211. Intramolecular Site Exchange of Carbonyl Ligands in the Cluster Compounds Nonacarbonyl{μ_3-[η^3-(1,3,5-trithiane)]}triruthenium ([Ru$_3$(CO)$_9$$\{\mu_3$-($\eta^3$-C$_3H_6S_3$)$\}$]) and (*tert*-Butyl Isocyanide)octacarbonyl-$\{\mu_3$-[η^3-(1,3,5-trithiane)]$\}$triruthenium ([Ru$_3$(*t*-BuNC)(CO)$_8$$\{\mu_3$-($\eta^3$-C$_3H_6S_3$)$\}$])

by Gábor Laurenczy, André E. Merbach, Bertrand Moullet, and Raymond Roulet*

Institut de Chimie Minérale et Analytique, Université de Lausanne, 3, place du Château, CH–1005 Lausanne

and Lisa Hoferkamp and Georg Süss-Fink*

Institut de Chimie, Université de Neuchâtel, 51, avenue de Bellevaux, CH–2000 Neuchâtel

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Variable-temperature and -pressure ^{13}C-NMR studies of the 1,3,5-trithiane-capped triruthenium clusters [Ru$_3$(CO)$_9${μ_3-(η^3-1,3,5-trithiane)}] (**1**) and [Ru$_3$(*t*-BuNC)(CO)$_8${μ_3-(η^3-1,3,5-trithiane)}] (**2**) revealed that CO site exchanges occur *via* an intramolecular merry-go-round process, involving a transition state mostly dissociative in character.

Introduction. – Cyclic thioethers are at present extensively studied as multidentate ligands in coordination chemistry [1–6]. Ruthenium carbonyl was reacted with 1,4,7-trithiacyclononane and 1,5,9-trithiacyclododecane by *Lewis* and coworkers; a series of tri-, tetra-, penta-, and hexanuclear clusters was isolated from this reaction and characterized [7]. The reaction of 1,3,5-trithiane (C$_3$H$_6$S$_3$) with [Ru$_3$(CO)$_{12}$] was investigated independently by us [8] and by *Pakkanen* and coworkers [9]; the resulting trinuclear complex [Ru$_3$(CO)$_9${μ_3-(η^3-C$_3$H$_6$S$_3$)}] (**1**) was shown crystallographically to consist of a trinuclear metal core with the 3 S-atoms of the cyclic ligand coordinated to the 3 Ru-atoms in a nearly perfect C_{3v} symmetry.

In this paper, we report a variable-temperature and -pressure NMR study of the intramolecular CO exchange occurring in solutions of the trinuclear ruthenium cluster **1** as well as of its monosubstituted derivative [Ru$_3$('BuNC)(CO)$_8${μ_3-(η^3-C$_3$H$_6$S$_3$)}] (**2**), prepared in order to explore perturbations to the exchange process caused by changes in the ligand envelope.

Results and Discussion. – The ^{13}C-NMR spectrum of a sample of [Ru$_3$(CO)$_9${μ_3-(η^3-C$_3$H$_6$S$_3$)}] (**1**) enriched in ^{13}CO (*ca.* 30%) in (D$_8$)THF is blocked at 178 K and presents 3 signals of equal intensities in the CO region (see *Fig. 1*). The resonances at 264.8, 200.8, and 199.1 ppm can be attributed to the bridging, axial, and equatorial CO's, respectively [8]. The C_{3v} geometry in solution is, therefore, similar to the structure of **1** in the solid state which was determined by X-ray analysis [8]. With increasing temperature, the signals at 264.8 and 199.1 ppm start to broaden, indicating an intramolecular exchange process between the bridging and equatorial CO's, similar to that found for [Ir$_4$(CO)$_9${μ_3-(η^3-C$_3$H$_6$S$_3$)}] [5]. The axial CO ligands do not participate in this 'merry-go-round' scrambling
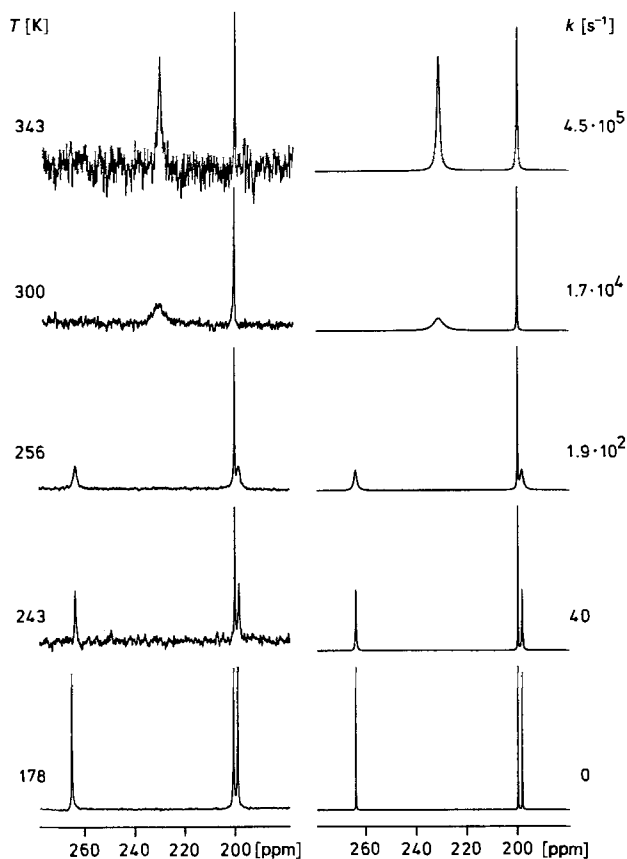
Fig. 1. *Experimental* (left) *and calculated* (right) *variable-temperature* ^{13}C-*NMR spectra of* **1** *in* (D₈)THF

process. *Fig. 1* shows the measured (*left*) and calculated (*right*) spectra at five different temperatures. The rate constants of the merry-go-round were determined at different temperatures, using a non-linear, least-squares fitting procedure [10]. The activation parameters were calculated using the *Eyring* equation [11] and are summarized in the *Table*.

The C_s geometry of **2** in solution is similar to that of **1** with the isocyanide ligand replacing an axial CO. Indeed, the ^{13}C-NMR spectrum of a sample of **2** enriched in [13]CO (*ca*. 30%) in (D₈)THF is blocked at 223 K and shows two resonances in the region of bridging CO's with an intensity ratio 2:1 (a, b), two resonances with relative intensities

Table. *Kinetic Parameters for the Merry-go-round Process in* [Ru₃(CO)₉{μ₃-(η³-C₃H₆S₃)}] *and* [Ru₃(t-BuNC)(CO)₈{μ₃-(η³-C₃H₆S₃)}] *Clusters*

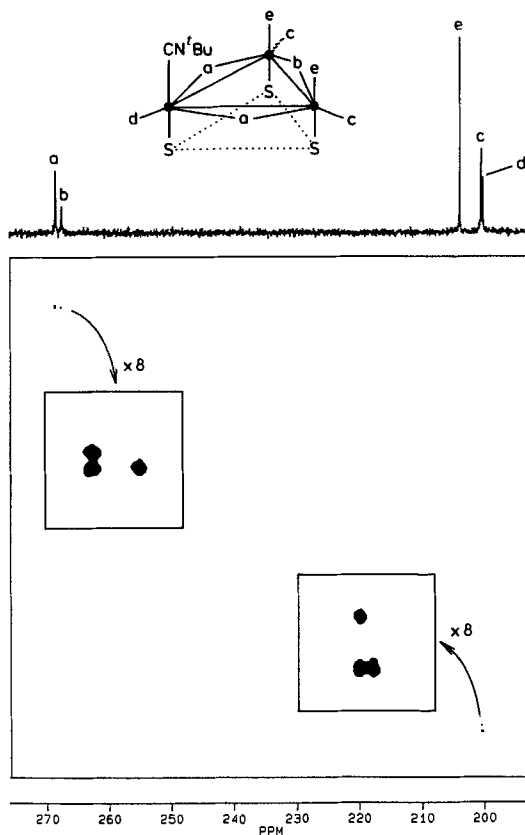|	k_{298} [s⁻]	$\Delta H^{\neq}$ [kJ mol⁻¹]	$\Delta S^{\neq}$ (J mol⁻¹ K⁻¹)	$\Delta G^{\neq}_{298}$ [kJ mol⁻¹]	$\Delta V^{\neq}$ [cm³ mol⁻¹]
1	$(1.4 \pm 0.2) \cdot 10^4$	62.7 ± 3	$+ 45.1 \pm 11$	49.3 ± 0.4	$+ 13.3 \pm 1.2$
2	71 ± 11	102.6 ± 7	$+ 153.9 \pm 26$	56.7 ± 0.6	$+ 14.1 \pm 1.8$

Fig. 2. *EXSY ^{13}C-NMR Spectrum of* 2 *in* (D$_8$)*THF at 263 K.* Mixing time: 100 ms.

2:1 for equatorial CO's (*c*, *d*), and a single resonance for the axial CO's (*e*) (*Fig. 2*). The half-width of that latter resonance is unaffected upon raising the temperature, while the former four resonances start to broaden. The increase in temperature causes an exchange process in this cluster, also. A ^{13}C-EXSY spectrum of 2 in (D$_8$)THF at 263 K (*Fig. 2*) shows the dynamic connectivities *a* ↔ *c*, *b* ↔ *c* and *a* ↔ *d*, which correspond to the merry-go-round of the bridged and equatorial CO's analogous to that of 1. The simulation of the ^{13}C-NMR spectra of 2 at different temperatures by the same procedure as that used for 1 led to the activation parameters reported in the *Table*.

The intramolecular CO site exchange for 1 and 2 was further studied as function of pressure (1–2000 bar). The rate constants of the merry-go-round were obtained by the same fitting procedure as that used in the variable-temperature work. The determined rate constants at different pressures were fitted to *Eqn. 1*, where k_0 is the rate constant at zero pressure and $\Delta V^{\neq}$ is the activation volume (*Fig. 3*; according to *Eqn. 2*, the slope of the fitted line gives the activation volume). The values obtained are $\ln k_0 = 5.1 \pm 0.1$, $\Delta V^{\neq} = +13.3 \pm 1.2 \ \text{cm}^3 \text{mol}^{-1}$ at 253.1 K for 1 and $\ln k_0 = 3.8 \pm 0.6$, $\Delta V^{\neq} = +14.1 \pm 1.8$ cm^3 mol^{-1} at 279.5 K for 2.
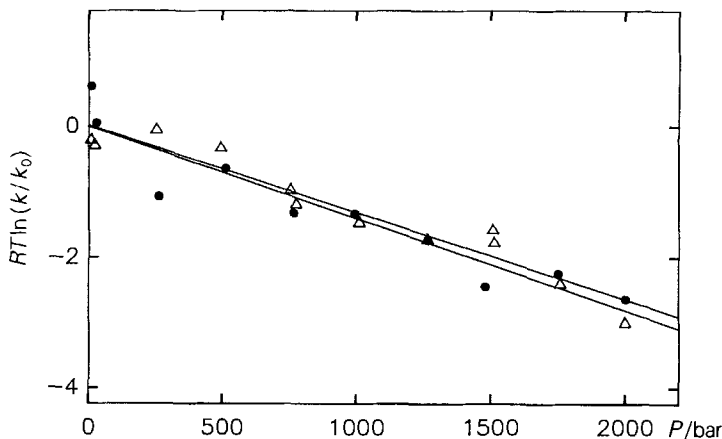
Fig. 3. *Pressure effect on the normalized natural logarithm of the rate constants for the CO scrambling in* **1** *at 253.1 K* (●) *and in* **2** *at 279.5 K* (△)

$$\ln(k) = \ln(k_0) - \Delta V^{\neq}\; P/RT \tag{1}$$

$$RT\ln(k/k_0) = -\Delta V^{\neq}\; P \tag{2}$$

Introducing the t-BuNC ligand in an axial position of **1** slows the CO scrambling process. The isocyanide ligand is a better σ-donor and weaker π-acceptor than CO, and a μ_2-CO group is a better π-acceptor than a terminal one. Therefore, the CO-bridged ground-state geometry of **2** is stabilized relative to that of **1**, and an increase in activation enthalpy should be expected (see *Table*).

The activation volumes of the merry-go-round process in **1** and **2** are equal within experimental error. A similar study of the merry-go-round of $[Ir_4(CO)_9\{\mu_3\text{-}(\eta^3\text{-}C_3H_6S_3)\}]$

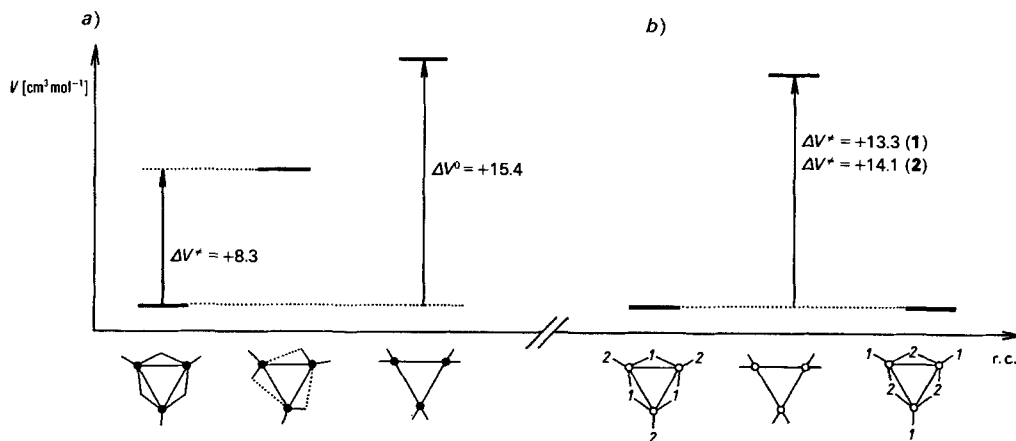Fig. 4. *Volume profiles for the merry-go-round process* a) *in* $[Ir_4(CO)_9\{\mu_3\text{-}(\eta^3\text{-}C_3H_6S_3)\}]$ (● = Ir) *and* b) *in* **1** *and* **2** (○ = Rh). Only the basal face of the Ir cluster is shown; r.c. = reaction coordinate.

was published [12], which offers the only activation volume available for comparison. In contrast to **1** and **2**, 2 isomers of the Ir_4 cluster are present in solution, one with 3 edge-bridging CO's and the other with all CO's terminal. The difference in volume between the 2 isomers ($+15.4$ cm^3 mol^{-1}; see *Fig. 4a*) was attributed to the conversion of the 3 bridging CO's to the unbridged form. Since the activation volume ($+8.3$ cm^3 mol^{-1}) was about half of the reaction volume ($+15.4$ cm^3 mol^{-1}), and since the isomerization involves the breaking of three Ir–CO bonds to form 3 additional terminal CO's, a transition state characterized by 3 semi-bridging CO's was proposed. An unbridged transition state would have required a change of volume of $15.4/3 \approx 5.1$ cm^3 mol^{-1} per CO ligand. For the present Ru_3 clusters, the activation volume is greater than that of the Ir_4 cluster by *ca.* 6 cm^3 mol^{-1} (see *Fig. 4b*, showing the merry-go-round about the triangular face capped by the μ_3-(η^3-1,3,5-trithiane) ligand). One can, therefore, propose that the transition state of the merry-go-round has a geometry which is closer to the limiting dissociative case (with 6 equatorial, terminal CO's) than the semi-bridging transition state proposed for the Ir cluster.

Experimental Part

1. *General.* [$Ru_3(CO)_{12}$] was prepared according to a standard procedure [13], [$Ru_3(CO)_9\{\mu_3$-(η^3-$C_3H_6S_3$)\}] (**1**) [14] and [$Ru_3(CO)_{11}$ (*'BuNC*)] [15] according to published methods. The 1,3,5-trithiacyclohexane and *tert*-butyl isocyanide were purchased from *Fluka* and used as received. All operations were carried out under N_2 using standard *Schlenk* techniques. Solvents were purified, distilled from the appropriate drying agents, and stored under N_2. Prep. TLC: plates coated with Al_2O_3. IR Spectra: *Perkin-Elmer-FT-IR-1720* spectrophotometer. ^{1}H-NMR Spectra: *Bruker WM 400*; in (D_8)THF at normal temp. and atmospheric pressure; δ in ppm. Mass spectra were carried out by Prof. *T. A. Jenny*, Université de Fribourg. Elemental analysis was performed by the Mikroelementaranalytisches Laboratorium der Eidgenössischen Technischen Hochschule Zürich.

2. *(tert-Butyl isocyanide)octacarbonyl{μ_3-[η^3-(1,3,5-trithiane)]}triruthenium* (**2**). A soln. of [Ru_3('BuNC) (CO)$_{11}$] (50 mg, 0.072 mmol) and 1,3,5-trithiane (10 mg, 0.072 mmol) in hexane (30 ml) was refluxed in a 125-ml *Schlenk* tube for 8 h resulting in a light yellow precipitate and soln. The yellow solid was isolated and separated by prep. TLC (CH_2Cl_2). The lower of the two yellow bands contained **1**, while the fast-moving band contained the desired **2** (24 mg, 44%). IR (THF): 2159m, 2021s, 1988vs, 1956s, 1943vs, 1794vs. ^{1}H-NMR ((D_8)THF): 2.52 (s, 6 H); 1.31 (s, 9 H). FAB-MS (MeOH): 749 (M^+). Anal. calc. for $C_{16}H_{15}NO_8Ru_3S_3 \cdot 0.5$ C_4H_8O (784.7): C 27.55, H 2.44, N 1.78; found: C 27.51, H 2.47, N 1.78.

3. *^{13}C-Enrichment.* The ^{13}C-enriched compounds **1** and **2** were prepared starting from ^{13}C-enriched [$Ru_3(CO)_{12}$], prepared according to [16]. The enrichment in ^{13}C of the CO ligands of **1** and **2** was *ca.* 30%. ^{13}C-NMR ((D_8)THF, 178 K): **1**: 264.8, 200.8, 199.1; **2**: 269.3 (a), 268.3 (b), 203.6 (e), 200.2 (c), 199.9 (d; see *Fig. 2* for a–d). The molalities of the solns. used for the variable-temp. and -pressure experiments were between 0.03 and 0.04 m.

4. *NMR Measurements.* The spectra at variable temp. were recorded using a *Bruker AC-200* spectrometer (4.7 T) working at 50.323 MHz. The measurements were made between 178 and 343 K for **1** and 178 and 323 K for **2**. The variable-pressure experiments were performed using a *Bruker AM-400* spectrometer (9.4 T) working at 100.626 MHz. The measurements were made up to 2000 bar using a home-built high-pressure probe, designed for a *Bruker* wide-bore cryomagnet [17]. A built-in Pt resistor allowed temp. measurements with an accuracy of ± 1 K. By pumping a thermostated liquid through the bomb, the temp. was stabilized to ± 0.2 K at 253.1 K for **1** or 279.5 K for **2**. The spectra were obtained by using 32 K data points resulting from 17000 to 25000 scans accumulated over a total spectral width of 17 kHz for **2** or 23 kHz for **1**. To improve the signal to noise ratio, exponential filters (line-broadening) of 1 Hz for **1** or 10 Hz for **2** were used. $\delta(C)$'s are referred to Me_4Si and measured with respect to the THF signal at 68.6 ppm. The EXSY ^{13}C-NMR spectra of **2** were obtained in (D_8)THF at 263 K from NOESY experiments using TPPI [18]. The spectral width was 7575.7 Hz in both $F1$ and $F2$ domains, a shifted squared cosine bell was applied in both domains prior to *Fourier* transformation. The mixing time was 100 ms.

REFERENCES

[1] S. R. Cooper, *Acc. Chem. Res.* **1988**, *21*, 141; S. C. Rawle, B. J. Sewell, S. R. Cooper, *Inorg. Chem.* **1987**, *26*, 3769.

[2] A. J. Blake, R. O. Gould, A. J. Holder, T. I. Hyde, G. Reid, M. Schröder, *J. Chem. Soc., Dalton Trans.* **1990**, 1759.

[3] A. F. Hill, N. W. Alcock, J. C. Cannadine, G. R. Clark, *J. Organomet. Chem.* **1992**, *426*, C40.

[4] R. J. Crowte, J. Evans, M. Webster, *J. Chem. Soc., Chem. Commun.* **1984**, 1344.

[5] G. Suardi, A. Strawczynski, R. Ros, R. Roulet, F. Grepioni, D. Braga, *Helv. Chim. Acta* **1990**, *73*, 154.

[6] S. Rossi, K. Kallinen, J. Pursiainen, T. T. Pakkanen, T. A. Pakkanen, *J. Organomet. Chem.* **1992**, *75*, 2227.

[7] S. J. Edwards, B. F. G. Johnson, J. K. Khan, J. Lewis, P. R. Raithby, *J. Organomet. Chem.* **1992**, *426*, C44.

[8] L. Hoferkamp, G. Rheinwald, H. Stoeckli-Evans, G. Süss-Fink, *Helv. Chim. Acta* **1992**, *75*, 2227.

[9] S. Rossi, J. Pursiainen, T. A. Pakkanen, *J. Organomet. Chem.* **1992**, *436*, 55.

[10] 'EXCHANGE', program library, Computing Center, University of Lausanne.

[11] 'EYRING', program library, Computing Center, University of Lausanne.

[12] A. Orlandi, U. Frey, G. Suardi, A. E. Merbach, R. Roulet, *Inorg. Chem.* **1992**, *31*, 1304.

[13] M. I. Bruce, C. M. Jensen, M. L. Jones, 'Reagents for Transition Metal Complex and Organometallic Syntheses', Ed. R. J. Angelici, John Wiley & Sons, Inc., New York, 1990, p. 216.

[14] L. Hoferkamp, G. Rheinwald, H. Stoeckli-Evans, G. Süss-Fink, *Helv. Chim. Acta* **1992**, *75*, 2227.

[15] M. I. Bruce, J. G. Matisons, R. C. Wallis, *Aust. J. Chem.* **1982**, *35*, 935.

[16] D. J. Darensbourg, R. L. Gray, M. Pala, *Organometallics* **1984**, *3*, 1928.

[17] U. Frey, L. Helm, A. E. Merbach, *High Pres. Res.* **1990**, *2*, 237.

[18] G. Bodenhausen, H. Kogler, R. R. Ernst, *J. Magn. Res.* **1984**, *58*, 370.