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vergence with a final *R* factor of 0.061 for 348 variables refined against 2693 data with $|F_o| > 4.0\sigma|F_o|$. All other details regarding the crystal structure are reported in the supplementary material.

Syntheses of 2–4. One equivalent of the appropriate trichloride (i.e., PCl_3, $AsCl_3$, $SbCl_3$) was added with vigorous stirring to a solution of **1** (200 mg, 0.205 mmol) and triethylamine (75 mg, 0.743 mmol) in benzene (10 mL). After stirring at 25 °C for 1 h, solid Et_3NHCl was removed by vacuum filtration, and then the volatiles were evaporated (0.1 Torr, 25 °C). Hexane extraction of the residue, filtration (to remove Et_3NHCl or any unreacted **1**), and evaporation of the volatiles (0.1 Torr, 25 °C) afforded the respective pnictites (**2–4**) in virtually quantitative yield (by ^{13}C NMR). Analytically pure samples were obtained by the slow diffusion of acetonitrile in benzene solutions of **2–4**.

Characterization Data for 2. ^1H NMR (25 °C, $CDCl_3$): δ 1.78 (br m, 35 H), 1.24 (br m, 35 H), 0.80 (br m, 7 H). $^{13}C\{^1H\}$ NMR (25 °C, $CDCl_3$): δ 27.49, 27.46, 27.42, 26.90, 26.88, 26.79, 26.67, 26.56, 26.40 (s, CH_2), 23.25, 23.20 (s, 3:4 for CH). $^{29}Si\{^1H\}$ NMR (25 °C, C_6D_6): δ −66.95 (s, 3 Si), −67.99 (s, 1 Si), −71.44 (d, 3 Si, $^2J_{Si-P}$ = 35.8 Hz). $^{31}P\{^1H\}$ NMR (25 °C, C_6D_6): δ 86.12 ($^2J_{P-Si}$ = 35.8 Hz for ^{29}Si satellites). MS (65 eV, 200 °C; relative intensity): *m/e* 1000 (M^+, 100%), 918 ($M^+ - C_6H_{10}$, 40.2%), 836 ($M^+ - 2C_6H_{10}$, 8.5%). Anal. Calcd for $C_{42}H_{77}O_{12}PSi_7$ (Found): C, 50.36 (50.45); H, 7.75 (7.52). Mp 258–265 °C (dec).

Characterization Data for 3. ^1H NMR (25 °C, $CDCl_3$): δ 1.73 (br m, 35 H), 1.23 (br m, 35 H), 0.75 (br m, 7 H). $^{13}C\{^1H\}$ NMR (25 °C, $CDCl_3$): δ 27.53, 27.49, 26.90, 26.85, 26.73, 26.64, 26.58 (s, CH_2), 23.80, 23.27, 23.17 (s, 3:3:1 for CH). $^{29}Si\{^1H\}$ NMR (25 °C, C_6D_6): δ −67.65, −67.84, −70.48 (s, 3:1:3). MS (65 eV, 200 °C; relative intensity): 1044 (M^+, 0.2%), 961 ($M^+ - C_6H_{10}$, 100%), 879 ($M^+ - 2C_6H_{10}$, 52%). Anal. Calcd for $C_{42}H_{77}AsO_{12}Si_7$ (Found): C, 48.25 (48.49); H, 7.42 (7.47). Mp 249–252 °C.

Characterization Data for 4. ^1H NMR (25 °C, $CDCl_3$): δ 1.74 (br m, 35 H), 1.22 (br m, 35 H), 0.75 (br m, 7 H). $^{13}C\{^1H\}$ NMR (25 °C, $CDCl_3$): δ 27.67, 27.55, 27.05, 26.95, 26.67 (s, CH_2), 24.26, 23.44, 23.24 (s, 3:3:1 for CH). $^{29}Si\{^1H\}$ NMR (25 °C, C_6D_6): δ −67.76, −68.53, −69.65 (s, 1:3:3). MS (65 eV, 200 °C; relative intensity): 1008 ($M^+ - C_6H_{10}$, 100%), 926 ($M^+ - 2C_6H_{10}$, 32%). Anal. Calcd for $C_{42}H_{77}O_{12}SbSi_7$ (Found): C, 46.18 (46.67); H, 7.10 (7.13). Mp 266–69 °C.

Synthesis of 5. A solution of $(t\text{-}BuO)_3Bi^2$ (88 mg, 0.205 mmol) in ~3 mL of benzene was added to a suspension of **1** (200 mg, 0.205 mmol) in 5 mL of benzene. Stirring for 2 min at 25 °C produced a homogeneous solution, which was evaporated to give a virtually quantitative yield of **5**. ^1H, ^{13}C, and ^{29}Si NMR spectra of the crude product indicate that the purity is >95%. Unfortunately, the compound decomposes on standing in solution to a complex mixture of unidentified products, and could not successfully recrystallized under a variety of conditions. ^1H NMR (25 °C, C_6D_6): δ 2.17, 1.78, 1.65, 1.37, 1.29 (br m, 70 H); 1.07 (br m, 7 H). $^{13}C\{^1H\}$ NMR (25 °C, $CDCl_3$): δ 28.31, 28.14, 27.93, 27.87, 27.54, 27.50, 27.40, 27.32 (s, CH_2); 26.21, 24.33, 23.97 (s, 3:3:1 for CH). $^{29}Si\{^1H\}$ NMR (25 °C, C_6D_6/C_7H_8): δ −67.83, −67.88, −69.27 (s, 1:3:3).

Reaction of 2 with Me_3Al: Synthesis of 6. Neat $AlMe_3$ (19.4 μL, 14.6 mg, 0.200 mmol) was added via syringe to a solution of **2** (200 mg, 0.200 mmol) in 5 mL of benzene. After stirring for ~10 min at 25 °C, the volatiles were removed in vacuo to afford a quantitative yield of **6** as a white powder. The material obtained in this manner is spectroscopically pure. Unfortunately, all attempts to recrystallize the complex failed because of its extremely high solubility in all organic solvents with which it does not react. ^1H NMR (25 °C, C_6D_6): δ 2.05–1.10 (br m, 70 H), 1.02 (m, 7 H), −0.094 (s, 9 H). $^{13}C\{^1H\}$ NMR (25 °C, C_6D_6): δ 27.63, 27.58, 27.42, 27.15, 27.11, 27.04; 26.98, 26.88, 26.59 (s, 6:6:6:6:3:3:2:2:1 for CH_2), 23.59, 23.46, 23.27 (s, 1:3:3 for CH), −8.88 (br s). $^{29}Si\{^1H\}$ NMR (25 °C, C_6D_6): δ −66.97, −67.91 (s 3:1 Si), −70.76 (d, 3 Si, $^2J_{Si-P}$ = 35.6 Hz). $^{31}P\{^1H\}$ NMR (25 °C, C_6D_6): δ 62.89 (s).

Oxidation of 2 to 7. Dry ozone (~2% in O_2) was introduced at a rate of 8 mL/min into a solution of **2** (200 mg, 0.200 mmol) in 5 mL of benzene. After 10 min, the solvent was removed in vacuo (0.1 Torr, 25 °C) to afford a quantitative yield of analytically pure **6**. ^1H NMR (25 °C, $CDCl_3$): δ 1.73 (br m, 35 H), 1.24 (br m, 35 H), 0.929 (m, 3 H), 0.83 (m, 4 H). $^{13}C\{^1H\}$ NMR (25 °C, $CDCl_3$): δ 27.34, 27.68, 27.68, 27.09, 26.74, 26.68, 26.48, 26.46, 26.34, 25.87 (s, 6:6:6:6:3:3:2:2:1 for CH_2), 22.87, 22.62 (s, 1:3 for CH), 22.32 (d, 3 CH, $^3J_{C-P}$ = 3.6 Hz). $^{29}Si\{^1H\}$ NMR (25 °C, $CDCl_3$): δ −67.21, −68.27 (s, 3:1), −69.18 (d, 3 Si, $^2J_{Si-P}$ = 10.2 Hz). $^{31}P\{^1H\}$ NMR (25 °C, $CDCl_3$): δ −44.95 (m). MS (65 eV, 200 °C; relative intensity): 1016 (M^+, 100%), 934 ($M^+ - C_6H_{10}$, 89%), 852 ($M^+ - 2C_6H_{10}$, 11%), 770 ($M^+ - 3C_6H_{10}$, 5%). Anal. Calcd for $C_{42}H_{77}O_{13}PSi_7$ (Found): C, 49.57 (49.50); H, 7.63 (7.50).

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Supplementary Material Available: X-ray crystal data for **2** including experimental procedures and tables of crystal data, atomic coordinates, thermal parameters, bond lengths, and bond angles (9 pages); a listing of calculated and observed structure factors (12 pages). Ordering information is given on any current masthead page.

Isotopic Exchange Studies on the Cluster Anion $[HRu_3(CO)_{11}]^-$ in Solution: Direct Evidence for Intramolecular Fluxionality in Clusters

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Summary: Variable-temperature ^{13}C NMR studies on a 1:1 mixture of $[K(18\text{-crown-6})][HRu_3(CO)_{11}]$ (^{13}C enriched) and $[K(18\text{-crown-6})][DRu_3(CO)_{11}]$ (nonenriched) in CD_2Cl_2–$CHFCl_2$ reveal that the ligand mobilities in the cluster anions are indeed *intramolecular* fluxional processes.

Fluxional processes are a common feature of transition-metal carbonyl clusters in solution. The coalescence phenomena in the variable-temperature ^{13}C NMR spectra of a vast number of polynuclear metal carbonyl complexes have been interpreted in terms of an *intramolecular* stereodynamic behavior based on either ligand migration within the cluster or metal rearrangement within the ligand envelope.[1-3] While this interpretation provides a con-

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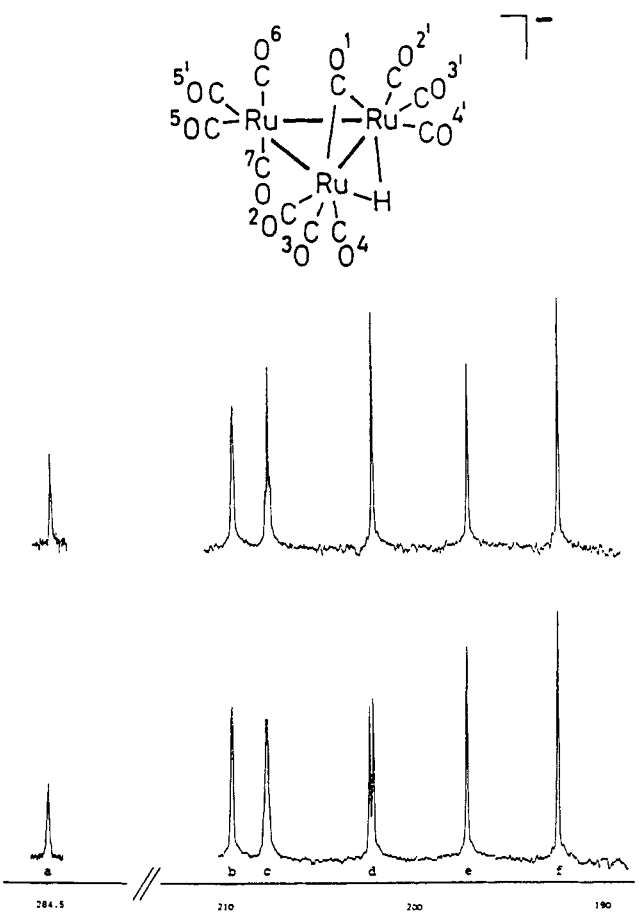
sistent model for the temperature dependence, to our knowledge, an *intermolecular* ligand exchange between the carbonyl cluster species has never been ruled out as an alternative explanation, although kinetic studies of substitution reactions[4] show that an intermolecular ligand exchange involving a dissociative pathway should be significantly slower than the dynamic processes considered here. We now report the findings of isotope labeling experiments which demonstrate that the fluxional processes observed in the cluster anion $[HRu_3(CO)_{11}]^-$ (1)[5] must indeed proceed through an *intramolecular* mechanism.

In order to prove unambiguously that the ligand mobility in a transition-metal cluster is intramolecular, the $^{13}C-^{1}H$ coupling of a carbonyl hydrido cluster must be shown to be unaffected by the presence of the deuterated analogue. Since the $^{13}C-^{2}D$ coupling constants[6] are 6.5 times smaller than the corresponding $^{13}C-^{1}H$ coupling constants, the choice of carbonyl hydrido clusters is limited by the requirement of a $^{13}C-^{1}H$ coupling of at least 10 Hz for reliable results. We therefore selected the cluster anion $[HRu_3(CO)_{11}]^-$ (1), in which one of the $^{13}C-^{1}H$ couplings is as high as 13 Hz.

The low-temperature limiting spectrum of 1 at −110 °C, reproduced in Figure 1, is identical with that published earlier.[5] However, the original assignment of the ^{13}C NMR signals to the individual carbonyl ligands in 1 has to be modified on the basis of decoupling experiments, as already suggested by Shore et al.[7] The measurements at different field strengths and an 8000-Hz broad-band decoupling experiment proves the two peaks d to be a doublet and not two singlets as originally proposed.[5] The two unique carbonyl ligands 6 and 7, which were supposed to give rise to these two peaks, are almost indistinguishable and show up as one signal (b), as proposed by Shore et al.[7] To make sure that it is indeed signal b which should be attributed to the nonequivalent carbonyl ligands 6 and 7, we carried out a ^{13}C-shift experiment: By addition of 300 mg of $Pr(fod)_3$ (fod = 7,7-dimethyl-1,1,1,2,2,3,3-heptafluoro-4,6-octanedionate) as the shift reagent to 50 mg of $[K(18\text{-crown-}6)][HRu_3(CO)_{11}]$ (enriched) in 3 mL of a 1:2 mixture of CD_2Cl_2 and $CHFCl_2$, signal b splits into two signals in the proton-decoupled ^{13}C NMR spectra. The same effect is also observed with the tetraethylammonium salt of ^{13}C-enriched cluster anion 1. These findings are in accordance with the assumption of strong ion-pairing effects in solution based on infrared studies.[8] The complete reassignment of the ^{13}C NMR signals of anion 1 is given in Figure 1.

On the basis of the reassignment of the ^{13}C NMR signals of 1 the interpretation of the fluxional processes[5] has to be modified. We therefore repeated the variable-temperature ^{13}C NMR measurements of 1 (tetraethylammonium salt) over the temperature range of −90 to +33 °C (Figure 2). The spectra show that pseudorotation of both the $Ru(CO)_4$ moiety (carbonyls 5, 5′, 6, and 7) and the $HRu_2(CO)_6$ moiety start at about the same temperature; at −60 °C both signals b and e as well as signals a, c, and f broaden. The fact that signal d stays unaffected at this temperature suggests that carbonyls 2 and 2′ (trans with respect to the hydrido bridge) are not involved in the exchange process with the carbonyl bridge 1 unless the temperature is raised to −40 °C. The complete carbonyl scrambling is observed only above 0 °C.



signal	∂[ppm]	$J(^{13}C-^{1}H)$ [Hz]	carbonyl
a	284.5	6.3	1
b	209.5	-	6,7
c	207.7	5.3	4,4′
d	202.2	13.0	2,2′
e	197.1	-	5,5′
f	192.2	-	3,3′

Figure 1. Carbonyl region of the ^{13}C NMR spectra (67.88 MHz) of $[K(18\text{-crown-}6)][HRu_3(CO)_{11}]$ (anion 1) in CD_2Cl_2–$CHFCl_2$ (1:2) at −110 °C: (bottom) ^{1}H-coupled spectrum; (top) 8000 Hz ^{1}H-decoupled spectrum.

For the crossover experiment, equivalent amounts of $[K(18\text{-crown-}6)][HRu_3(^{13}CO)_{11}]$ (anion 1 27% enriched in ^{13}C) and $[K(18\text{-crown-}6)][DRu_3(CO)_{11}]$ (anion 2) were dissolved in a mixture of CD_2Cl_2 and $CHFCl_2$. The ^{13}C NMR spectrum ($^{13}C-^{1}H$ coupled, 100 scans) of this solution at −110 °C showed only the signals of 1, since 2 was not ^{13}C-enriched. After it was warmed to +10 °C, at which temperature the spectrum indicated complete carbonyl scrambling, the solution was again cooled to −10 °C. The spectrum recorded at this point showed no change with regard to the spectrum before warming. If the fluxional processes in 1 involved an intermolecular mechanism, either carbonyl or hydride exchange between the cluster anions would lead to a mixed deuterated and ^{13}C-enriched species. Such an intermolecular exchange should therefore be reflected in the ^{13}C NMR spectra. Hence, although the

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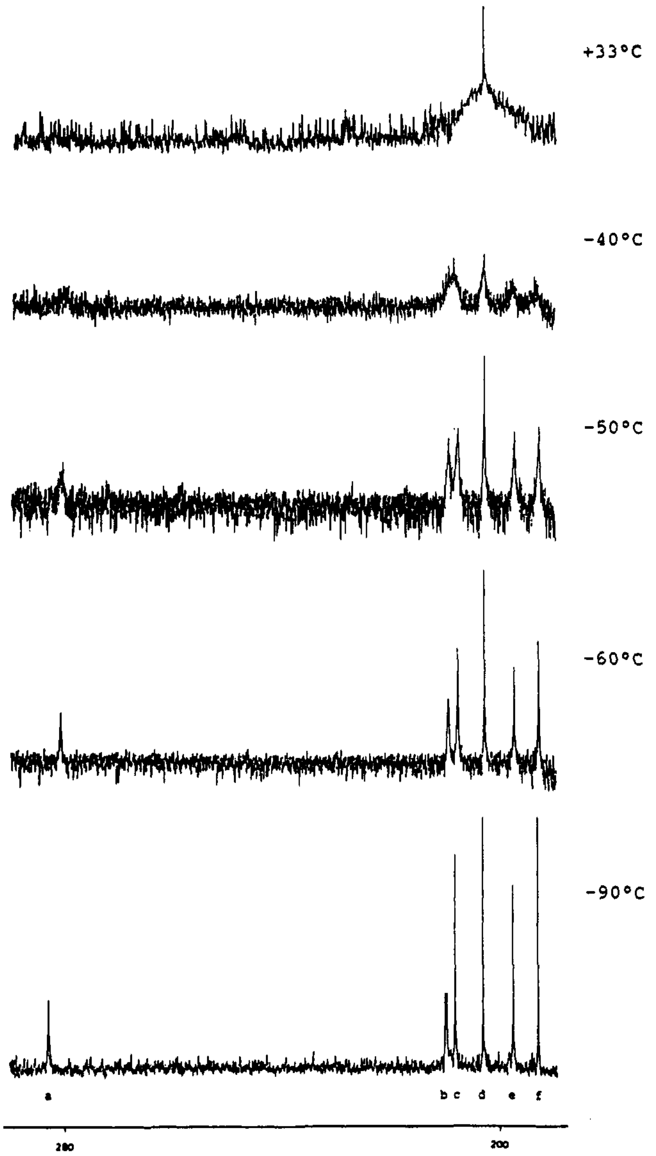

Figure 2. Variable-temperature ^{13}C NMR spectra (^1H decoupled) of $[NEt_4][HRu_3(CO)_{11}]$ (anion 1) in CD_2Cl_2–$CHFCl_2$ (1:2) from −90 to −40 °C and the spectrum at +33 °C in CD_2Cl_2 (^{13}C enriched, 67.88 MHz).

^{13}C–^1H coupling constants of the doublets a and b are perhaps too small to show the additional ^{13}C–^2D coupling, the deuterium coupling should be clearly seen by the signal d ($J(^{13}C$–$^1H) = 13.0$ Hz). For mixed $^2D/^{13}C$-enriched species, as expected for an intermolecular exchange, the doublet d should be split into a 1:1:1 triplet by the additional deuterium coupling.

The results showed that there are no signals for the isotope exchange product, ^{13}C-enriched $[DRu_3(CO)_{11}]^-$, which would be expected in the case of an intermolecular carbonyl exchange at 10 °C. Therefore, an intermolecular carbonyl exchange mechanism must be ruled out. These findings are presumably also significant for other transition-metal clusters.

Experimental Section

Starting Materials. The cluster anion $[HRu_3(CO)_{11}]^-$ (1) was synthesized from $Ru_3(CO)_{12}$ by following a procedure analogous to that published in ref 5; an equivalent mixture of KBH_4 and 18-crown-6 was used instead of $NaBH_4$. The salt was crystallized from methanol. The ^{13}C-enriched anion 1 was synthesized analogously from ^{13}C-enriched $Ru_3(CO)_{12}$, obtained by the enrichment method of Darensbourg et al.[9] The deuterated anion $[DRu_3(CO)_{11}]^-$ (2) was prepared from 1 as the [K(18-crown-6)] salt under D_2 pressure (10 bar, 12 h, 20 °C) in acetone-d_6. All the compounds were handled under purified nitrogen with use of degassed and N_2-saturated solvents.

Spectroscopic Studies. A mixture of 25 mg of $[K(18\text{-crown-}6)][HRu_3(^{13}CO)_{11}]$ (anion 1 27% ^{13}C enriched) and 25 mg of $[K(18\text{-crown-}6)][DRu_3(CO)_{11}]$ (anion 2) was placed in a 10-mm NMR tube and dissolved in a mixture of 1 mL of CD_2Cl_2 and 2 mL of $CHFCl_2$. This solution was used for the variable-temperature measurements under standard conditions (100 scans, ^{13}C–^1H coupled). Since 1 was exclusively enriched, only the ^{13}C NMR signals of 1 were observed at −110 °C. A control experiment with pure $[K(18\text{-crown-}6)][DRu_3(CO)_{11}]$ confirmed that the ^{13}C NMR resonances of nonenriched 2 do not show up under these conditions. The mixture of 1 (^{13}C enriched) and 2 (not ^{13}C enriched) was warmed to +10 °C. After the ^{13}C NMR spectrum was recorded, the sample was kept 1 h at this temperature and then again cooled to −110 °C, at which temperature the initial spectrum was reproduced. The NMR spectra were recorded with a Bruker WM 270 spectrometer.

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