3.72; N, 13.06. λ_{max}(MLCT, CH_3CN) = 512 nm (ϵ 10 250 M^{-1} cm^{-1}); Λ_M(MeOH) = 180 Ω^{-1} cm^2 M^{-1}.

Acknowledgment. Financial assistance received from the CSIR, New Delhi, is gratefully acknowledged.

Registry No. $[Ru(L^1)_3](ClO_4)_2$, 15635-95-7; $[Ru(L^1)_3](NO_3)_2$, 67062-86-6; $[Ru(L^2)_3](ClO_4)_2$, 14767-24-9; $[Ru(L^2)_3](NO_3)_2$, 14126-11-5; $[Ru(L^3)_3](ClO_4)_2$, 139242-61-8; $[Rh(L^1)_3](ClO_4)_3$, 28018-83-9; $[Ru(L^1)_2(L^3)](ClO_4)_2$, 77321-15-4; $[Ru(L^1)(L^3)_2](ClO_4)_2$, 139342-07-7; $[Ag(L^1)_2](ClO_4)$, 86783-78-0; $[Ag(L^2)_2](ClO_4)$, 58034-59-6; $[Ag(L^3)_2](ClO_4)$, 131972-14-0; $RuCl_2(L^1)_2$, 15746-57-3; $RuCl_2(L^2)_2$, 85718-09-8; $RuCl_2(L^3)_2$, 81600-80-8; $[Ag(L^1)_2](NO_3)$, 33971-93-6; $[Ag(L^2)_2](NO_3)$, 60939-16-4.

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High-Pressure Thermodynamic and Kinetic NMR Study of Nonacarbonyl(μ_3-1,3,5-trithiane)tetrairidium: The "Merry-Go-Round" Process

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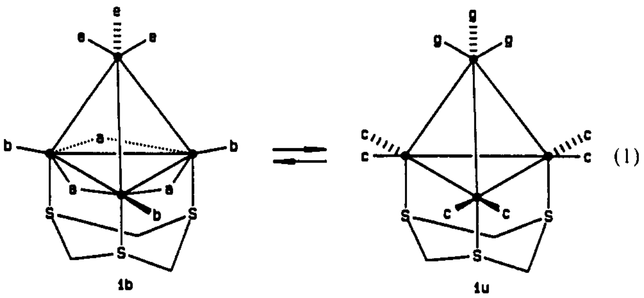
Introduction

Numerous studies have demonstrated the importance of including pressure as a kinetic parameter in the elucidation of inorganic reaction mechanisms.[1-4] These studies have led to a better understanding and a systematic classification of solvent exchange and ligand substitution reactions of octahedral complexes of transition metals. Data on the activation volumes of reactions involving organometallic compounds are, on the other hand, less numerous and generally deal with the intermolecular exchange of ligands. The only data on intramolecular processes involving carbonyl complexes are those concerning the isomerization of *ttt*-$RuCl_2(CO)_2(PR_3)_2$ and *trans*-$RuCl_2(CO)(PR_3)_3$.[5] In both cases a positive activation volume indicates a mechanism primarily dissociative in nature.

This paper deals with the quantitative characterization of a "merry-go-round" site exchange of CO's, commonly observed in carbonyl clusters but whose intermediate has never been observed.[6] In a previous paper,[7] we reported on the dynamic behavior of the cluster $[Ir_4(CO)_9(\mu_3$-1,3,5-trithiane)] (**1**) studied by IR and variable-temperature ^{13}C-NMR spectroscopy. Depending on the solvent used for crystallization, the title compound can be obtained in either the bridged **1b** (C_{3v} symmetry) or unbridged **1u** (T_d symmetry) forms whose crystal structures have been determined. An endothermic isomerization equilibrium **1b** ⇄ **1u** (eq 1) takes place in solution and involves an exchange mechanism on the NMR time scale which corresponds to a merry-go-round of the bridging and terminal CO's of the basal face.



(1)

This system is therefore the first example where the unbridged intermediate of a merry-go-round process is sufficiently stable to be observed. We have thus studied this system by variable-pressure ^{13}C-NMR spectroscopy to quantitatively characterize the CO site exchange process by the determination of the activation and reaction volumes. This system is particularly suitable for a variable-pressure study as there is no charge creation or annihilation on forming the transition state or the product. Therefore, in this case the electrostriction can be neglected. The resulting activation and reaction volumes reflect molecular volume changes and can be directly used for mechanistic studies. The reaction volume will subsequently be compared to the value obtained from crystallographic data.

Experimental Section

Chemicals and Solutions. Nonacarbonyl(μ_3-1,3,5-trithiane)tetrairidium, $[Ir_4(CO)_9(SCH_2)_3]$ (**1**), was synthesized as previously described.[7] The ^{13}C-enrichment of CO was ca. 50%. ^{13}C-NMR (THF, 168 K): **1b**, δ 233.3 (a), 183.5 (b), 160.2 (e); **1u**, δ 169.8 (c), 160.8 (g). The concentration of the solution used for the variable-pressure ^{13}C-NMR study was 0.04 m, where m are moles per kilogram of solvent, in tetrahydrofuran, THF.

NMR Measurements. Spectra at variable pressure were recorded using a Bruker AC-200 spectrometer working at 50.323 MHz for carbon-13. Measurements were made up to 200 MPa using a home-built high-pressure probe, designed for a Bruker wide-bore cryomagnet, which has been previously described.[8] The resonance frequency was tuned to 50.3 MHz using the same capacitive network as used for ^{17}O NMR at 9.4 T (54.2 MHz) adjusting the matching/tuning capacitors. The 90° pulse length was found to be 35 μs. A built-in platinum resistor allowed temperature measurements with an accuracy ±1 K after all corrections.[9] By the pumping of thermostated synthetic oil through the bomb, the temperature was stabilized to ±0.2 K. Spectra were obtained by using 4K data points resulting from 35 000–45 000 scans accumulated over a total spectral width of 11 kHz. To improve the signal to noise ratio, a zero-filling to 16K data points and an exponential filter (line-broadening) of 5 Hz were used. ^{13}C-NMR chemical shifts are referred to TMS and measured with respect to the solvent THF signal at 68.8 ppm.

Computation Method. The analysis of the equilibrium and rate constant data, using the required equations, was performed using ITERAT,[10] a nonlinear least-squares program fitting the values of the desired parameters. Reported errors are one standard deviation.

Results and Discussion

Equilibrium Constant. The equilibrium between the bridged **1b** and unbridged **1u** isomers was followed as a function of pressure at 274 K. At this temperature the two species are in fast exchange on the NMR time scale, and therefore, only an average chemical shift δ can be measured. The equilibrium constants, defined as $K = [\mathbf{1u}]/[\mathbf{1b}]$, were obtained from the population dependence of the ^{13}C chemical shift (see Figure 1). The shift variation is given by eq 2, where P_i is the population of site i and δ_i is the

$$\delta = P_a\delta_a + P_b\delta_b + P_c\delta_c \tag{2}$$

$$P_a + P_b + P_c = 1 \qquad P_a = P_b$$

chemical shift of the corresponding site (see eq 1) obtained at low temperature in the slow exchange region. It is assumed that CO chemical shifts within both species (δ_a, δ_b, δ_c) do not vary significantly with pressure. This is substantiated by the observation that no pressure dependence was detected for the shifts of car-

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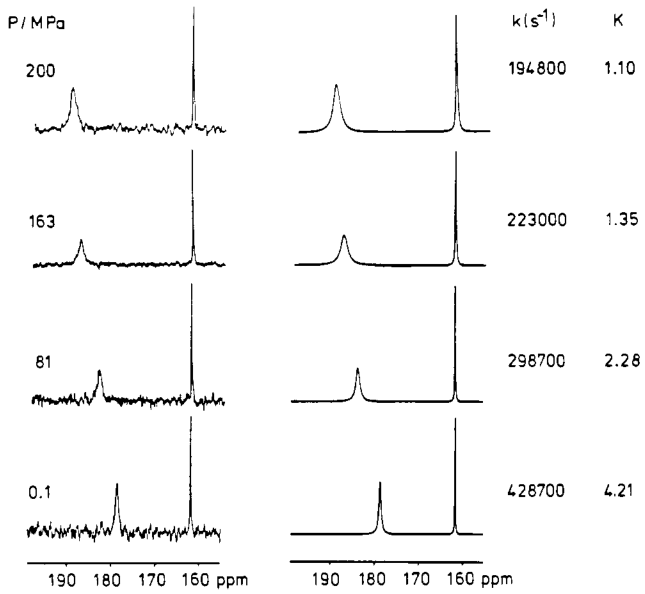

Figure 1. Variable-pressure 200-MHz ^{13}C NMR spectra of ^{13}C-enriched nonacarbonyl(μ_3-1,3,5-trithiane)tetrairidium in THF at 274.4 K. A least-squares fitting program was used to calculate the spectra on the right.

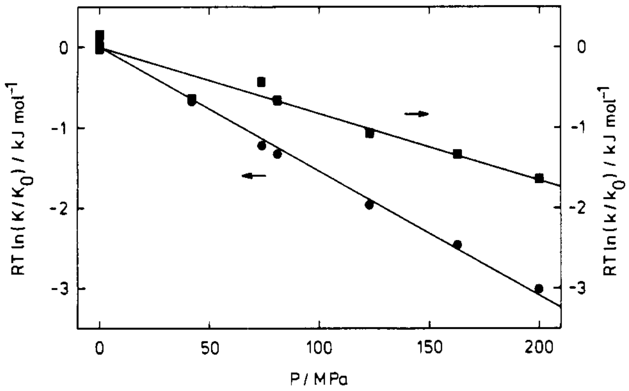

Figure 2. Pressure effect on the normalized natural logarithm of the **1u** ⇄ **1b** equilibrium constant (●) and on the rate constant for CO exchange (■) in nonacarbonyl(μ_3-1,3,5-trithiane)tetrairidium in THF (274.4 K).

bonyls e and g which do not participate in the exchange. The equilibrium constants were calculated from eq 3 and were fitted

$$K = [\mathbf{1u}]/[\mathbf{1b}] = P_c/(P_a + P_b) \tag{3}$$

$$\ln K = \ln K_0 - \Delta V_0 P/RT \tag{4}$$

to eq 4 (Figure 2), where K_0 is the equilibrium constant at 0.1 MPa and ΔV_0 the reaction volume. This leads to $\Delta V_0 = +15.4 \pm 0.4$ cm^3 mol^{-1} and $K_0 = 4.12 \pm 0.08$ at 274.4 K. The latter value was in good agreement with that found by IR spectroscopy. Indeed, a ratio of 4.6 ± 0.4 at 274 K was obtained for the absorbances of **1u** (ν(CO) > 1970 cm^{-1}) and **1b** ($\nu(\mu_2$-CO) = 1795 cm^{-1}).

The molar volumes of the two isomers were calculated both from the crystal cell data (V_{cell}/Z) and from molecular parameters, respectively, giving the following values in cm^3 mol^{-1}: 311 and 209 (**1u**); 291 and 196 (**1b**). The ratios between the volume values for each species are the same (1.48). This means that an equal distribution of vacuum and matter is present within the cell since $Z = 4$ for both isomers. The differences in molar volumes of the two isomers, as calculated by the two methods, are 20 and 13 cm^3 mol^{-1}, respectively. The reaction volume ΔV_0 obtained from variable-pressure ^{13}C-NMR experiments is closer to the one calculated from molecular parameters. This is expected since the volumes calculated from crystal cell data take into account additional constraints due to crystal packing. This experimental value is of particular importance as it allows the estimation of the volume variation for the breaking of a M–CO bridging bond in an organometallic compound. The difference in volume between the two isomers is attributable to the conversion of the three bridging CO's in **1b** to the unbridged form even if a synergic contraction of the metallic cage has to be taken into consideration.[7] It implies that the minimal volume variation associated with the transformation of a bridging CO to an unbridged one in an intramolecular process is ca. 5 cm^3 mol^{-1}. This value is a one-third of that found for the activation volume of CO substitution by Ph_3P in $Cr(CO)_6$, where the Cr–CO bond is essentially broken in the transition state.[11] This is further substantiated by more recent values that indicate a ΔV^* of ca. +20 cm^3 mol^{-1} for typical CO dissociation reactions.[12]

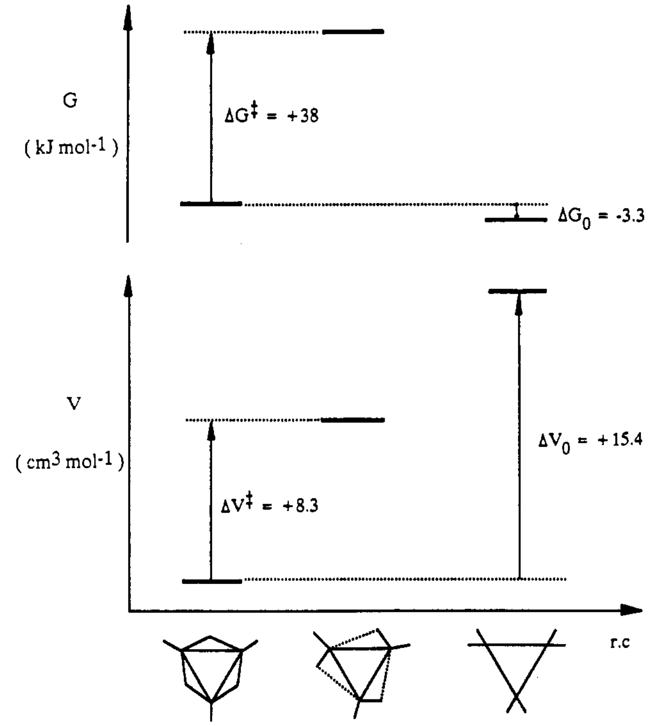

Figure 3. Free enthalpy and volume profiles for the merry-go-round process in nonacarbonyl(μ_3-1,3,5-trithiane)tetrairidium.

"Merry-Go-Round" Process. The CO intramolecular exchange (see eq 1) was followed as a function of pressure (0.1–200 MPa). Rate constants for the exchange reaction were obtained by line shape analysis using a program derived from EXCNG,[13] fitting by least-squares procedures the calculated spectra to the experimental ones (see Figure 1).

The following exchange matrix elements were used: (a,a) = (b,b) = $-k$, (a,c) = (b,c) = $k/2K$ and (c,c) and $-k/K$, with k = rate constant of CO exchange in s^{-1} and K = [**1u**]/[**1b**]. Data were fitted to eq 5 (Figure 2), where k_0 is the rate constant at

$$\ln k = \ln k_0 - \Delta V^* P/RT \tag{5}$$

0.1 MPa and ΔV^* the activation volume. The obtained values are $\Delta V^* = +8.3 \pm 0.8$ cm^3 mol^{-1} and $k_0 = (4.0 \pm 0.2) \times 10^5$ s^{-1} at 274.4 K. The latter values was in good agreement with that obtained from the variable-temperature ^{13}C-NMR spectra ($k_0 = 3.5 \times 10^5$ s^{-1}). A summary of the quantitative, thermodynamic, and activation parameters is shown in Figure 3.

Since the activation volume is about half the reaction volume and since the isomerization involves the breaking of three M–CO bonds to form three additional terminal CO's, one can assume a transition state characterized by three semibridging CO's. Such a transition state implies that the merry-go-round is a concerted process. The present carbonyl cluster system gives the first detailed

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characterization of the common CO site exchange process first reported by Cotton in 1966.[6] It should however be stressed that all merry-go-round processes in carbonyl clusters are not necessarily concerted. Indeed, we have already shown that the merry-go-round process in $[Ir_4(CO)_8(\mu_2\text{-}CO)_3Br]^-$ does not pass through an unbridged intermediate or transition state. This can be related to the ground-state structure of this anion, which features two asymmetrical bridging CO's with shorter bonds to the same Ir atom.[14] Formation of an unbridged intermediate would require the rupture of one of the two shorter bonds and is, therefore, not the lowest activation energy process. On the other hand, a concerted process can take place in **1b**, as the three bridging CO's have equal Ir–CO distances.[7]

Acknowledgment. Financial support from the Swiss National Science Foundation is gratefully acknowledged. We thank Professor Braga for the calculation of the reaction volume from molecular parameters.

Registry No. **1**, 127435-82-9.

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Lithium–Transition Metal Complexes Derived from *meso*-Octaethylporphyrinogen Which Display σ- and π-Bonding Modes

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Until recently,[2,3] *meso*-octaalkylporphyrinogens,[4] which are the precursors of porphyrin-type ligands,[5,6] have never been considered for metal complexation reactions. The anionic form of octaalkylporphyrinogen (Figure 1) has a number of characteristics which are virtually unique for a macrocyclic ligand: (i) The tetraanion should allow the stabilization of unusually high oxidation states for transition metals;[2] (ii) the pyrrolyl anion can function as a σ (2 e) or π (6 e) donor group;[3] (iii) the meso substituent should allow a variety of functionalities to be easily introduced into the macrocycle,[4] and at the same time the conformation of the metallacycle[7] may serve to force a special metal–hydrocarbon interaction.

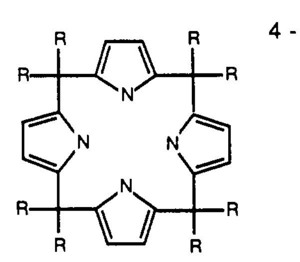

Figure 1.

Table I. Crystal Data for Complex **4**

formula	$C_{52}H_{80}CoLi_2N_4O_4$	*Z*	4
cryst system	monoclinic	no. of unique obsd data	3349
space group	*C*2/*c*	intens measmt	*a*
cell params at 295 K		struct refinement	*b*
a/Å	20.698 (4)	$R = \sum\|\Delta F\|/\sum\|F_o\|$	0.043
b/Å	10.942 (4)		
c/Å	22.791 (4)		
β/deg	104.79 (2)		

[a] For intensities and background individual profiles were analyzed by the following: Lehman, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A: Struct. Crystallogr. Cryst. Chem.* **1974**, *A30*, 580. [b] Refinement was by blocked full-matrix least squares first isotropically and then anisotropically for all non-hydrogen atoms. The hydrogen atoms except those associated with THF molecules (which were ignored) were located from different Fourier maps and introduced as fixed contributors prior to the final stage of refinement.

Table II. Atomic Coordinates (×10⁴) and Thermal Parameters for Complex **4**

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq},[a] Å^2
Co	0	2259.1 (5)	2500	274 (2)
N1	842 (1)	2213 (2)	2300 (1)	305 (7)
N2	452 (1)	2190 (2)	3339 (1)	305 (6)
C1	969 (1)	1544 (3)	1831 (1)	344 (10)
C2	1654 (1)	1510 (3)	1897 (1)	448 (11)
C3	1956 (1)	2196 (3)	2422 (1)	448 (11)
C4	1443 (1)	2616 (3)	2663 (1)	344 (9)
C5	1465 (1)	3345 (3)	3235 (1)	366 (9)
C6	1082 (1)	2633 (3)	3609 (1)	361 (9)
C7	1247 (1)	2321 (3)	4217 (1)	485 (11)
C8	701 (1)	1654 (3)	4320 (1)	456 (10)
C9	226 (1)	1585 (3)	3781 (1)	334 (9)
C10	419 (1)	858 (3)	1388 (1)	347 (10)
C11	1125 (2)	4595 (3)	3062 (2)	477 (12)
C12	1457 (2)	5449 (3)	2701 (2)	656 (16)
C13	2203 (1)	3526 (4)	3594 (1)	542 (13)
C14	2336 (2)	4430 (4)	4120 (2)	808 (19)
C15	634 (2)	496 (3)	812 (1)	473 (12)
C16	813 (2)	1529 (4)	443 (2)	629 (15)
C17	259 (2)	−337 (3)	1696 (1)	492 (11)
C18	847 (2)	−1132 (4)	1993 (2)	927 (21)
Li	1472 (3)	3425 (6)	1561 (3)	697 (27)
O1S	859 (1)	4646 (2)	1139 (1)	726 (11)
C1S	175 (2)	4726 (4)	1176 (2)	844 (19)
C2S	−79 (3)	5951 (5)	929 (3)	1331 (32)
C3S	449 (3)	6509 (5)	686 (3)	1162 (31)
C4S	1050 (3)	5740 (5)	877 (3)	1321 (32)
O2S	2247 (1)	3849 (3)	1246 (1)	804 (11)
C5S	2811 (3)	4414 (7)	1634 (3)	1433 (36)
C6S	3368 (3)	4271 (8)	1348 (3)	1516 (39)
C7S	3060 (4)	3897 (9)	720 (4)	1962 (51)
C8S	2380 (3)	3535 (8)	679 (3)	1673 (43)

[a] U_{eq} is in the form $^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$.

Experimental Section

All operations were carried out under an atmosphere of purified nitrogen. All solvents were purified by standard methods and freshly

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