Organometallics **2006,** *25,* 4913−4916

A Kinetic Study of the Competition between Carbon Monoxide and Alkenes in Chloro Complexes of Platinum(II)

Daniela Belli Dell'Amico*, Riccardo Bini, Fausto Calderazzo, Laura Carbonaro,
Luca Labella, and Anna Vitullo

*Dipartimento di Chimica e Chimica Industriale, University of Pisa,
via Risorgimento 35, I-56126 Pisa, Italy*

Received June 6, 2006

*Summary: Alkenes (cyclohexene; 1-octene) react with cis-$PtCl_2(CO)_2$, leading to cis-$PtCl_2(CO)$(alkene) (**1a**, alkene = cyclohexene; **1b**, alkene = 1-octene). The substitution kinetics to **1a** and **1b** in 1,2-dichloroethane in the temperature range 273−308 K have the following second-order rate constants at 298 K, respectively: cyclohexene, $(0.94 \pm 0.07) \times 10^{-3}$ M^{-1} s^{-1}; 1-octene, $(2.33 \pm 0.05) \times 10^{-2}$ M^{-1} s^{-1}. The activation parameters are $\Delta H^* = 37 \pm 4$ kJ mol^{-1}, $\Delta S^* = -180 \pm 10$ J K^{-1} mol^{-1} for the reaction affording **1a** and $\Delta H^* = 36.5 \pm 0.7$ kJ mol^{-1}, $\Delta S^* = -154 \pm 2$ J K^{-1} mol^{-1} for the reaction to **1b**. The large negative values of the activation entropies are consistent with an associative mechanism. The reverse reactions proceed with a similar rate constant.*

Introduction

Ligand substitution kinetics of square-planar complexes containing d^8 metal centers have been widely studied,[1] especially for platinum(II), which, being characterized by moderate reaction rates, can be monitored by conventional methods.[2] However, to the best of our knowledge, kinetic studies concerning competitive CO/alkene substitution reactions are not available in the literature, although they are certainly relevant to processes involving both carbon monoxide and olefins, such as hydroformylation and alkene/CO copolymerization.[3] On the other hand, the kinetics of exchange of carbon monoxide have been reported for Pt(II), Pd(II), Rh(I), and Ir(I),[4] and a certain number of data concerning olefin exchange,[5a−d] or the displacement of an olefin by another olefin,[5f,g] are available in the literature.

Olefin exchange in $[MCl_3(C_2H_4)]^-$ (M = Pd, Pt) shows that the second-order rate constant at 298 K (k_2^{298}) in THF as solvent is 9×10^2 and 1.3×10^3 M^{-1} s^{-1} for platinum and palladium, respectively.[5c] The CO exchange in $[MCl_3(CO)]^-$ is considerably slower, k_2^{298} values being, in $CDCl_3$ as solvent, 3.4×10^{-3} and 5.70×10^{-1} M^{-1} s^{-1} for platinum and palladium, respectively.[4a] It is interesting to note that ethene exchange is quite fast for both platinum and palladium, while the reactions involving CO are rather slow, especially for platinum, which is more than 100 times slower than palladium. As these reactions proceed by an associative path, the energy of a pentacoordinated activated complex with respect to the starting compound should play the major role in determining the rate constant. In this connection, it is to be noted that platinum(II) adopts pentacoordination in some alkene or carbonyl complexes normally in the presence of a bidentate nitrogen donor ligand.[6,7]

In earlier papers we have reported that *cis*-$PtCl_2(CO)_2$[8] undergoes CO substitution by cyclohexene or 1-octene (see eq 1) through equilibrium reactions favoring the dicarbonyl.[9] Here we report the kinetic studies carried out on the same systems operating in 1,2-dichloroethane in the temperature range 273−308 K.

$$cis\text{-}PtCl_2(CO)_2 + \text{alkene} \rightleftharpoons cis\text{-}PtCl_2(CO)(\text{alkene}) + CO \qquad (1)$$

Earlier data have established spectroscopically that only the *cis* geometrical isomer is obtained through reaction 1.[9] This has been confirmed crystallographically in the case of alkene = cycloheptene.[9b]

Experimental Section

General Procedures. K_2PtCl_4 was purchased from Aldrich Chemical Co. or from Chimet S.p.A., Badia al Pino, Arezzo, Italy. Carbon monoxide (research grade) was purchased from Rivoira and purified by passing it through concentrated sulfuric acid and KOH. 1,2-Dichloroethane was freshly distilled from P_4O_{10} under a dinitrogen atmosphere. Toluene and heptane were distilled from sodium. Benzene-d_6 (99.9%) was purchased from Aldrich and distilled after treatment with activated molecular sieves.

IR spectra were obtained with a Perkin-Elmer 1725X Fourier transform spectrophotometer with an IR Data Manager station.

---

[1] Wilkins, R. G. *Kinetics and Mechanism of Reactions of Transition Metal Complexes*, 2nd ed.; VCH: Weinheim, 1991.

[2] Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions. A Study of Metal Complexes in Solution*, 2nd ed.; Wiley: New York, 1967.

[3] (a) Pino, P.; Piacenti, F.; Bianchi, M. *Reactions of Carbon Monoxide and Hydrogen with Olefinic Substrates: The Hydroformylation (Oxo) Reaction.* In *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P., Eds.; J. Wiley: New York 1977; Vol. 2. (b) van Leeuwen, P. N. W. M.; Claver C. *Rhodium Catalysed Hydroformylation*; Kluwer: Dordrecht, 2000. (c) Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663. (d) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc*. **1996**, *118*, 4746. (e) Consiglio, G. In *Late Transition Metal Polymerization Catalysis*; Wiley-VCH: Weinheim, 2003; pp 279−305.

[4] (a) Olsson, A.; Roodt, A.; Bojczuk, M.; Heaton, B. T.; Elding, L. I. *J. Chem. Soc., Dalton Trans*. **1994**, 3723. (b) Churlaud, R.; Frey, U.; Metz, F.; Merbach, A. E. *Inorg. Chem*. **2000**, *39*, 304.

[5] (a) Cramer, R. *Inorg. Chem*. **1965**, *4*, 445. (b) Natile, G.; Maresca, L.; Cattalini, L. *J. Chem. Soc., Dalton Trans.* **1977**, 651. (c) Olsson, A.; Kofod, P. *Inorg. Chem*. **1992**, *31*, 183. (d) Plutino, M. R.; Otto, S.; Roodt, A.; Elding, L. I. *Inorg. Chem*. **1999**, *38*, 1233. (e) Otto, S.; Samuleev, P. V.; Polyakov, V. A.; Ryabov, A. D.; Elding, L. I. *Dalton Trans.* **2004**, 3662. (f) Hupp, S. S.; Dahlgren, G. *Inorg. Chem*. **1976**, *15*, 2349. (g) Miya, S.; Kashiwabara, K.; Saito, K. *Inorg. Chem*. **1980**, *19*, 98.

[6] Albano, V. G.; Natile, G.; Panunzi, A. *Coord. Chem. Rev*. **1994**, *133*, 67.

[7] De Felice, V.; De Renzi, A.; Ferrara, M. L.; Panunzi, A. *J. Organomet. Chem.* **1996**, *513*, 97.

[8] Bagnoli, F.; Belli Dell'Amico, D.; Calderazzo, F.; Englert, U.; Marchetti, F.; Herberich, G. E.; Pasqualetti, N.; Ramello, S. *J. Chem. Soc., Dalton Trans*. **1996**, 4317.

[9] (a) Alper, H.; Huang, Y.; Belli Dell'Amico, D.; Calderazzo, F.; Pasqualetti, N.; Veracini, C. A. *Organometallics* **1991**, *10*, 1665. (b) Belli Dell'Amico, D.; Calderazzo, F.; Pasqualetti, N.; Maichle-Mössmer, C.; Strähle, J.; Wurst, K *Organometallics* **1994**, *13*, 1582. (c) Belli Dell'Amico, D.; Bini, R.; Calderazzo, F.; Carbonaro, L.; Labella, L.; Vitullo, A. *Organometallics* **2005**, *24*, 4427.

10.1021/om060499r CCC: $33.50

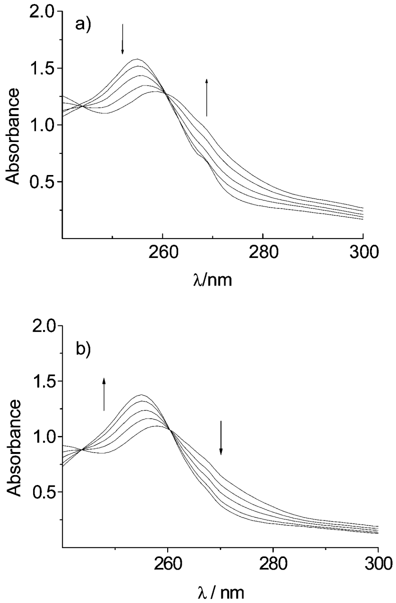


Figure 1. (a) UV−vis spectra of the reaction of *cis*-$PtCl_2(CO)_2$ (~1 × 10^{-4} M) with cyclohexene (~0.7 M), in 1,2-dichloroethane at 25.0 ± 0.2 °C, under a dinitrogen atmosphere. Following the arrows: *cis*-$PtCl_2(CO)_2$ and spectra recorded 45, 180, 1080, and 3900 s after mixing the reagents. (b) Spectra for the reaction of *cis*-$PtCl_2$(CO)(cyclohexene) (~1 × 10^{-4} M) with CO (5.5 × 10^{-3} M in 1,2-dichloroethane at 25.0 °C under a CO atmosphere. Following the arrows: *cis*-$PtCl_2$(CO)(cyclohexene) and spectra recorded 60, 180, 270, 480, and 1140 s after mixing the reagents.

Spectrophotometric and kinetic measurements were carried out by using 1.00 or 0.10 cm quartz Suprasil cells, on a Perkin-Elmer Lambda9 spectrophotometer equipped with a cell compartment maintained at constant temperature (±0.2 °C).

All reactions and manipulations were carried out under a dinitrogen atmosphere using Schlenk tube techniques. *cis*-$PtCl_2(CO)_2$,[8] *cis*-$PtCl_2$(CO)(cyclohexene), **1a**,[9a,b] and *cis*-$PtCl_2$(CO)(1-octene), **1b**,[9c] were prepared as previously described. Because of the high sensitivity of the platinum(II) carbonyls, extreme care was devoted to avoiding moisture traces, especially when dilute solutions were used.

Kinetics Measurements. All glassware was thoroughly dried prior to use. The spectrophotometric measurements were carried out in quartz cells, 1 cm thick, of about 5 mL capacity, supplied with a stopcock for their use under a controlled atmosphere. A freshly prepared 1,2-dichloroethane solution of *cis*-$PtCl_2(CO)_2$ of known concentration (between 2 × 10^{-4} and 5 × 10^{-4} M) was mixed with a solution of the olefin (between 2 × 10^{-2} and 5 × 10^{-1} M) in the quartz cell under a dinitrogen atmosphere. The reaction was monitored by UV−vis spectroscopy at the wavelength of the largest change of absorbance, i.e., between 265 and 275 nm. For the reverse reaction, solutions of complexes **1a**,**b** (ca. (2−5) × 10^{-4} M) were similarly prepared in 1,2-dichloroethane under a dinitrogen atmosphere. An aliquot of such a solution (ca. 0.2 mL, corresponding to an amount ranging from 0.4 × 10^{-4} to 1 × 10^{-4} mmol of **1a** or **1b**) was introduced into the quartz cell. The required amount (about 2.5 mL) of 1,2-dichloroethane saturated with CO at atmospheric pressure (1 mL contains about 5 × 10^{-3} mmol of CO[10a] under our conditions, taking into account the vapor pressure of the solvent[10b]) was added under CO. Identical kinetic curves were obtained either when the cell was closed with its Teflon stopcock or when it was connected to a 500 mL CO reservoir. Kinetic runs

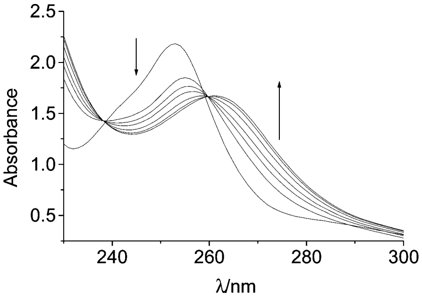


Figure 2. UV−vis spectra of the reaction of *cis*-$PtCl_2(CO)_2$ (~1 × 10^{-4} M) with 1-octene (~5 × 10^{-3} M) in 1,2-dichloroethane at 25.0 ± 0.2 °C, under a dinitrogen atmosphere. Following the arrows: spectrum of *cis*-$PtCl_2(CO)_2$ and spectra recorded 75, 150, 240, 330, 420, and 600 s after mixing the reagents.

were also conducted by mixing, under a CO atmosphere, solutions of *cis*-$PtCl_2$(CO)(1-octene) and saturated solutions of CO containing an excess of olefin, i.e., under pseudo-first-order conditions for both the forward and reverse reactions. Good first-order kinetic curves were normally obtained for both the forward and the reverse reactions, which were quantified by nonlinear least-squares fitting of the absorbance versus time plots to the equation $A = A_\infty + (A_0 - A_\infty)\exp(-k_{obs}t)$, where A, A_∞, and A_0 are absorbances at time t_∞ and 0, respectively. Satisfactory first-order dependence was normally observed for at least 6 half-lives. The analysis of data was accomplished with the nonlinear least-squares fitting program OriginLab 5.0. The reported errors correspond to one standard deviation.

Results

Pure *cis*-$PtCl_2$(CO)(alkene), **1a**,**b**, were obtained by reacting *cis*-$PtCl_2(CO)_2$ with excess olefin and by pumping off the produced CO. The olefin complex *cis*-$PtCl_2$(CO)(alkene), alkene = cyclohexene, 1-octene, dissolved in 1,2-dichloroethane saturated with CO at room temperature, was completely converted into *cis*-$PtCl_2(CO)_2$ in a few minutes. The IR spectra of the resulting solution, recorded ca. 1 h after mixing the reagents, confirmed the formation of *cis*-$PtCl_2(CO)_2$, as monitored by the ν_{CO} bands at 2178 and 2136 cm^{-1}.

For the kinetic studies reactions 2 and 3 were monitored by UV−vis spectroscopy (Figures 1 and 2) in 1,2-dichloroethane as solvent, and the forward reactions were initiated under dinitrogen ($T = 25.0$ °C) by mixing the appropriate volumes of

$$cis\text{-}PtCl_2(CO)_2 + \text{cyclohexene} \underset{k_{CO}}{\overset{k_{alk}}{\rightleftharpoons}} \underset{\mathbf{1a}}{cis\text{-}PtCl_2(CO)(\text{cyclohexene})} + CO \quad (2)$$

$$cis\text{-}PtCl_2(CO)_2 + \text{1-octene} \underset{k_{CO}}{\overset{k_{alk}}{\rightleftharpoons}} \underset{\mathbf{1b}}{cis\text{-}PtCl_2(CO)(\text{1-octene})} + CO \quad (3)$$

cis-$PtCl_2(CO)_2$ and olefin solutions, under pseudo-first-order conditions (high excess of olefin), directly in the quartz cell. After addition of the olefin, the intensity of the maximum at 255 nm ($\epsilon = 4831$ M^{-1} cm^{-1}), due to *cis*-$PtCl_2(CO)_2$, started to decrease and a new band at 260 ($\epsilon = 4839$ M^{-1} cm^{-1}) or 262 nm ($\epsilon = 4225$ M^{-1} cm^{-1}) was observed, due to the formation of **1a** or **1b**, respectively. For both reactions the presence of isosbestic points (at about 240 and 260 nm) suggests that two absorbing species dominate in solution. In both cases, the reverse sequence of the spectra recorded in the carbonylation

---

[10] (a) Lühring, P.; Schumpe, A. *J. Chem.-Eng. Data* **1989**, *34*, 250. (b) *Handbook of Chemistry and Physics*, 82nd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 2001−2002; pp 6−72.

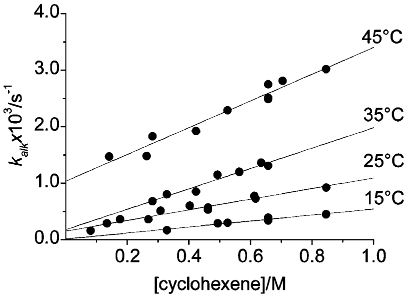


Figure 3. Observed rate constant k_{alk} of reaction 2 vs cyclohexene concentration in 1,2-dichloroethane at different temperatures.

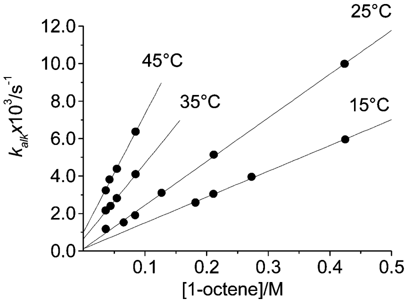


Figure 4. Observed rate constant k_{alk} of reaction 3 vs 1-octene concentration in 1,2-dichloroethane at different temperatures.

of the olefin complexes (shown in Figure 1b for reaction 2) confirms the reversible nature of the processes.

The processes were studied at different olefin concentrations. The kinetic traces, recorded at the suitable wavelength under pseudo first-order conditions, after exclusion of the first few data points, can be described by single exponentials with rate constants k_{alk}.

Figures 3 and 4 report plots of k_{alk} versus the olefin concentration at different temperatures for the direct reactions 2 and 3, respectively. Linear dependences were obtained up to the highest olefin concentrations.

These findings are in agreement with the accepted scheme for ligand substitution in square-planar complexes, as for the rate law of eq 4.

$$k_{\mathrm{alk}} = k_{\mathrm{I}} + k_{\mathrm{II}}[\mathrm{alkene}] \tag{4}$$

The second-order rate constant k_{II} refers to the olefin-dependent pathway, while k_{I} may include contributions related to (a) the reverse reaction, (b) the solvent-dependent substitution pathway, and (c) concurrent decomposition reactions. In our case the intercept values are usually small, the contribution of these paths appearing not to be relevant, and the error is fairly large relative to their magnitude. The relatively high k_{I} values at the highest temperatures are probably due to a decomposition reaction.

As reported in Table 1 and Figures 3 and 4, the temperature dependence of the forward reaction was studied between 15 and 45 °C. The overall activation parameters were calculated from Eyring plots (Figure 5) and correspond to $\Delta H^* = 37 \pm 4$ kJ mol^{-1}, $\Delta S^* = -180 \pm 10$ J K^{-1} mol^{-1} for reaction 2 and $\Delta H^* = 36.5 \pm 0.7$ kJ mol^{-1}, $\Delta S^* = -154 \pm 2$ J K^{-1} mol^{-1} for reaction 3. The large negative values of the activation entropies strongly support an associative mechanism. Thus, the activated complex must be characterized by well-formed Pt−alkene and Pt−CO bonds.

Table 1. Temperature Dependence of k_{I} and k_{II} for the Substitution Reaction of CO by Alkene in *cis*-PtCl$_2$(CO)$_2$ Affording the Complexes 1a,b (eqs 2 and 3) in 1,2-Dichloroethane

	T/°C	$10^2 \times k_{\mathrm{II}}$/M^{-1} s^{-1}	$10^2 \times k_{\mathrm{I}}$ /s^{-1}
reaction 2	15.0	0.053 ± 0.006	0.001 ± 0.003
	25.0	0.094 ± 0.007	0.015 ± 0.003
	35.0	0.18 ± 0.02	0.018 ± 0.009
	45.0	0.24 ± 0.02	0.10 ± 0.01
reaction 3	15.0	1.38 ± 0.03	0.01 ± 0.01
	25.0	2.33 ± 0.05	0.01 ± 0.01
	35.0	4.0 ± 0.1	0.06 ± 0.01
	45.0	6.3 ± 0.3	0.1 ± 0.02

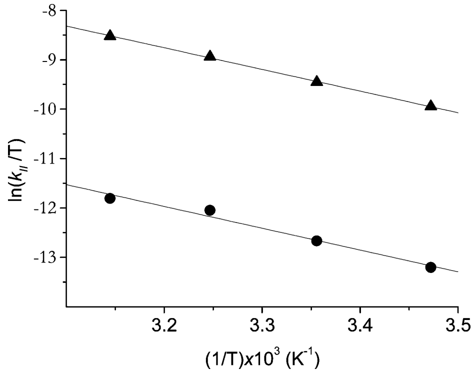


Figure 5. Eyring plots for the forward reactions 2 and 3 carried out in 1,2-dichloroethane at $p = 1$ atm. Solid circles for reaction 2 and triangles for reaction 3 at the following temperatures (±0.2): 15.0; 25.0; 35.0; 45.0 °C.

The reaction may proceed through one step with synchronous bond formation and bond breaking or, alternatively, with a two-step mechanism and a five-coordinate intermediate (Scheme 1). In the latter case, by applying the steady-state approximation and neglecting the intercepts as discussed above, the expressions 5 and 6 for the pseudo-first-order kinetic constants of the forward (k_{alk}) and the reverse (k_{CO}) reactions, respectively, can be derived.

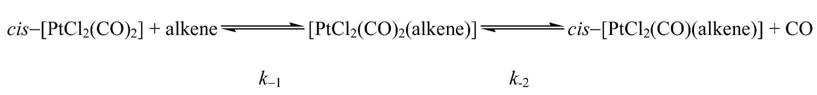
Although we have no spectroscopic or kinetic evidence for the formation of a reaction intermediate, we cannot exclude its presence in a low concentration, as required by the steady-state approximation. For this reason we propose the following scheme (Scheme 1) and the corresponding eqs 5 and 6.

$$k_{\mathrm{alk}} = \frac{k_1 k_2}{k_{-1} + k_2}[\mathrm{olefin}] \tag{5}$$

$$k_{\mathrm{CO}} = \frac{k_{-1} k_{-2}}{k_{-1} + k_2}[\mathrm{CO}] \tag{6}$$

The reverse reactions were studied under pseudo-first-order conditions, the concentration of dissolved carbon monoxide

Scheme 1



$$cis\text{-}[\mathrm{PtCl_2(CO)_2}] + \text{alkene} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{PtCl_2(CO)_2(alkene)}] \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} cis\text{-}[\mathrm{PtCl_2(CO)(alkene)}] + \mathrm{CO}$$

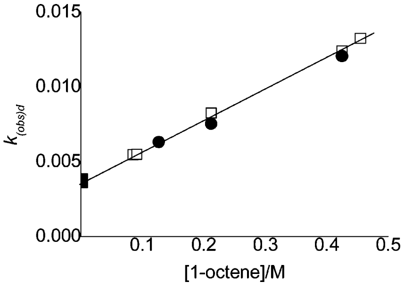


Figure 6. Plot of k_{obsd} vs 1-octene concentration, for the reactions carried out under CO (p = 1 atm; [CO] = 5.5×10^{-3} M) between (a) *cis*-$PtCl_2(CO)_2$ (~1×10^{-4} M) and 1-octene, solid circles, ●; (b) *cis*-$PtCl_2$(CO)(1-octene) (~1×10^{-4} M) and CO in the presence of 1-octene, open squares, □; and in the absence of 1-octene (rectangle). Solvent is 1,2-dichloroethane, $T = 25.0 \pm 0.2$ °C.

being 5.5×10^{-3} M,[10] about 40-fold greater than that of the metal complex. The pseudo-first-order rate constant for the disappearance of the olefin complex was determined from a one-exponential plot of the absorbance versus time up to 80−90% conversion of the reagent with respect to the equilibrium concentration. Data fitting for at least three independent kinetic runs gave a mean value of $k_{CO} = (3.5 \pm 0.2) \times 10^{-3}$ s^{-1} for reaction 2 and $k_{CO} = (3.6 \pm 0.2) \times 10^{-3}$ s^{-1} for reaction 3.

Kinetic runs for the reverse reaction 3 were also carried out in the presence of an excess olefin over the metal complex, under CO at atmospheric pressure at 25.0 °C. The kinetics were largely controlled by one exponential. A very small drift of the absorbance at longer reaction times, likely depending on some side reactions, was observed in the reaction profile only by increasing the concentration of the olefin. By fitting the data of the first part of the reaction to one exponential, the k_{obsd} were determined. Under these conditions, the rate constant is a combination of the forward and reverse reaction constants, $k_{obs} = k_{alk} + k_{CO}$. It is linearly dependent on the concentration of olefin, as shown in Figure 6.

The intercept, $(3.6 \pm 0.1) \times 10^{-3}$ M^{-1} s^{-1}, satisfactorily matches the value of the rate constant for the reaction carried out in the absence of olefin (see above). The slope of $(2.06 \pm 0.05) \times 10^{-2}$ M^{-1} s^{-1} is in good agreement with the result obtained for reaction 3 followed under a dinitrogen atmosphere.

It can be noted that the ratios $\{k_{alk}/[\text{alkene}]\}/\{k_{CO}/[\text{CO}]\}$ give the equilibrium constants of eq 2 and 3 [$K_2 = (1.5 \pm 0.2) \times 10^{-3}$ and $K_3 = (3.6 \pm 0.3) \times 10^{-2}$ at 25 °C], in good agreement with the data previously reported (calculated from $\Delta G°$ at T = 25 °C: $K_2 = 2.5 \times 10^{-3}$, $K_3 = 4.5 \times 10^{-2}$).[9c]

As discussed in the Introduction, the second-order rate constant of the L exchange for the substrates $[PtCl_3L]^-$ is reported to be about 10^{-3} M^{-1} s^{-1} for L = CO[4a] and about 10^3 M^{-1} s^{-1} for L = C_2H_4,[5c] the large difference being related to the differences in both activation parameters, ΔH^* and ΔS^*, acting in the same direction. Our results show that the CO substitution by a simple olefin in *cis*-$PtCl_2(CO)_2$ proceeds with a second-order rate constant (10^{-2}−10^{-3} M^{-1} s^{-1}) that depends on the nature of the olefin, as expected for an associative process, the terminal olefin 1-octene substituting CO about 10 times faster than the cyclic C_6H_{10}. This difference has to be ascribed to the different activation entropy of the two processes, the terminal olefin showing a less negative value. It is to be noted that the two reverse reactions proceed, probably by a fortuitous combination of factors, essentially with the same rate constant.

Acknowledgment. The authors wish to thank the Ministero dell' Istruzione, dell' Università e della Ricerca (MIUR), Programmi di Ricerca Scientifica di Rilevante Interesse Nazionale, Cofinanziamento 2004−2005, and the COST ACTION D17/003 of the European Community for promoting this scientific activity. Thanks are due to CRCC (Consorzio Interuniversitario Reattività Chimica e Catalisi) for a postgraduate fellowship to R.B.

OM060499R