic configuration d$^{10}$ or d$^8$ [gold(I),[8] platinum(II),[9] palladium(II),[10] and rhodium(I)[11]] has been studied in our laboratories and elsewhere. For instance, while electron-poor olefins are not able to displace CO in complexes of platinum(II) and gold(I), equilibria are observed with unsubstituded alkenes.[8,9]

We now report the thermodynamic parameters of the equilibria corresponding to the substitution of one carbonyl ligand in *cis*-PtCl$_2$(CO)$_2$ by cyclohexene or 1-octene (eq 1). On the other hand, we have observed that *cis*-PtCl$_2$(CO)$_2$ reacts with some dienes (1,5-cyclooctadiene, norbornadiene) with fast and complete CO substitution (eq 2).

$$cis\text{-PtCl}_2(\text{CO})_2 + \text{alkene} \rightleftharpoons$$
$$cis\text{-PtCl}_2(\text{CO})(\text{alkene}) + \text{CO} \quad (1)$$

$$cis\text{-PtCl}_2(\text{CO})_2 + \text{diene} \rightarrow \text{PtCl}_2(\text{diene}) + 2 \text{ CO} \quad (2)$$

## Results

As early as 1870, Schützenberger reported the isolation of a product analyzing as PtCl$_2$(CO)(C$_2$H$_4$).[12] However, only recently have complexes of composition PtX$_2$(CO)(alkene), X = Cl, Br, been fully characterized,[9] good yields being obtained by treating the dinuclear

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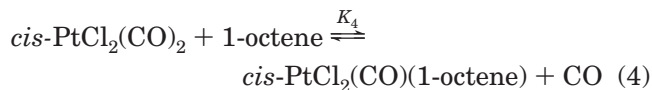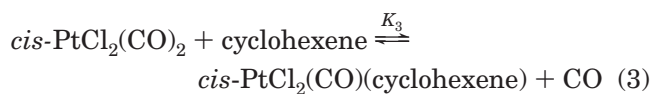(11) Cramer, R. *J. Am. Chem. Soc.* **1964**, *86*, 217.

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halide-bridged $Pt_2X_4(CO)_2$ with the olefin or by reacting *cis*-$PtX_2(CO)_2$ with an excess of the olefin under constant removal of the displaced CO. This route has now been used for the preparation of the cyclohexene (**1a**) and 1-octene (**1b**) derivatives. No evidence of formation of $PtCl_2(alkene)_2$ and/or $Pt_2Cl_4(alkene)_2$ was found, even after a prolonged treatment in vacuo. On the other hand, the $PtCl_2(alkene)_2$ derivatives are described in the literature as being labile.[13–16]

The cyclohexene derivative **1a** has already been described,[9] while *cis*-$PtCl_2(CO)(1\text{-octene})$, **1b**, is a new compound. By monitoring the reaction of *cis*-$PtCl_2(CO)_2$ with 1-octene, the growth of a unique new band in the carbonyl stretching region was attributed to the formation of **1b**. Accordingly, the IR spectrum of the product in the solid state shows two bands at 345 and 320 $cm^{-1}$ due to the Pt–Cl stretching vibrations (400–200 $cm^{-1}$).[17] Bands at 2121 and 1509 $cm^{-1}$ are assigned to the C≡O and C=C stretching vibrations, respectively, of the coordinated ligands, the latter corresponding to a bathochromic shift of about 130 $cm^{-1}$ with respect to the free olefin, in agreement with the literature data.[18] In the $^{195}Pt$ NMR spectrum ($C_6D_6$) only one sharp resonance at −3708 ppm was observed, as expected for a single geometrical isomer. The other NMR data (see the Experimental Section) are consistent with the structural assignment.

The platinum dicarbonyl *cis*-$PtCl_2(CO)_2$ reacts with the dienes COD and NBD under CO with prompt and complete carbonyl substitution (see eq 2), as proved by gas-volumetric[19a] measurements, yielding platinum derivatives of the type $PtCl_2(diene)$.[19b–d]

As the alkene/*cis*-$PtCl_2(CO)_2$ systems produce equilibria (eq 1), we could compare the relative binding affinity of CO and alkenes for platinum(II) and obtain the thermodynamic parameters of substitution reactions 3 and 4. These reactions were checked by IR spectroscopy in 1,2-dichloroethane; see Figures 1 and 2. In the carbonyl stretching region the intensity of the two bands of *cis*-$PtCl_2(CO)_2$ decreases and a new absorption due to the olefin-carbonyl complex at 2117 $cm^{-1}$ (**1a**) or at 2124 $cm^{-1}$ (**1b**) appears.

$$cis\text{-}PtCl_2(CO)_2 + \text{cyclohexene} \overset{K_3}{\rightleftharpoons}$$
$$cis\text{-}PtCl_2(CO)(\text{cyclohexene}) + CO \quad (3)$$

$$cis\text{-}PtCl_2(CO)_2 + 1\text{-octene} \overset{K_4}{\rightleftharpoons}$$
$$cis\text{-}PtCl_2(CO)(1\text{-octene}) + CO \quad (4)$$

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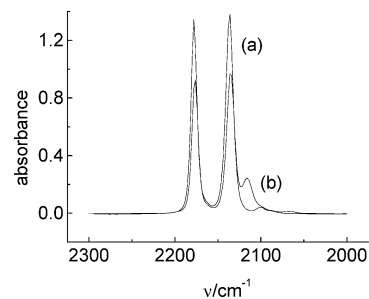


**Figure 1.** IR study of the *cis*-$PtCl_2(CO)_2$/cyclohexene equilibrium in 1,2-dichloroethane (eq 3) at 21 °C. [cyclohexene] = 2.468 M, [CO] = $5.5 \times 10^{-3}$ M. (a) *cis*-$PtCl_2(CO)_2$, (b) equilibrium mixture.



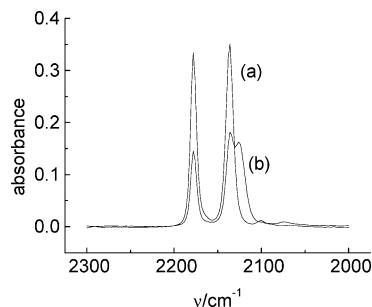**Figure 2.** IR study of the *cis*-$PtCl_2(CO)_2$/1-octene equilibrium in 1,2-dichloroethane (eq 4) at 21 °C. [1-octene] = 0.255 M, [CO] = $5.5 \times 10^{-3}$ M. (a) *cis*-$PtCl_2(CO)_2$, (b) equilibrium mixture.

*K* values were determined through the equilibrium concentrations in solution according to eq 5, the subscript *e* standing for equilibrium.

$$K = \frac{[PtCl_2(CO)(\text{alkene})]_e[CO]_e}{[PtCl_2(CO)_2]_e[\text{alkene}]_e} \quad (5)$$

According to the Lambert–Beer law, the concentration of the two complexes in equilibrium are expressed by the initial ($A_0$) and equilibrium ($A_\infty$) absorbance of the band at 2178 $cm^{-1}$ (see eqs 6 and 7), where the subscript *i* means "initial", $\epsilon$ is the extinction coefficient, and *d* is the cell thickness.

$$[PtCl_2(CO)_2]_i = [PtCl_2(CO)_2]_e +$$
$$[PtCl_2(CO)(\text{alkene})]_e = \frac{A_0}{\epsilon d} \quad (6a)$$

$$[PtCl_2(CO)_2]_e = \frac{A_\infty}{\epsilon d} \quad (6b)$$

$$[PtCl_2(CO)(\text{alkene})]_e = \frac{A_0 - A_\infty}{\epsilon d} \quad (6c)$$

$$K_{eq} = \frac{A_0 - A_\infty}{A_\infty} \frac{[CO]_e}{[\text{alkene}]_e} \quad (7)$$

Equilibrium constants (see eqs 3 and 4) at 21 °C correspond to $(2.4 \pm 0.5) \times 10^{-3}$ and $(2.8 \pm 0.4) \times 10^{-2}$, respectively.

Experiments were carried out at different temperatures, in the range 288–313 K, and monitored via UV spectroscopy (400–200 nm) in order to determine the thermodynamic parameters. The UV technique allowed
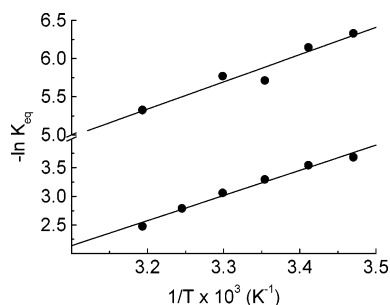
**Figure 3.** Plots of $-\ln K$ vs $1/T$ for the reactions of *cis*-PtCl$_2$(CO)$_2$ with cyclohexene (eq 3, upper plot) and with 1-octene (eq 4) in 1,2-dichloroethane.

us to operate in a cell supplied with a sidearm and a stopcock, to maintain the reagents and the equilibrium mixture under a controlled atmosphere.

The equilibrium concentrations of the metal complexes were obtained by using eqs 8–10, where $\epsilon_1$ and $\epsilon_2$ are the extinction coefficients of *cis*-PtCl$_2$(CO)$_2$ and *cis*-PtCl$_2$(CO)(alkene), respectively. The plots of $-\ln K$ vs $1/T$ are reported in Figure 3.

$$[PtCl_2(CO)_2]_i = \frac{A_0}{d\epsilon_1} \qquad (8)$$

$$A_\infty = (\epsilon_1[PtCl_2(CO)_2]_e + \epsilon_2[PtCl_2(CO)(alkene)]_e)d \quad (9)$$

$$[PtCl_2(CO)_2]_e + [PtCl_2(CO)(alkene)]_e = [PtCl_2(CO)_2]_i \qquad (10)$$

$$K = \frac{\epsilon_1(A_\infty - A_0)}{(\epsilon_2 A_0 - \epsilon_1 A_\infty)} \frac{[CO]_e}{[alkene]_e} \qquad (11)$$

The $\Delta H°$ (kJ mol$^{-1}$) and $\Delta S°$ (J mol$^{-1}$ K$^{-1}$) values of the reactions, as obtained by the slopes and the intercepts of the plots, correspond to 30 ± 4 and 51 ± 15 for cyclohexene and 36 ± 2 and 95 ± 8 for 1-octene. According to these data, the interpolated $K$ values at 21 °C are $2.2 \times 10^{-3}$ and $3.7 \times 10^{-2}$ for cyclohexene and 1-octene, respectively, in good agreement with the values obtained by the IR experiments.
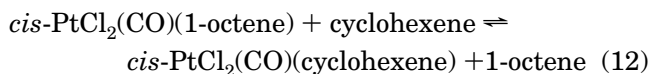
The displacements of CO by cyclohexene and 1-octene are slightly endothermic, with similar values of $\Delta H°$. The slight preference for 1-octene with respect to cyclohexene appears to depend mainly on entropy. If we assume that solvation enthalpies of reagents and products are similar, the positive $\Delta H°$ associated with these reactions can be considered to mainly arise from the rupture of the Pt−CO bond and the formation of the Pt−alkene bond. Thus, the former is about 30 kJ mol$^{-1}$ stronger than the latter.

The complete displacement of coordinated CO by COD and NBD (see eq 3) presumably arises from a favorable entropy change, two CO molecules being transferred to the gas phase.

For the sake of comparison it is appropriate to recall that quantitative CO/alkene competition studies on palladium(II) [10] complexes have been reported for [Pd-(phen)R(CO)]$^+$/C$_2$H$_4$, phen =1,10-phenanthroline. Carbon monoxide is largely preferred with respect to ethylene, the equilibrium constant at 298 K, R = Me, for the displacement of coordinated CO being $(2 \pm 1) \times 10^{-4}$. The results of our studies point out that CO is

favored, with respect to simple alkenes, also for uncharged square-planar complexes of platinum(II).

From the thermodynamic parameters of reactions 3 and 4, and by summing eq 3 and the reverse of eq 4, the equilibrium constant of reaction 12, corresponding to about $10^{-1}$ at 21 °C, was calculated.

*cis*-PtCl$_2$(CO)(1-octene) + cyclohexene $\rightleftharpoons$
  *cis*-PtCl$_2$(CO)(cyclohexene) +1-octene  (12)

The competition of differently substituted alkenes for the coordination sphere of platinum(II) has been the subject of several studies,[20] showing that metal complexes are stabilized by olefins with electron-donating groups.[21] Spectroscopic[22a] and theoretical[22b] studies confirm the dominant contribution of $\sigma$-donation in the formation of the Pt(II)−olefin bond.

For the systems here reported, a negligible difference in the bond dissociation enthalpy of the two Pt−alkene bonds results, as expected in view of the similar electronic features of the two olefins. In this connection, it is interesting to note that enthalpy of hydrogenation is similar ($-128.3$ kJ mol$^{-1}$ for 1-octene and $-117.9$ kJ mol$^{-1}$ for cyclohexene).

## Experimental Section

**General Comments.** Potassium tetrachloroplatinate(II), K$_2$[PtCl$_4$], was purchased (Aldrich) or loaned (Chimet S.p.A., I-52041 Badia al Pino, Arezzo). Research grade CO was purchased from Rivoira and purified by passing it in sequence through concentrated H$_2$SO$_4$ and a concentrated solution of KOH. 1,2-Dichloroethane was freshly distilled from P$_4$O$_{10}$ under a dinitrogen atmosphere. Toluene and heptane were distilled from sodium. Olefins were refluxed over sodium and distilled before use. Benzene-$d_6$ (99.9%) was purchased from Aldrich and distilled after refluxing over sodium.

$^1$H, $^{13}$C, and $^{195}$Pt NMR spectra were recorded with a Varian Gemini 200 MHz spectrometer. The experiments were carried out at room temperature (about 22 °C), and chemical shifts were measured in ppm ($\delta$) and referenced to external TMS via residual solvent peaks for $^1$H and $^{13}$C and to aqueous (D$_2$O) hexachloroplatinic acid for $^{195}$Pt. IR spectra were obtained by using Perkin-Elmer spectrophotometers (model 283 B or FTIR1725X equipped with IR Data Manager software). In the range 4000−600 and 600−200 cm$^{-1}$, cells equipped with CaF$_2$ (or KBr) and polyethylene windows, respectively, were used. Spectrophotometric measurements were carried out by using 1.00 or 0.10 cm quartz Suprasil cells, with a Perkin-Elmer Lambda9 spectrophotometer equipped with a cell whose temperature was kept constant by the use of a thermostat. Cells were equipped with a side inlet supplied with a stopcock to allow all the operations to be carried out under CO.

Elemental analyses (C, H, N) were performed by Laboratorio di Microanalisi, Dipartimento di Scienze Farmaceutiche, Università di Pisa, with a C. Erba model 1106 elemental analyzer.

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All reactions and manipulations were carried out under a controlled (dinitrogen, or carbon monoxide, as specified) atmosphere. The gas-volumetric measurements were carried out according to the method described by Calderazzo and Cotton.[19a]

The compounds cis-Pt(CO)$_2$Cl$_2$[23] ($\lambda_{max}$ 255, $\epsilon_{max}$ 4831 M$^{-1}$ cm$^{-1}$), PtCl$_2$(COD),[19] and cis-[PtCl$_2$(CO)(1-cyclohexene)][9a] (**1a**, $\lambda_{max}$ 261 nm, $\epsilon_{max}$ 4839 M$^{-1}$ cm$^{-1}$) were prepared according to the literature. PtCl$_2$(NBD) was prepared either according to the literature[19c] or by an original method described below.

**Synthesis of PtCl$_2$(NBD).** An aqueous solution of K$_2$[PtCl$_4$] (6.0 mmol) was introduced in a 250 mL flask. NBD (3.2 mL, 30 mmol) in 1,2-dichloroethane and a catalytic amount of [NBu$_4$]Cl (1.0 mmol) were added. The biphasic reaction mixture was refluxed for 5 h. The substantially colorless aqueous layer was separated at room temperature and discarded. Heptane (25 mL) was added to the organic colorless layer, and the resulting suspension was filtered. The solid product was washed with heptane (3 × 10 mL) and dried in vacuo (1.34 g, 62.3% yield). Anal. Calcd for C$_7$H$_8$Cl$_2$Pt: C, 23.5; H, 2.3. Found: C, 23.3; H, 2.2. IR (Nujol, KBr windows): 1440w, 1310s, 1254w, 1242w, 1226m, 1180m, 1115w, 1030w, 992w, 980m, 951m, 936w, 906w, 882w, 848m, 832w, 774m, 678w and 612 cm$^{-1}$. $^1$H NMR (C$_2$D$_2$Cl$_4$): 5.3 (m, 4 H, $^2J_{Pt-H}$ 68 Hz); 4.3 (m, 2 H); 1.6 (s, 2 H) ppm. $^{195}$Pt NMR (CH$_2$Cl$_2$ + CD$_2$Cl$_2$): −3117 ppm.

**Synthesis of cis-[PtCl$_2$(CO)(1-octene)], 1b.** Under carbon monoxide, to a solution of cis-PtCl$_2$(CO)$_2$ (502 mg, 1.56 mmol) in 1,2-dichloroethane (200 mL) was added dropwise 1-octene up to an olefin/Pt molar ratio of 60. The reaction was IR monitored through the bands at 2178 and 2136 cm$^{-1}$ due to cis-PtCl$_2$(CO)$_2$ and at 2124 cm$^{-1}$, due to the substitution product. After consumption of the starting platinum complex, the solution was evaporated to dryness and the solid residue was treated with heptane (25 mL). The suspension was filtered, and the colorless product was dried in vacuo and sealed in vials under N$_2$ (360 mg, 57% yield). Due to its air sensitivity, reliable elemental analyses could not be obtained. However, the substance is spectroscopically pure. IR, Nujol, KBr windows: $\nu_{CO}$ 2121 cm$^{-1}$; 1,2-dichloroethane, CaF$_2$ windows: $\nu_{CO}$ 2124 cm$^{-1}$. UV−vis (1,2-dichloroethane, quartz cells): $\lambda_{max}$ 261 nm ($\epsilon$ = 4225 M$^{-1}$ cm$^{-1}$). $^1$H NMR (C$_6$D$_6$) (see structure below): 3.75 (d, H$^b$, 1 H, $^3J_{H-H}$ 14.6 Hz, $^2J_{Pt-H}$ 53.5 Hz); 4.35 (d, H$^a$, 1 H, $^3J_{H-H}$ 7.3 Hz, $^2J_{Pt-H}$ 68.9 Hz); 5.35 (m,H$^c$, 1 H); 1.61 (m, 2 H) ppm and a group of multiplets at about 1 ppm (m, 11 H). $^{13}$C NMR (C$_6$D$_6$): 152.1 (CO, $^1J_{Pt-C}$ 1635 Hz); 112.5 (CH$_2$=CH, $^1J_{Pt-C}$ 104 Hz); 76.9 (CH$_2$=CH, $^1J_{Pt-C}$ 123 Hz); 37.8; 31.6; 29.7; 28.8; 22.8; 14.3 ppm. $^{195}$Pt NMR (C$_6$D$_6$): −3708 ppm.
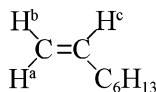


**Synthesis of PtCl$_2$(COD) from cis-PtCl$_2$(CO)$_2$.** By operating in a gas-volumetric apparatus,[19a] 20 mL of toluene was saturated at room temperature with CO, and COD (0.203 mL, 1.65 mmol) and a fragile flame-sealed glass ampule containing cis-PtCl$_2$(CO)$_2$ (267 mg, 0.83 mmol) were then introduced. At 21.2 °C (total pressure 752 Torr), the fragile ampule was mechanically broken and the evolved gas was measured. At the end of the reaction (about 1 h) a volume of CO corresponding to a CO/Pt molar ratio of 1.94 had been evolved. The content of the reactor was evaporated to dryness, and the residue was added of 1,2-dichloroethane (40 mL). The suspension was filtered, the filtrate was evaporated to dryness, and heptane (10 mL) was added to the residue. The suspension

was filtered, and the solid was washed with heptane (3 × 5 mL). The solid was dried in vacuo (101 mg) and identified as PtCl$_2$(COD) by comparison with an authentic sample (IR in Nujol, $^1$H NMR, and $^{195}$Pt NMR [peak at −3329 ppm] in 1,2-dichloroethane). An analogous experiment was carried out in 1,2-dichloroethane, where the product is soluble, with similar results. No carbonylation of PtCl$_2$(COD) was observed at 20 °C in toluene at atmospheric pressure.

**Synthesis of PtCl$_2$(NBD) from cis-PtCl$_2$(CO)$_2$.** In a gas-volumetric apparatus,[19a] 20 mL of 1,2-dichloroethane was saturated at room temperature with CO, and NBD (0.074 mL, 0.69 mmol) and a fragile glass ampule containing cis-PtCl$_2$-(CO)$_2$ (147 mg, 0.46 mmol) were then introduced. At 21.7 °C (total pressure 772 Torr), the ampule was broken and the evolved gas was measured. At the end of the reaction (about 1 h) a volume of CO corresponding to a CO/Pt molar ratio of 1.94 was measured. No carbonyl bands (IR) were observed in the supernatant solution. In the $^{195}$Pt NMR spectrum of the solution (with some C$_6$D$_6$ added), only one signal at −3117 ppm due to PtCl$_2$(NBD) was present. The carbonylation of PtCl$_2$-(NBD), monitored gas-volumetrically, did not proceed at 22 °C in 1,2-dichloroethane, at atmospheric pressure of CO.

**Equilibrium Constants and Thermodynamic Parameters Determination. IR Measurements.** The CO/olefin substitutions on cis-PtCl$_2$(CO)$_2$ were studied by IR spectroscopy in the CO stretching region (2200−2000 cm$^{-1}$) at atmospheric pressure. After addition of the olefin under CO, the reaction mixture was monitored by IR until equilibrium was reached. The final and initial absorbance of the $\nu_{CO}$ band of cis-Pt(CO)$_2$Cl$_2$ at 2178 cm$^{-1}$ was used for the evaluation of the equilibrium constants according to eq 5. In each spectrum the solvent contribution was subtracted, the olefin and CO contribution being negligible. The measurements were performed at $P_{TOT}$ = 1 atm and $T$ = 21 °C by using a Specac P/N 21000 variable-temperature cell, consisting of a 0.1 mm cell equipped with CaF$_2$ windows inserted in a container supplied with KBr windows. In all cases the equilibrium constants were approximated to the concentration ratio according to eq 5. The olefin was always used in large excess, and its equilibrium concentration was considered to coincide with the initial one. The CO concentration in saturated 1,2-dichloroethane at 1 atm (5.5 × 10$^{-3}$ M)[24a] was calculated after taking into account the solvent vapor pressure.[24b]

In a typical experiment, a solution of cis-PtCl$_2$(CO)$_2$ (∼10$^{-2}$ M) was prepared in a Schlenk tube under CO. Olefin solutions of known concentration were stored under CO. A 1.0 mL sample of the platinum-containing solution was added to 1.0 mL of the olefin solution, and the mixture was stirred (3 h) under CO and then used to fill the IR cell, which was kept at the same temperature as the reaction mixture.

Equilibrium constants for reactions 3 and 4 at 21 °C have been obtained as the averaged values of five independent experiments carried out by using alkene concentrations in the range 0.9−2.4 M (cyclohexene) and (0.8−1.3) × 10$^{-1}$ M (1-octene).

**UV Measurements.** For equilibria 3 and 4, a series of experiments at different temperatures were carried out and studied by UV spectroscopy in the range 400−200 nm. In each spectrum the solvent and olefin contribution was subtracted. Corrections for the variation of solvent density with temperature were not applied. The CO concentration was calculated as in the case of the IR experiments,[24] and its value (5.5 × 10$^{-3}$ M) was assumed to be constant in the experimental temperature range. This approximation is justified by the low value of the solution enthalpy of CO (0.79 kJ mol$^{-1}$ in CCl$_4$ in the range 283−318 K[25]) and by the fact that the partial

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pressure of CO was essentially constant in the course of the experiment. The carbonylation experiments were carried out in a cell kept at the desired temperature by the use of a thermostat, with the gas phase maintained at room temperature ($\sim$20 °C). Equilibrium constants were calculated through eq 11 by using the absorbance values at 253 nm ($\epsilon_{PtCl_2(CO)(cyclohexene)}$ = 4108 $M^{-1}$ $cm^{-1}$; $\epsilon_{PtCl_2(CO)(1\text{-octene})}$ = 3675 $M^{-1}$ $cm^{-1}$; $\epsilon_{PtCl_2(CO)_2}$ = 4771 $M^{-1}$ $cm^{-1}$).

In a typical experiment a solution of *cis*-PtCl$_2$(CO)$_2$ [concentration in the range (4−9) × 10$^{-3}$ M] was prepared in a Schlenk tube under CO. An olefin solution of known concentration (0.4−2.5 M) was prepared in 10 mL flasks stored in a large Schlenk tube under CO. Then 2.0 mL of the platinum solution was added to 2.0 mL of the olefin solution, and the mixture was stirred (3 h) under CO. The cell, once filled with the reaction mixture under CO at 293 K, was sealed, and spectra at variable temperature were recorded after the system had reached the equilibrium conditions.

**Supporting Information Available:** Table reporting the *K* values, calculated according to eq 11. Figures reporting UV spectra of the *cis*-PtCl$_2$(CO)$_2$/alkene equilibrium in 1,2-dichloroethane (eqs 3 and 4) at different temperatures.

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