Kinetics of Carbon Monoxide Exchange in Chloro and Bromo Carbonyl Complexes of Palladium(II) and Platinum(II)‡

Anders Olsson,[a] **Andreas Roodt,**[*,†] **Maria Bojczuk,**[b] **Brian T. Heaton**[*,b] **and Lars I. Elding**[*,a]
[a] *Inorganic Chemistry 1, Chemical Center, University of Lund, PO Box 124, S-221 00 Lund, Sweden*
[b] *Department of Chemistry, University of Liverpool, PO Box 147, Liverpool L69 3BX, UK*

Carbonyl exchange between $[MX_3(^{13}CO)]^-$ (MX = PdCl, PtCl or PtBr) and ^{12}CO has been studied by IR and ^{13}C NMR spectroscopies as a function of temperature. The exchange is first-order in both CO and complex concentration, and the activation entropies are negative, suggesting an associative reaction mechanism. There is a small solvent effect, but no chloride dependence. Activation parameters and rate constants, in the order $\Delta H^{\ddagger}$/kJ mol^{-1}, $\Delta S^{\ddagger}$/J K^{-1} mol^{-1}, k_{ex}^{298}/dm^3 mol^{-1} s^{-1}, are for $[PdCl_3(CO)]^-$ 60 ± 8, −47 ± 30, 0.57 ± 0.07; for $[PtCl_3(CO)]^-$ 60 ± 7, −91 ± 22, (3.3 ± 0.3) × 10^{-3} and for $[PtBr_3(CO)]^-$ 49 ± 6, −104 ± 19, (6.0 + 0.2) × 10^{-2} (95% confidence interval). This is three to six orders of magnitude slower than ethene exchange in analogous ethene halide complexes.

Carbonyl exchange in transition-metal complexes has been an area of great interest since the early 1960s,[1] but the attention has never really included the square-planar carbonyl halide complexes of the platinum metals. To our knowledge the only report is the observation made by Wojcicki and Basolo[2] that carbonyl exchange in $[Pt_2(\mu\text{-}Cl)_2Cl_2(CO)_2]$ is complete in less than 2 min and thus faster than could be measured by the methods available. Here we present a kinetic study of carbonyl exchange in $[PdCl_3(CO)]^-$ and $[PtX_3(CO)]^-$ (X = Cl or Br) using both IR and NMR spectroscopies. The work is a continuation of previous studies[3] on ethene exchange in analogous ethene halide complexes of palladium and platinum,[3] and of the electronic structures of these complexes.[4]

Experimental

Chemicals and Solutions.—$CDCl_3$ (Janssen, 99.6% D) was dried over activated molecular sieves. Acetone, tetrahydrofuran (thf), CH_2Cl_2 and cyclohexanone were distilled under nitrogen from an appropriate drying agent prior to use. The compounds $[NBu^n_4][MX_3(CO)]$ (MX = PdCl, PtCl, PtBr or PtI) were prepared from $[NBu^n_4]_2[M_2(\mu\text{-}X)_2X_4]$ and CO(g) enriched to > 90% in ^{13}C (MSD Isotopes or Aldrich) according to literature methods.[5]

NMR Measurements.—Carbon-13 NMR spectra were collected at 75.429 MHz on a Varian Unity 300 spectrometer. Solutions were prepared by weighing the sample and $CDCl_3$ into the NMR tube. Concentrations were in the range 5–20 mmol dm^{-3} for $[NBu^n_4][PdCl_3(CO)]$ and 20–100 mmol dm^{-3} for $[NBu^n_4][PtCl_3(CO)]$. The tube was placed in a cooling bath at least 10 °C below the intended measuring temperature. The kinetics was started by bubbling ordinary CO through the solution by means of a glass capillary for about 2 min. To eliminate the gas phase, a tight-fitting, sealed glass tube was inserted into the NMR tube and sealed to it with parafilm. The NMR tube was then quickly transferred to the pre-thermostatted NMR probe, and acquisition started. Spectra were collected using 90° pulses and 5 × T_1 as the relaxation delay. Values of T_1 for the complexes and free CO were determined using the inversion–recovery technique. Peak areas were calculated from the peak heights and widths at half height.

IR Measurements.—The IR spectra were recorded on a Perkin-Elmer 683 infrared spectrometer using 0.1 mm CaF_2 solution cells. The compound $[NBu^n_4][PtX_3(^{13}CO)]$ (X = Cl, Br or I) (0.21 mmol) was weighed into a 250 cm^3 round bottomed flask, and dissolved in 10 cm^3 of solvent (acetone, thf, dichloromethane or cyclohexanone). The flask was sealed, the contents were freeze–thaw–degassed, refrozen and evacuated. The flask was placed in a water-bath, allowed to equilibrate for 15 min, then filled with a known, but variable, CO–N_2 mixture to atmospheric pressure, and stirred rapidly in order to equilibrate the gas with the solution. The IR spectra of 0.1 cm^3 aliquots were recorded between 2300 and 1950 cm^{-1} until more than 95% of the exchange had occurred.

Calculations

Treatment of NMR Data.—From the NMR measurements two curves were obtained from each run, corresponding to free and co-ordinated ^{13}CO respectively. Since isotopic exchange always follows first-order kinetics a single exponential was computer-fitted directly to the peak areas in a least-squares fashion. From the rate constants, k_{obs} obtained, the exchange rates were calculated using the McKay equation (1),[6] where R_{ex}

$$R_{ex} = k_{obs}\frac{ab}{a+b} \qquad (1)$$

is the overall rate of exchange, irrespective of isotope, a the total complex concentration and b the total CO concentration. The value of a was determined by weighing the sample and solvent, and b was calculated from $b = ay_\infty/x_\infty$ where x_∞ and y_∞ denote the equilibrium concentrations of $[MCl_3(^{13}CO)]^-$ and ^{13}CO respectively. Fig. 1 shows plots of R_{ex} as a function of the total concentrations of metal complex.

Treatment of IR Data.—From the IR spectra, the absorbance of the CO stretching vibration corresponding to co-ordinated ^{12}CO and ^{13}CO (^{12}A and ^{13}A respectively) and the ratio of

---

† On leave from Department of Chemistry, University of the Orange Free State, Bloemfontein 9300, South Africa.

‡ *Supplementary data available* (SUP No. 57044, 5 pp.): Observed first-order rate constants for reactions between ^{12}CO and $[MX_3(^{13}CO)]^-$ (MX = PdCl, PtCl or PtBr). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: atm ≈ 101 325 Pa.

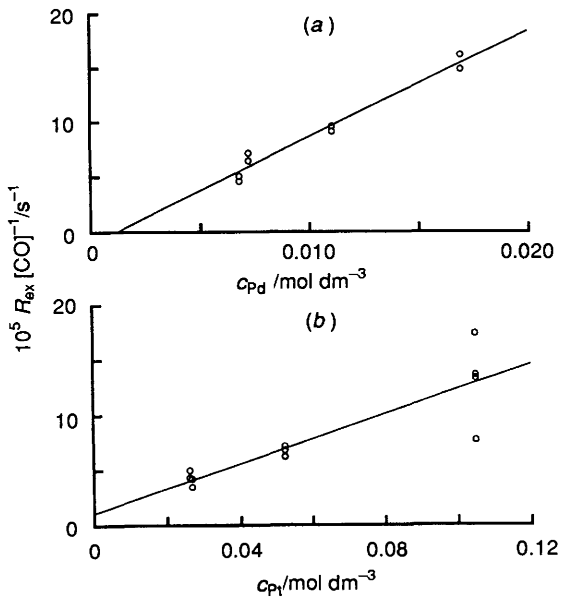

Fig. 1 The overall rate of exchange R_{ex} as calculated from the NMR measurements, equation (1), as a function of the total concentration of metal complex: (*a*) $[PdCl_3(CO)]^-$ at −15 °C; (*b*) $[PtCl_3(CO)]^-$ at 15 °C [experimental errors in (*b*) increase with increasing platinum concentration]

enrichment, $Q = {}^{12}A/({}^{12}A + {}^{13}A)$, were computed. The k_{obs} was determined by a least-squares fit to equation (2).

$$\ln\left(\frac{Q_0 - Q_\infty}{Q - Q_\infty}\right) = k_{obs}t \qquad (2)$$

Since the solubility of CO is rather low, the volume of CO in the gas phase had to be included in the total concentration of CO for the IR measurements in order to make a reliable determination of the CO dependence feasible. This makes a modification to the McKay equation necessary.* Considering equation (3), where X = Cl or Br, and since rapid stirring of the solution was assured, the distribution of ^{12}CO and ^{13}CO between the gas phase and the solution can be assumed to be close to equilibrium. The equilibrium constant is defined by equation (4).

$$\begin{tikzcd}[PtX_3(^{13}CO)]^- + {}^{12}CO \arrow[r, shift left, "k_{ex}"] \arrow[d, shift left, "\text{fast}"] & {[PtX_3(^{12}CO)]^- + {}^{13}CO} \arrow[l, shift left] \arrow[d, shift left, "\text{fast}"] \\ {}^{12}CO(g) \arrow[u, shift left] & {}^{13}CO(g) \arrow[u, shift left]\end{tikzcd} \qquad (3)$$

$$K = \frac{[CO]/1 \text{ mol dm}^{-3}}{P_{CO}/1 \text{ atm}} \qquad (4)$$

The concentrations are abbreviated as follows: $a = [PtX_3(^{13}CO)^-] + [PtX_3(^{12}CO)^-]$, $b = ([^{13}CO] + [^{12}CO])(K + 1)/K$, $x = [PtX_3(^{13}CO)^-]$, $y = [^{13}CO]$, $a - x = [PtX_3(^{12}CO)^-]$ and $z = [^{12}CO] = bK/(K + 1) - y$; b is the total CO concentration, considering all CO as dissolved. The net rate of reaction is given by the total rate multiplied by the fraction of events which lead to an exchange of isotopes [eqn. (5)].

$$\frac{-dx}{dt} = R_{ex}\frac{x}{a}\frac{z}{b} - R_{ex}\frac{a-x}{a}\frac{y}{b} \qquad (5)$$

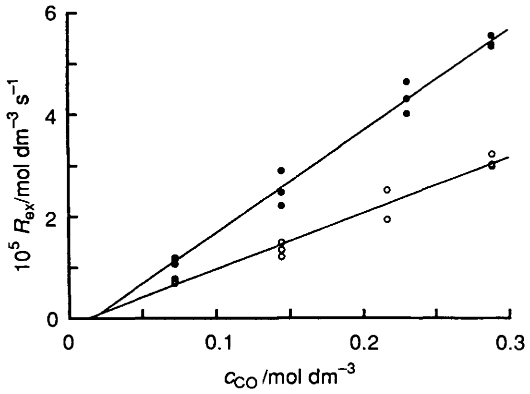

Fig. 2 The overall rate of exchange R_{ex} as calculated from the IR measurements, equation (9), as a function of the concentration of free carbon monoxide, considering all CO as dissolved: (○) $[PtCl_3(CO)]^-$, (●) $[PtBr_3(CO)]^-$, both at 30.3 °C; c_{Pt} = 0.021 mol dm^{-3}

Substitution of z and rearrangement gives equation (6). But,

$$\frac{-dx}{dt} = \frac{R_{ex}}{ab}\left(\frac{bxK}{K+1} - ay\right) \qquad (6)$$

since $x + y(K + 1)/K = x_\infty + y_\infty(K + 1)/K$ and $a/b = x_\infty K/y_\infty(K + 1)$ insertion and rearrangement gives equation (7) which can be integrated between the usual limits to give

$$\frac{-dx}{dt} = R_{ex}\frac{K}{K+1}\frac{a+b}{ab}(x - x_\infty) \qquad (7)$$

equation (8). The modified McKay equation thus becomes (9).

$$\ln\left(\frac{x_0 - x_\infty}{x - x_\infty}\right) = R_{ex}\frac{K}{K+1}\frac{a+b}{ab}t \qquad (8)$$

Fig. 2 shows a plot of R_{ex} from equation (9) *vs.* the total concentration of carbon monoxide.

$$k_{obs} = R_{ex}\frac{K}{K+1}\frac{a+b}{ab} \qquad (9)$$

The solubility of CO in chloroform and acetone expressed as a mole fraction is 6.6 × 10^{-4} (mean of two values) and 7.80 × 10^{-4} respectively at 298.2 K and a CO pressure of 1 atm.[7] The corresponding values of K are 8.25 × 10^{-3} and 1.06 × 10^{-2}. For the other solvents used there are no published data on the solubility of CO. In the calculations, K for CH_2Cl_2 was assumed to be the same as for $CHCl_3$, and K for cyclohexanone and thf the same as for acetone. In the absence of solubility data for CO in these solvents, it does not seem unreasonable to equate the solubility of CO in solvents with similar functional groups/polarity. The value of a was determined by weighing the sample, and b was calculated from the volume of the reaction flask and the partial pressure (p) of CO. Vapour pressures of the solvents used were taken from the literature (CH_2Cl_2, acetone, cyclohexanone[8] and thf[9]).

Results

The carbonyl exchange rate is first-order in $[PdCl_3(CO)^-]$ and $[PtCl_3(CO)^-]$, Fig. 1. The CO dependence was examined for $[PtCl_3(CO)]^-$ and $[PtBr_3(CO)]^-$, and also found to be first-order, as shown in Fig. 2. The CO dependence for $[PdCl_3(CO)]^-$ was not measured since the reaction is too fast at the temperatures needed for IR measurements, but there is no reason to doubt that this reaction is also first-order. The rate

---

* An alternative formulation of this equation appears in ref. 2.

Table 1 Rate constants and activation parameters for carbonyl exchange. The error limits quoted define a 95% confidence interval

Complex	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}	$k_{ex}{}^{298}$/dm^3 mol^{-1} s^{-1}	Temp. range/K	Method
$[PtCl_3(CO)]^-$	69 ± 6	−61 ± 20	(3.0 ± 0.1) × 10^{-3}	293–303	IR[a]
$[PtCl_3(CO)]^-$	61 ± 8	−88 ± 27	(3.4 ± 0.4) × 10^{-3}	288–308	NMR[b]
$[PtCl_3(CO)]^-$	60 ± 7	−91 ± 22	(3.3 ± 0.3) × 10^{-3}	288–308	IR, NMR[c]
$[PtBr_3(CO)]^-$	49 ± 6	−104 + 19	(6.0 ± 0.2) × 10^{-2}	293–303	IR[a]
$[PdCl_3(CO)]^-$	60 ± 8	−47 + 30	0.57 ± 0.07	248–268	NMR[b]

[a] In CH_2Cl_2. [b] In $CDCl_3$. [c] IR and NMR data fitted simultaneously.

Table 2 Solvent dependence of carbonyl exchange rate constant for $[PtBr_3(CO)]^-$ at 303.5 K

Solvent	k_{ex}/dm^3 mol^{-1} s^{-1}
Acetone	0.041
Cyclohexanone	0.037
Dichloromethane	0.090
thf	0.069

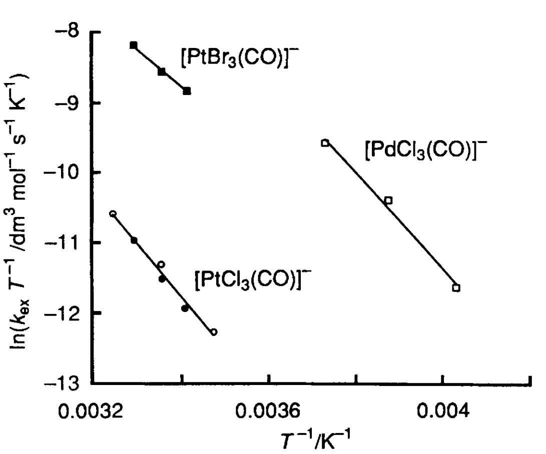

Fig. 3 Eyring plots for the carbonyl exchange. (●, ■) IR data, (○, □) ^{13}C NMR data

law is thus the usual one found for platinum(II) and palladium(II) complexes, equation (10), where k_{ex} is the

$$R_{ex} = k_{ex}[\text{complex}][\text{CO}] \qquad (10)$$

second-order exchange rate constant, and the solvent path is negligible. Combination with equations (1) and (9) then gives the relations between k_{obs} and k_{ex} [eqns. (11) and 12)]

$$k_{obs} = k_{ex}(a + b) \qquad (11)$$

$$k_{obs} = k_{ex}(a + b)K/(K + 1) \qquad (12)$$

for the reactions without and with a gas-phase included, respectively.

The temperature dependence of k_{ex} was also measured. Activation parameters determined from the Eyring plots in Fig. 3 are summarized in Table 1. There is a pleasing agreement between the IR and NMR measurements for $[PtCl_3(CO)]^-$. Addition of chloride did not affect the rate significantly. There is a small solvent effect on the exchange rate for $[PtBr_3(CO)]^-$, as shown in Table 2, but the absolute values depend on the assumptions for the solubility of CO being correct. Carbonyl exchange for $[PtI_3(CO)]^-$ at 25 °C has a half-life of *ca.* 2 min, which is too fast to be followed accurately by the methods used in this study. An estimation of the lower limit of the rate constant leads to a value of $k_{ex} > 2$ dm^3 mol^{-1} s^{-1}.

Discussion

The exchange is first-order in both complex and CO concentration, and the activation entropy is negative for all three complexes studied. We suggest a common, associative mechanism, with a five-co-ordinate, 18-electron transition state.

Wojcicki and Basolo[2] found that carbonyl exchange in $[Pt_2(\mu\text{-}Cl)_2Cl_2(CO)_2]$ was 'instantaneous', or complete in less than 2 min. This corresponds to a half-life of less than *ca.* 25 s, and $k_{ex} > \approx 10$ dm^3 mol^{-1} s^{-1}, which is at least three orders of magnitude faster than the values for $[PtCl_3(CO)]^-$ found in the present study. Similarly, the analogous bridged ethene complexes $[M_2(\mu\text{-}Cl)_2Cl_2(C_2H_4)_2]$ (M = Pd or Pt) exchange ethene about three orders of magnitude faster than the mononuclear $[MCl_3(C_2H_4)]^-$.[3] It is also known[10] that pyridine cleaves the bridge in $[Pt_2(\mu\text{-}Br)_2Br_4]^{2-}$ about three orders of magnitude faster than it substitutes bromide in the corresponding mononuclear complex $[PtBr_4]^{2-}$. Thus, the halide-bridged, d^8 square-planar complexes are in general labile compared to their mononuclear analogues, possibly due to strain in the four-membered ring and weaker bonds to the bridging halides.

For carbonyl exchange in the dinuclear carbonyl complexes, Wojcicki and Basolo[2] suggested a mechanism in which one of the chloride bridges is split, which also seems reasonable for $[Pt_2(\mu\text{-}Cl)_2Cl_2(C_2H_4)_2]$[3] bearing in mind the large *trans* effect of both CO and C_2H_4.[11]

Some ground-state properties of $[MX_3(CO)]^-$ (MX = PdCl, PtCl, PtBr or PtI) and $[PtCl_3(C_2H_4)]^-$ are listed in Table 3. Whereas $d(M\text{–}X_{trans}) > d(M\text{–}X_{cis})$ in the ethene complex, $d(M\text{–}X_{trans})$ and $d(M\text{–}X_{cis})$ do not differ significantly in the carbonyl complexes. The force constants (f) for the $M\text{–}Cl_{trans}$ bond, on the other hand, are slightly higher than for $M\text{–}Cl_{cis}$ in the carbonyl complexes $[MCl_3(CO)]^-$ (M = Pd or Pt), whereas the opposite is true for $[PtCl_3(C_2H_4)]^-$. The values of f(M–CO) for $[PtCl_3(CO)]^-$ and $[PtBr_3(CO)]^-$ are identical and much higher than for $[PdCl_3(CO)]^-$. How these similarities/variations in ground-state properties translate to the five-co-ordinate intermediates involved in the present exchange reactions have still to be elucidated. The replacement of substituted pyridines (R) by chloride in *trans*-$[PtCl_2L(R)]$ (L = CO or C_2H_4), is about three orders of magnitude faster for the ethene complexes than for the carbonyl complexes,[17] showing that the *trans* effect is considerably larger for ethene than for carbon monoxide. It is also well known that second-row metal carbonyls are more labile than first- and third-row analogues. According to a theoretical calculation, this fact stems from the different M–CO σ-/π-interactions.[18] This has been quantified by a recent report on the substitution of CO in the complexes $[M(\eta^3\text{-}C_3Bu^t{}_3)(CO)_3]$ (M = Co, Rh or Ir), which shows that the activation enthalpy for CO dissociation for Rh is about 50 kJ mol^{-1} lower than that for Co and about 14 kJ mol^{-1} lower than that for Ir.[19] The increased rate of carbonyl exchange in $[PdCl_3(CO)]^-$ *vs.* $[PtCl_3(CO)]^-$ found in the present study might indicate that there is a similar trend in the nickel triad.

For $[PtX_3(CO)]^-$ (X = Cl, Br or I), the value of k_{ex} increases in the order Cl < Br < I, which parallels the order of increasing kinetic *trans* effect of the halide (approximately 1:10:130).[20]

Table 3 Force constants, bond distances and ^{13}C chemical shifts of $[MX_3(CO)]^-$ (MX = PdCl, PtCl, PtBr or PtI) and $[PtCl_3(C_2H_4)]^-$

Complex	f(M–CO)[a]/ 10^2 N m^{-1}	f(M–X_{cis})/ 10^2 N m^{-1}	f(M–X_{trans})/ 10^2 N m^{-1}	d(M–X_{cis})/Å	d(M–X_{trans})/Å	$\delta(^{13}C)$[b]
$[PtCl_3(CO)]^-$	3.90	2.02[a]	2.13[a]	2.292(4)[c]	2.289(3)[c]	152
$[PtBr_3(CO)]^-$	3.90	1.83[a]	1.83[a]			153
$[PtI_3(CO)]^-$	3.83	1.60[a]	1.56[a]			156.2
$[PdCl_3(CO)]^-$	2.36	1.79[a]	1.83[a]	2.292(3)[d]	2.284(2)[d]	163.4
$[PtCl_3(C_2H_4)]^-$		1.82[c]	1.78[e]	2.302(2)[f]	2.340(2)[f]	

[a] Ref. 12. [b] Ref. 5. [c] Ref. 13. [d] Ref. 14. [e] Ref. 15. [f] Ref. 16.

The relative values of k_{ex} found in the present study are: 1:18:≈500 for Cl:Br:I.

The observed exchange rate of $[MCl_3(CO)]^-$ is between three and six orders of magnitude slower than that of $[MCl_3(C_2H_4)]^-$ determined previously.[3] This large difference in reactivity is probably due to differences in chemical bonding between the metals and carbonyl and ethene, respectively. The four bonding electrons (one σ and one π bond) between M and ethene in $[MX_3(C_2H_4)]^-$ are considerably less localized than the six bonding ones (one σ, two π bonds) between M and carbonyl in $[MX_3(CO)]^-$. Thus, carbonyl is expected to be more strongly bound than ethene to these soft metal centres and therefore also to be a less efficient leaving ligand. There seems to be no data available so far for a comparison of these two ligands as entering nucleophiles. Moreover, the possibility of different exchange mechanisms for the carbonyl and ethene complexes cannot be excluded at present.

Acknowledgements

Financial support from the Swedish Natural Science Research Council (NFR) is gratefully acknowledged. A. R. thanks the NFR for a travel grant, the South African FRD and the UOFS for financial assistance, and M. B. thanks the SERC for a studentship.

References

1 F. Basolo, *Inorg. Chim. Acta*, 1981, **50**, 65 and refs. therein.
2 A. Wojcicki and F. Basolo, *J. Am. Chem. Soc.*, 1961, **83**, 525.
3 A. Olsson and P. Kofod, *Inorg. Chem.*, 1992, **31**, 183.
4 A. Olsson and L.-F. Olsson, *Inorg. Chem.*, in the press.
5 J. Browning, P. L. Goggin. R. J. Goodfellow, M. G. Norton, A. J. M. Rattray, B. F. Taylor and J. Mink, *J. Chem. Soc., Dalton Trans.*, 1977, 2061.
6 J. W. Moore and R. G. Pearson, *Kinetics and Mechanism,* Wiley-Interscience, New York, 1981, p. 311.
7 P. G. T. Fogg and W. Gerrard, *Solubility of Gases in Liquids*, John Wiley and Sons, Chichester, 1991, p. 277.
8 *Handbook of Chemistry and Physics*, ed. R. C. Weast, CRC Press, Cleveland, 55th edn., 1974.
9 D. F. Shriver and M. A. Drezdzov, *The Manipulation of Air-sensitive Compounds*, Wiley-Interscience, New York, 1986.
10 R. G. Pearson and M. M. Muir, *J. Am. Chem. Soc.*, 1966, **88**, 2163.
11 R. G. Wilkins, *Kinetics and Mechanism of Reactions of Transition Metal Complexes*, VCH, Weinheim, 1991, p. 237.
12 P. L. Goggin, M. G. Norton and J. Mink, *Inorg. Chim. Acta*, 1978, **26**, 125.
13 D. R. Russell, P. A. Tucker and S. Wilson, *J. Organomet. Chem.*, 1976, **104**, 387.
14 B. P. Andreini, D. Belli Dell'Amico, F. Calderazzo, M. G. Venturi and G. Pelizzi, *J. Organomet. Chem.*, 1988, **354**, 369.
15 M. J. Grogan and K. Nakamoto, *J. Am. Chem. Soc.*, 1966, **88**, 5454.
16 R. A. Love, T. F. Koetzle, G. J. B. Williams, L. C. Andrews and R. Bau, *Inorg. Chem.*, 1975, **14**, 2653.
17 L. Canovese, M. L. Tobe and L. Cattalini, *J. Chem. Soc., Dalton Trans.*, 1985, 27.
18 T. Ziegler, V. Tschinke and C. Urschenbach, *J. Am. Chem. Soc.*, 1987, **109**, 4825.
19 Jian-Kun Shen, D. S. Tucker, F. Basob and R. P. Huges, *J. Am. Chem. Soc.*, 1993, **115**, 11312.
20 L. I. Elding, *Inorg. Chim Acta*, 1978, **28**, 255.

Received 17*th June* 1994; *Paper* 4/03695F