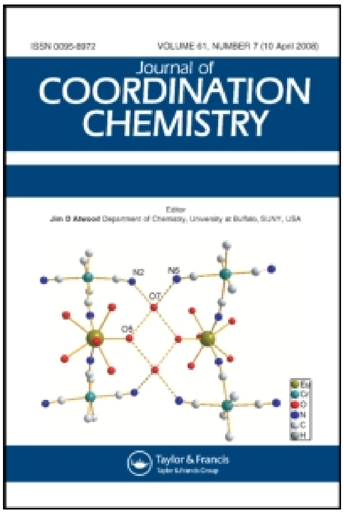


Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A MECHANISTIC STUDY OF THE FORMATION OF $[Ru_6C(CO)_{16}]^{2-}$ FROM $[Ru_6(CO)_{18}]^{2-}$

Stanley A. Roth[a]; John R. Shapley[a]
[a] Department of Chemistry, University of Illinois, Urbana, Illinois

To cite this Article Roth, Stanley A. and Shapley, John R.(1994) 'A MECHANISTIC STUDY OF THE FORMATION OF $[Ru_6C(CO)_{16}]^{2-}$ FROM $[Ru_6(CO)_{18}]^{2-}$', Journal of Coordination Chemistry, 32: 1, 163 — 172
To link to this Article: DOI: 10.1080/00958979408024246
URL: http://dx.doi.org/10.1080/00958979408024246

J. Coord. Chem., 1994, Vol 32, pp. 163–172
Reprints available directly from the publisher
Photocopying permitted by license only

A MECHANISTIC STUDY OF THE FORMATION OF $[Ru_6C(CO)_{16}]^{2-}$ FROM $[Ru_6(CO)_{18}]^{2-}$

STANLEY A. ROTH and JOHN R. SHAPLEY*

Department of Chemistry, University of Illinois, 505 South Mathews, Urbana, Illinois 61801

(Received August 28, 1993; in final form December 10, 1993)

The kinetics of the transformation of $[Ru_6(CO)_{18}]^{2-}$ into $[Ru_6C(CO)_{16}]^{2-}$ in diglyme over the temperature range 130–160°C have been determined. The results are consistent with reversible loss of a carbonyl ligand from $[Ru_6(CO)_{18}]^{2-}$, followed by formation of carbon dioxide and reassociation of carbon monoxide to give the observed product. Mass spectral analysis of the evolved carbon dioxide trapped as barium carbonate supports an intramolecular pathway for the disproportionation of carbon monoxide.

KEYWORDS: Ruthenium carbonyl clusters, kinetics, carbide

INTRODUCTION

The role of bulk and surface carbides in heterogeneous Fischer-Tropsch catalysis[1] has been extensively studied in relation to their proposed intermediacy in carbon monoxide reduction reactions.[2] It has been established that carbon monoxide disproportionation, the Boudouard reaction, (eq 1), occurs on many metallic surfaces, *e.g.*, Fe, Ru, Co, and Ni, and that subsequent hydrogenation of this surface carbon produces varying quantities of light hydrocarbons.[3]

$$2CO \longrightarrow CO_2 + C \qquad (1)$$

In a previous study[4] we showed that $Ru_6(CO)_{18}^{2-}$ was converted in essentially quantitative fashion into $Ru_6C(CO)_{16}^{2-}$. This reaction activates carbon monoxide and produces an encapsulated carbide, with oxygen removal in the form of carbon dioxide (eq 2). In this paper we describe our further kinetics and labeling studies on this molecular analog of the Boudouard reaction.

$$Ru_6(CO)_{18}^{2-} \xrightarrow{\Delta} Ru_6C(CO)_{16}^{-} + CO_2 \qquad (2)$$

EXPERIMENTAL

General Procedures

$[PPN]_2[Ru_6(CO)_{18}]$ and $[PPN]_2[Ru_6C(CO)_{16}]$ were prepared from $Ru_3(CO)_{12}$ using previously published procedures.[4] Diglyme was freshly distilled from molten

---

* Author for correspondence.

sodium prior to use. Unless otherwise specified, all operations were carried out under a nitrogen atmosphere with the use of standard techniques. Infrared spectra of reaction mixtures were recorded on a Perkin-Elmer Model 281B spectrophotometer. Reaction temperatures were maintained to within ± 1 °C with a proportional temperature controller.

Kinetics Studies

To an oven dried 50 ml volumetric flask was added $[PPN]_2[Ru_6(CO)_{18}]$ (54.7 mg, 0.025 mmol). The volumetric flask was then fitted with a Y-adapter having a serum rubber stopper and a pressure equalizing separatory funnel filled with dry diglyme. After adding the solvent to the flask, the resulting 0.50 mM solution was transferred through a cannula to a 100 ml four-necked flask containing a magnetic stirring bar and fitted with a thermometer, a gas-inlet dispersion tube, a condenser/gas-outlet, and a serum rubber stopper. This yellow-brown solution was sparged for at least 30 min with the appropriate reaction gas and then heated in a silicone oil bath to the desired temperature. After attaining a stable reaction temperature (usually less than 10 min), samples were periodically withdrawn under N_2 and placed in septum-capped vials.

The kinetics runs were conducted with continuous sparging of the reaction solution by a CO/N_2 mixture. Gas mixtures of greater than 10% CO in N_2 were prepared by individually controlling the flow rates of N_2 and CO with fine metering valves (Nupro model 2MG). The flow rate of CO was initially set to the desired value using a soap bubble flow meter; then the total gas flow rate was adjusted to 50 ml/min by controlling the flow rate of N_2. Gas mixtures of less than 10% CO in N_2 were prepared in an analogous manner using premixed 10.35% CO in N_2 (Air Products) and pure N_2.

The progress of the reaction was followed by monitoring the infrared spectra in the 2100-1950 cm^{-1} region (see Figure 1). The reactant, $Ru_6(CO)_{18}^{2-}$, has infrared absorbance maxima in this region at 1999 and 1985 cm^{-1}. The product, $Ru_6C(CO)_{16}^{2-}$, has a more intense absorbance maximum at 1978 cm^{-1}. An isobestic point at 1984 cm^{-1} in the infrared spectra was observed. In the few cases where partial decomposition occurred, a consistent isobestic point was not obtained and the data from those kinetic runs were discarded. Initial reactions were monitored for more than three half-lives to establish linearity of the pseudo-first-order rate plots (see Figure 2). All reactions (except the 130 °C data set) were monitored for a minimum of two half-lives. At long reaction times (*i.e.*, low temperatures) a parallel decomposition pathway competes with the desired reaction; therefore, the 130 °C experiments were terminated after 12 h, and an initial rate was calculated. The reaction solutions were heated to reflux (162 °C) for 30 min in the absence of CO in order to drive the reaction to completion and to obtain A_∞. Absorbance data at 1978 cm^{-1} were used to obtain pseudo-first-order rate constants,K_{obs}, from $1n(A_\infty - A_t)$ time plots (correlation coefficients >0.990).

Preparation of ^{13}C labeled $Ru_3(*CO)_{12}$

Into a 250 ml glass pressure vessel was placed a solution of $Ru_3(CO)_{12}$ (500 mg) in cyclo-hexane (75 ml, distilled from Na/benzophenone ketyl) and a magnetic stirring bar. The solution was degassed by three freeze-pump-thaw cycles and the pressure

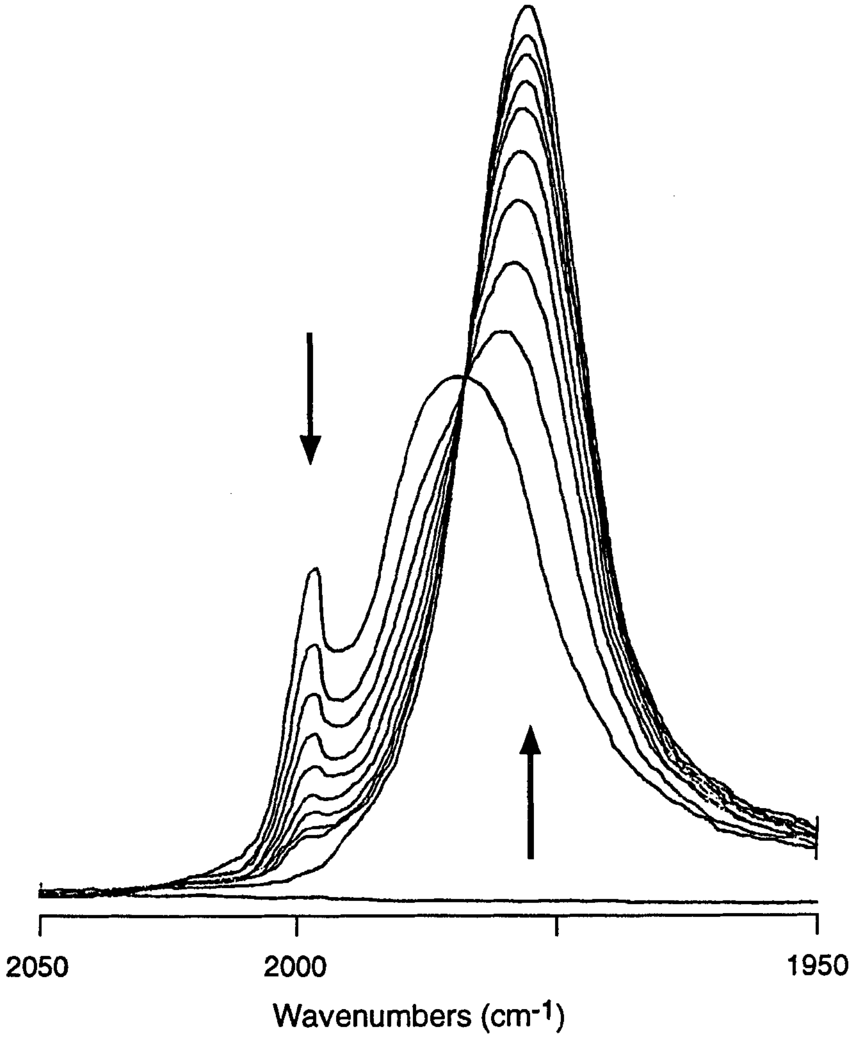


Figure 1 Infrared spectra, ν(CO), monitored during the conversion of $[Ru_6(CO)_{18}]^{2-}$ into $[Ru_6C(CO)_{16}]^{2-}$ in diglyme.

vessel was filled with 10 psig of ^{13}CO(92% ^{13}C, Mound Facility of Monsanto Research Corp). After 24 h of heating in an 80°C oil bath the solution was cooled, cycled through two freeze-pump-thaw degassing cycles, refilled to 10 psig with ^{13}CO, and reheated to 80°C for an additional 22 h. The solvent was removed, and the orange residue was washed first with methanol and then a small portion of pentane to produce an orange microcrystalline product (480 mg). IR(CH_2Cl_2):ν_{CO}2039(m), 2031(m), 2019(m,sh), 2013(s), 1999(m,sh), 1989(s), 1971(m) cm^{-1}.

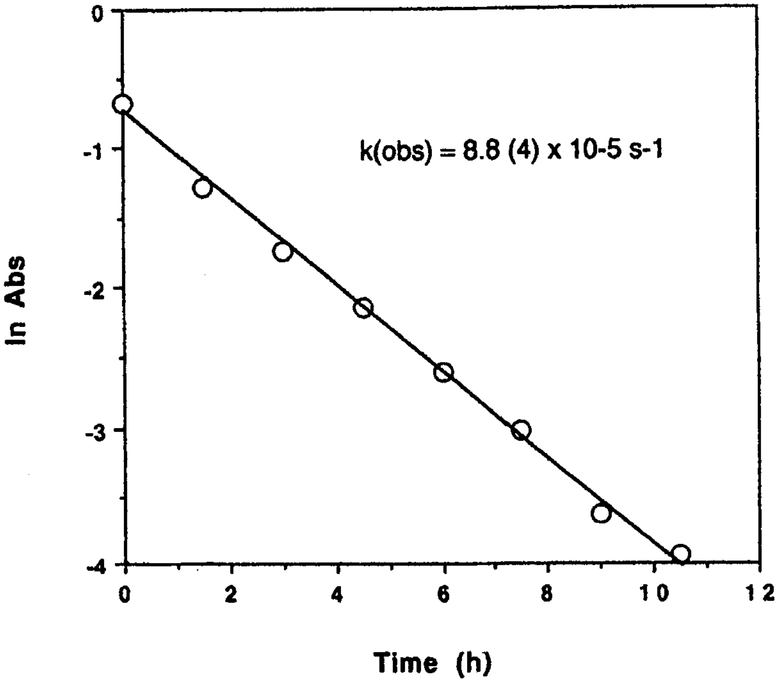


Figure 2 First order rate plot for the conversion of $[Ru_6(CO)_{18}]^{2-}$ into $[Ru_6C(Co)_{16}]^{2-}$ in diglyme at 150°C.

The calculated ^{13}C percentage, assuming complete equilibration of all ^{13}CO, was 77%.

Preparation of ^{13}CO labeled $[PPN]_2[Ru_6(*CO)_{18}]$

This compound was prepared from ^{13}CO labeled $Ru_3(*CO)_{12}$(218 mg, 0.345 mmol) by the procedure previously described.[4] IR(CH_2Cl_2): ν_{CO} 1961(s,br), 1942(s,br) cm^{-1}.

Preparation of ^{13}CO labeled $[PPN]_2[Ru_6{*C}(CO)_{16}]$

A 100 ml, three-necked round bottom flask containing $[PPN]_2[Ru_6(*CO)_{18}]$ (100 mg, 0.046 mmol) was fitted with a gas inlet, a glass stopper, a condenser with a gas outlet at the top, and a magnetic stirring bar. Dry diglyme (~60 ml) was distilled directly into the flask and the solution was sparged with 10.35% CO in N_2 for 30 min at a flow rate of 50 ml/min. The solution was then heated to reflux in a 175°C oil bath for two h. $[PPN]_2[Ru_6{*C}(CO)_{16}]$ was obtained from the diglyme reaction solutions and recrystallized as previously described.[4] IR(CH_2Cl_2):ν_{CO} 1978(s), 1952(m,sh) cm^{-1}. ^{13}C NMR:δ 459 (carbide), δ 218 (CO).

The purge gas from the reaction was bubbled through two successive bubblers filled with saturated aqueous BaOH (75 ml each). A small quantity of white, fluffy $BaCO_3$ was formed during the reaction. The aqueous solution was filtered through a small glass frit, and the precipitate was washed with distilled water (~25 ml), followed by acetone (~10 ml), and dried in a vacuum oven in the glass frit (8.0 mg, 0.0405 mmoles, 88%).

Isotope ratio mass spectral analysis of the Ba^*CO_3 showed it to have $^{13}C/^{12}C$ ratio of 0.227, which corresponds to an atom % ^{13}C of 18.5%.

RESULTS

Kinetics of $Ru_6C(CO)_{16}^{2-}$ Formation

The pyrolysis of $Ru_6(CO)_{18}^{2-}$ in refluxing diglyme (b.p. 162 °C) produces $Ru_6C(CO)_{16}^{2-}$ in greater than 95% isolated yield[4] together with carbon dioxide (eq 2). However, this is not solely an intramolecular reaction, since rate constants at 130–140°C were irreproducible unless the partial pressure of carbon monoxide was rigorously controlled. This was accomplished by continually sparging the reaction solution with a CO-containing gas mixture. Under these conditions a pseudo-first-order rate law (eq 3) was obeyed. For the reaction at 150°C the

$$d[Ru_6C(CO)_{16}^{2-}]/dt = k_{obs}[Ru_6C(CO)_{18}^{2-}] \tag{3}$$

first-order rate plot shown in Figure 2 was linear through five half-lives. Furthermore, the observed rate constant, k_{obs}, was independent of $[Ru_6(CO)_{18}^{2-}]_o$ over the range 0.1-0.7 mM (Table 1).

As the partial pressure of carbon monoxide in the purge gas was increased the observed rate decreased. Carbon monoxide inhibition experiments at temperatures between 130–160°C gave linear plots of $\ln(A_\infty - A_t)$ versus time (correlation coefficients >0.990). The corresponding rate constants from these kinetic experiments are listed in Table 2.

The observed pseudo-first-order rate law for the conversion of $Ru_6(CO)_{18}^{2-}$ into $Ru_6C(CO)_{16}^{2-}$ and the rate dependence on carbon monoxide partial pressure suggests that reversible loss of a carbonyl ligand precedes the product-forming step. The simplest reaction scheme suggested by these results is presented in eqs (4)–(6).

$$Ru_6(CO)_{18}^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru_6(CO)_{17}^{2-} + CO \tag{4}$$

$$Ru_6(CO)_{17}^{2-} \xrightarrow{k_2} Ru_6C(CO)_{15}^{2-} + CO_2 \tag{5}$$

Table 1 Rate constants for the pyrolysis of 0.5mM $[PPN]_2[Ru_6(CO)_{18}]$ at 150°C in diglyme with a continuous 50 ml/min sparge of CO/N_2 (1/9).

$[Ru_6(CO)_{18}^{2-}]_o$ mM	10^4k_{obs}[a] s^{-1}
0.13	1.76(6)
0.33	1.80(8)
0.50	1.84(6)
0.67	1.74(4)

[a] The estimated error in the last digit is indicated in parentheses.

Table 2 Rate constants for the pyrolysis of 0.5 mM $[PPN]_2[Ru_6(CO)_{18}]$ in diglyme with a continuous 50 ml/min CO/N_2 sparge.

Temp. °C	P_{CO} %	10^4k_{obs} s^{-1}	$\tau_{1/2}$ h
130°	1.01	0.456(15)	4.2
130°	2.07	0.309(8)	6.2
130°	3.85	0.218*5)	8.8
130°	5.70	0.159(3)	12.1
140°	4.78	0.740(14)	2.6
140°	9.65	0.521(8)	3.7
140°	13.9	0.346(8)	5.6
140°	19.8	0.279(20)	6.9
150°	9.45	1.84(3)	1.1
150°	21.3	1.29(3)	1.5
150°	29.4	0.97(3)	1.9
150°	37.3	0.88(4)	2.2
160°	30.2	7.56(5)	0.26
160°	39.0	6.61(18)	0.29
160°	48.7	5.37(19)	0.36
160°	58.8	5.32(7)	0.36

$$Ru_6C(CO)_{15}^{2-} \xrightarrow{+CO} Ru_6C(CO)_{16}^{2-} \qquad (6)$$

Application of the steady state approximation leads to the rate law in eq(7), and eq (8) defines k_{obs} for the pseudo-first-order conditions employed.

$$\frac{d[Ru_6C(CO)_{16}^{2-}]}{dt} = \frac{k_1k_2[Ru_6(CO)_{18}^{2-}]}{k_{-1}[CO] + k_2} \qquad (7)$$

$$k_{obs} = \frac{k_1k_2}{k_{-1}[CO] + k_2} \qquad (8)$$

Under moderate partial pressures of carbon monoxide both terms in the denominator (eq 8) contributed to k_{obs}. Although the precise [CO] was not known, the sparging conditions were assumed to keep [CO] constant and proportional to % CO in the gas stream. Graphing the data in terms of k_{obs}^{-1} versus (% CO) gave the linear plots shown in Figure 3 in agreement with eq (9).

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1k_2}\,(\%CO) \qquad (9)$$

The intercept of these plots provided values of k_1, the rate constant for the first-order dissociation of a carbonyl ligand from $Ru_6(CO)_{18}^{2-}$ (eq 4). The slopes of the plots allowed calculation of the ratio (k_1/k_2)(% CO), which provides a relative measure at a constant % CO — of this partition ratio at the different temperatures. The calculated values are displayed in Table 3.

Activation parameters for the carbonyl dissociation process are obtained by plotting the extrapolated k_1 values (Table 3) in the form of an Eyring plot (Figure 4). The enthalpy of activation, $\Delta H^{\ddagger}$, and entropy of activation, $\Delta S^{\ddagger}$, were determined as 32 ± 5 kcal/mole and 0 ± 12 eu, respectively. The large uncertainty in the entropy of activation arises from the errors in individual extrapolated k_1 values.

The partition ratio k_{-1}/k_2 at various temperatures is a function not only of the

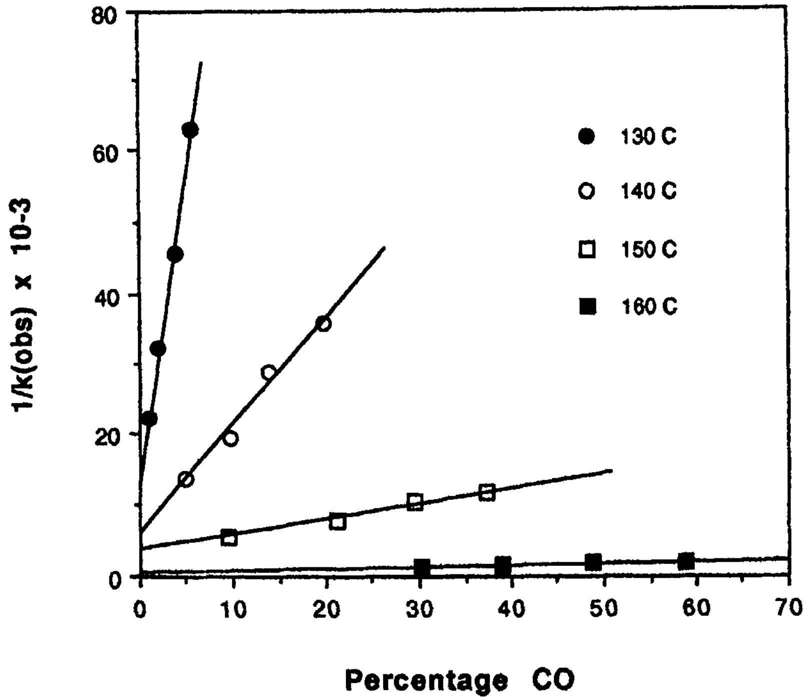


Figure 3 Plots of rate inhibition by carbon monoxide at various temperatures.

Table 3 Extrapolated rate constants for the pyrolysis of $[PPN]_2[Ru_6(CO)_{18}]$ in diglyme

Temp. °C	10^4k_1 s^{-1}	(k_{-1}/k_2)(% CO)
130°	0.73(5)	0.64
140°	1.7(6)	0.27
150°	3.0(5)	0.067
160°	14.(4)	0.029

activation energy difference between the competing reactions but also of the change in [CO]. Since the latter cannot be estimated with sufficient precision, no further analysis of these data was attempted.

The possibility that the elimination of carbon dioxide is a reversible equilibrium was investigated by substituting CO_2 for N_2 in the 10% CO sparge gas. At 140°C and 150°C the pseudo-first-order rate constants for $CO/CO_2 = 1/9$ and $CO/N_2 = 1/9$ were the same within experimental error, implying that the elimination of CO_2 is irreversible under these conditions.

^{13}C Labeling of Carbon Monoxide Disproportionation

^{13}C labeled $Ru_6(*CO)_{18}{}^{2-}$, prepared from *ca.* 77% ^{13}CO-labeled $Ru_3(^*CO)_{12}$, was pyrolyzed in refluxing diglyme with a concomitant 10% CO in N_2 sparge. Infrared

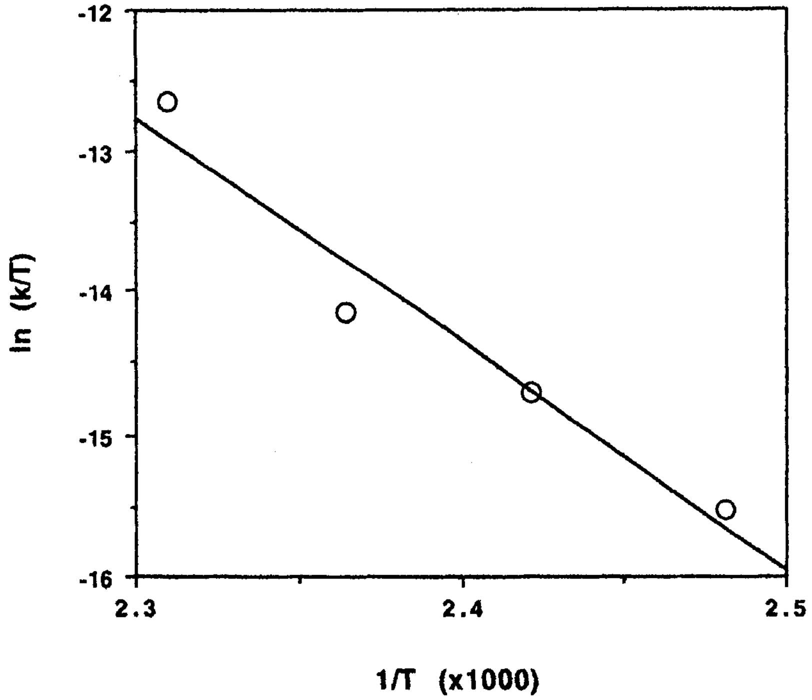


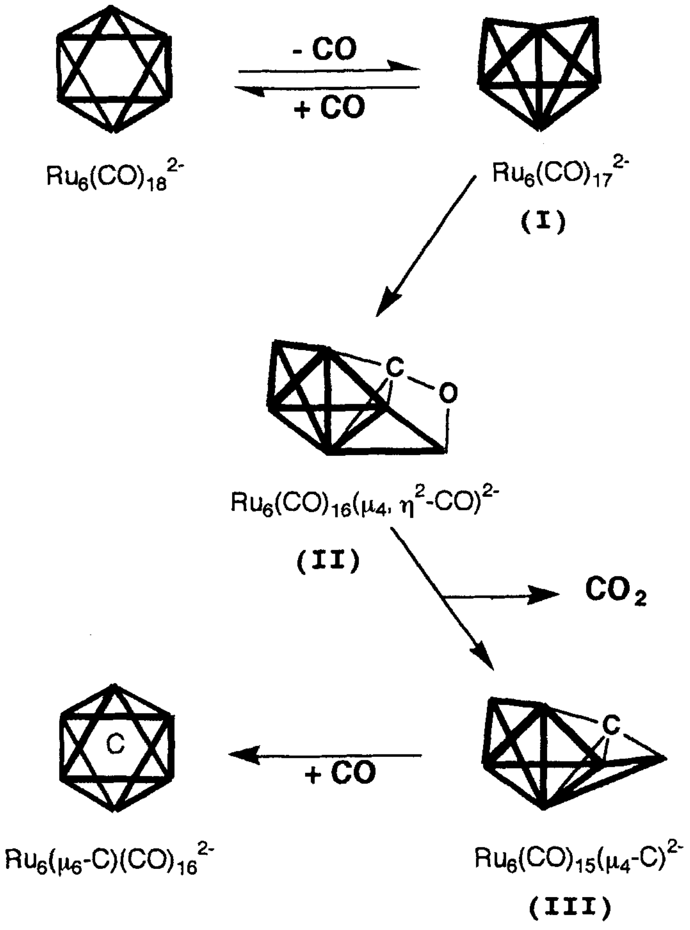
Figure 4 Eyring plot of extrapolated k_t values at various temperatures.

analysis of the $Ru_6{}^*C(CO)_{16}{}^{2-}$ product showed a carbonyl stretching pattern indistinguishable from that of the unlabeled complex. ^{13}C NMR analysis showed a CO/carbide signal intensity ratio of 2.4:1. Since the actual CO/carbide ratio was 16:1, the observed signal intensities (assuming equal relaxation times) suggested significant lost of ^{13}C from the carbonyl sites. If the carbide site was still 77% ^{13}C-labeled, then the maximum ^{13}CO labeling was 11%, a percentage that would have been difficult to observe by infrared spectroscopy. Mass spectral analysis of the CO_2 evolved, trapped as $BaCO_3$, showed 18.5% ^{13}C, which eliminated exogeneous CO as the sole source of the carbon dioxide. Thus, although the carbon monoxide exchange that occurs under reaction conditions served to dilute the ^{13}C label, the selective retention of label in both the carbide and the carbon dioxide is consistent with an intramolecular pathway for the disproportionation reaction. Related studies in closed systems have demonstrated that the encapsulated carbide ligand in $Ru_6C(CO)_{16}{}^{2-}$ or $Ru_6C(CO)_{17}$ arises from labeled carbon monoxide.[5]

DISCUSSION

Scheme I summarizes a proposed set of intermediates for the overall transformation of $Ru_6(CO)_{18}{}^{2-}$ into $Ru_6C(CO)_{16}{}^{2-}$. The kinetics imply that a reversible loss of carbon monoxide (eq 4) precedes the product-determining step (eq 5). The structure of the intermediate "$Ru_6(CO)_{17}{}^{2-}$" species (I) is shown as a bicapped tetrahedron. This is the structure typically observed for 84-electron hexanuclear clusters, in particular the isoelectronic $H_2Ru_6(CO)_{17}$,[6] which is formed by spontaneous loss of CO from octahedral $H_2Ru_6(CO)_{18}$. Insertion of a carbonyl into a Ru-Ru bond to give II provides a path for activation of the C–O bond. Several examples of such μ_4, η^2-CO ligands are known.[7,8] The specific structure shown is based on that established for the mesitylene derivative $Ru_6(CO)_{13}(\mu_4,\eta^2\text{-}CO)_2(\eta^6\text{-}C_6H_3Me_3)$[9], which upon pyrolysis gives the carbide compound $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)$. Insertion of an adjacent carbonyl ligand into the Ru-O bond followed by elimination of carbon dioxide would complete the carbon oxygen bond breaking

Scheme 1



process and generate the "surface" carbide species III. No compound of this specific structure is known, although $M_4(\mu_4\text{-}C)$ "butterfly" compounds are well known.[5,7] Addition of a carbon monoxide from solution causes rearrangement to the 86 electron octrahedron, encapsulating the carbon atom. The overall reaction is not reversible, as $Ru_6C(CO)_{16}^{2-}$ was found not to react with CO_2 at 160°C. However, the possibility of reversibility between I and II or even II and III is unknown.

Interestingly, the $\{Ru_6\}$ to $\{Ru_6C\}$ framework conversion has recently been effected under very mild conditions by treatment of $Ru_6(CO)_{18}^{2-}$ with triflic anhydride at room temperature to give $Ru_6C(CO)_{17}$ in high yield.[10]

Acknowledgements

This research was supported by grants from the National Science Foundation, including Grant CHE 89-15349. We thank Professor Thomas F. Anderson of the Department of Geology at the University of Illinois for the isotope ratio mass spectral measurements.

References

1. (a) R.B. Anderson, *The Fischer-Tropsch Synthesis* (Academic Press, Orlando, Florida, 1984). (b) M.E. Dry, *J. Organomet. Chem.* **372**, 117 (1989).
2. (a) R.C. Brady, III, and R. Pettit, *J. Am. Chem. Soc.* **102**, 6181 (1980). (b) C.K. Rofer-DePoorter, *Chem. Rev.* **81**, 447 (1981). (c) W.A. Herrmann, *Angew. Chem. Int. Ed. Engl.* **21**, 117 (1982).
3. D.W. Goodman, *Accounts Chem. Res.* **17**, 194 (1984), and references therein.
4. C.-M.T. Hayward and J.R. Shapley, *Inorg. Chem.* **21**, 3816 (1982).
5. J.S. Bradley, *Adv. Organomet. Chem.* **22**, 1 (1983), and references therein.
6. D.A. McCarthy, J.A. Krause, and S.G. Shore, *J. Amer. Chem. Soc.* **112**, 8587 (1990).
7. C.P. Horwitz and D.F. Shriver, *Adv. Organomet. Chem.* **23**, 219 (1984).
8. R.D. Adams, J.E. Babin, and M. Tasi, *Inorg. Chem.* **27**, 2618 (1988).
9. P.J. Bailey, M.J. Duer, B.F.G. Johnson, J. Lewis, G. Conole, M. McPartlin, H.R. Powell, and C. Anson *J. Organomet Chem.* **383**, 441 (1990).
10. P.J. Bailey, *J. Organomet. Chem.* **420**, C21 (1991).