present in the ^{11}B NMR spectra.[7]

Although transition metal dicarbollide complexes which are structurally similar to the "bent" metallacenes[12] are unknown, synthesis of the uranium complex[2] demonstrated that use of a larger metal permitted two $C_2B_9H_{11}^{2-}$ ligands to be configured in a bent fashion. A lanthanide metal in the +3 oxidation state should allow a more favorable accommodation of the high negative charge brought to a complex by two dicarbollide ligands. One rational approach to the synthesis of a 4f metallacarborane sandwich complex of this type is the addition of a second dicarbollide ligand to **2** or **3** with concomitant oxidation of the metal to the +3 state. Reaction of **2** with $[PPN]^+$[*closo*-3,1,2-$TlC_2B_9H_{11}]^-$ [13] affords the desired bis(dicarbollide) complex in accord with this strategy.

An equimolar amount of **2** (0.88 mmol) was added anaerobically as a solid to a THF solution of $[PPN]^+$[*closo*-3,1,2-$TlC_2B_9H_{11}]^-$, the resultant slurry was stirred for 12 h at room temperature and then filtered to remove the Tl metal that had formed. Reduction of the volume of the filtrate afforded greenish-yellow crystals; an X-ray diffraction study[14] established the composition and structure as $[PPN]^+[3,3\text{-}(THF)_2$-*commo*-3,3′-$Sm(3,1,2\text{-}SmC_2B_9H_{11})_2]^-$, **4**.[15] Compound **4** could be isolated in 47% yield in accord with eq 1.

$$Sm(C_2B_9H_{11})(THF)_4 + [PPN]^+[\textit{closo}\text{-}3,1,2\text{-}TlC_2B_9H_{11}]^- \xrightarrow[\text{rt}]{\text{THF}} [PPN]^+[3,3\text{-}(THF)_2\text{-}\textit{commo}\text{-}3,3'\text{-}Sm(3,1,2\text{-}SmC_2B_9H_{11})_2]^- + Tl^0 + 2THF \quad (1)$$

As shown in Figure 2, the coordination geometry of **4** can be described as a distorted tetrahedron (average ring centroid–Sm–O(THF) angle is 108.2°). The two η^5-dicarbollide ligands and the two THF solvate molecules comprise the coordination sphere about Sm. The centroid–Sm–centroid angle of 131.9 (5)° is similar to the values found for trivalent bis (C_5Me_5) lanthanide complexes that contain other ligands in the metal's coordination sphere.[16]

Raymond has advanced a structural model[17] that has been very successful in predicting metal to ligand bond lengths in organo-f-element complexes, lending support to the idea that the bonding in these compounds is predominantly ionic. By use of this criterion, an effective ionic radius for the dicarbollide ligand can be determined: 1.66 Å in both 7-coordinate **3b** and 8-coordinate **4**. The fact that the effective radius is the same in both complexes and is also similar to the value for the cyclopentadienyl ligand (1.64 ± 0.04 Å)[17] suggests that the bonding in these lanthanide dicarbollide compounds is largely ionic and does not differ greatly from the bonding observed in the analogous cyclopentadienyl compounds.

Complexes of Sm and Yb have also been synthesized with the $C_2B_{10}H_{12}^{2-}$ ligand,[19] and characterization data[20] supports their formulation as neutral monocage compounds analogous to **2** and **3**. Reactivity studies with these new classes of organo-f-element complexes[21] incorporating the $C_2B_9H_{11}^{2-}$ and $C_2B_{10}H_{12}^{2-}$ ligands are currently under way, and these results will be reported in a full paper.[20]

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Supplementary Material Available: Tables of positional and thermal parameters, interatomic distances and angles, and details of crystallographic data collection for **4** (10 pages). Ordering information is given on any current masthead page.

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(14) (a) A greenish-yellow crystal of **4** was mounted in a 0.5-mm glass capillary in a glovebox. Diffraction data were collected at 25 °C on a diffractometer equipped with a small Huber circle built by Prof. C. E. Strouse of this department, with Mo Kα radiation, to a maximum 2θ of 45°. Data were corrected for Lorentz, polarization, and absorption effects. The structure was solved by a combination of conventional Patterson, Fourier, and full-matrix least-squares techniques. (b) Crystallographic data for **4**: triclinic space group $P\bar{1}$; $a = 8.9374$ (3) Å, $b = 17.8703$ (6) Å, $c = 18.4989$ (7) Å, $\alpha = 107.5402$ (9)°, $\beta = 91.085$ (1)°, $\gamma = 90.705$ (1)°, $V = 2816$ Å^3, $Z = 2$; unique data ($I > 3\sigma(I)$), 5324; $R(R_w)$, 5.3% (6.5%). All calculations were performed on the DEC VAX 750 of the J. D. McCullough Crystallography Laboratory with the UCLA crystallographic package.

(15) Data for **4**: IR (Nujol mull, NaCl) ν_{BH} 2523 (s), ν_{THF} 1011 (s), 859 (s) cm^{-1}; $^{11}B\{^1H\}$ NMR (in CH_2Cl_2) −6.0 (2), −11.1 (1), −16.8 (2), −19.5 (1), −25.2 (3); ^1H NMR (in CD_2Cl_2, referenced to residual solvent protons at 5.32 ppm) B–H resonances 10.5 to 9.7, 4.0 to 2.6, −2.0 to −3.1 ppm, (weak and broad), carboranyl C–H 4.89 (s, broad), coordinated THF 2.74 (s, broad), 1.34 (s, broad).

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(21) Magnetic measurements on the paramagnetic complexes **2** and **4** are in progress and these results will be reported in a full paper.[20]

An EXAFS Study on the Morphology Change of Ru Catalyst by CO Adsorption

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Great attention has recently been paid to the reconstruction of clean metal surface upon adsorption.[1] Then a question naturally arises what happens to the small metal clusters in supported catalyst upon adsorption, which is the first step of catalytic reaction. Surface spectroscopic techniques like LEED are not available for small particles on the surface of supports, and mainly infrared absorption spectroscopy has provided information, rather indirectly, through the number of observed vibrations and the frequency shifts of adsorbed species such as CO. Recently Van't Blik et al. reported in a series of papers[2-4] direct evidence of a structural change of Rh clusters supported on Al_2O_3 upon CO adsorption. They observed a drastic change in EXAFS (extended X-ray absorption fine structure) by the admission of CO. It was concluded that this change was caused by the disruption of the metal–metal bond, resulting in formation of $Rh(CO)_2$ species. As far as we know, this is the only example of straightforward evidence of morphology changes caused by adsorption, and it is not certain whether or not this phenomenon is general. In this communication we present another example of the morphology change upon adsorption for Ru supported on γ-Al_2O_3 and show this phenomenon is not limited to Rh.

Highly dispersed Ru/γ-Al_2O_3 catalyst was prepared according to Okuhara et al.[5] In short, $Ru_3(CO)_{12}$ was adsorbed from hexane

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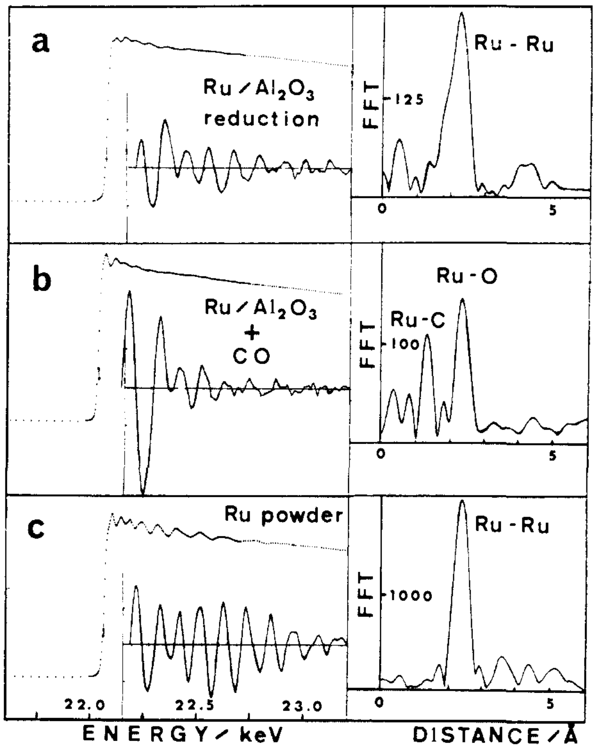

Figure 1. Observed Ru K edge EXAFS spectra, extracted oscillations, and associated Fourier transforms of (a) Ru/γ-Al_2O_3 reduced at 723 K in H_2, (b) after admission of 200 Torr CO, and (c) Ru powder. All the spectra were obtained at room temperature.

solution in a flow of nitrogen at room temperature onto γ-Al_2O_3, which had been pretreated by heating at 773 K in air for 10 h and under vacuum for 2 h. Then the solvent was removed in a flow of nitrogen at 323 K. The catalyst thus obtained was pressed into a self-supporting disk and was placed in an in situ EXAFS cell with Be windows and a heater. The decomposition of $Ru_3(CO)_{12}$ supported on γ-Al_2O_3 was carried out under vacuum at 723 K for 2 h. Then the catalyst was reduced with hydrogen at 723 K for 2 h, followed by evacuation at the same temperature for 1 h. The sample was kept in the vacuum tight cell in order to minimize the possible effect of water.[6] The dispersion of the catalyst was estimated to be 0.8 from the hydrogen chemisorption. The EXAFS measurements were performed by a double crystal X-ray spectrometer equipped with Ge(444) and LiF(220) bent crystals, which will be reported elsewhere.[7]

Figure 1a shows the Ru K EXAFS spectrum, extracted oscillation, and the associated k^3-weighted Fourier transform of the reduced 2 wt % Ru/γ-Al_2O_3 catalyst. For comparison, those of Ru powder as a reference are shown in Figure 1c. The long EXAFS oscillation of the catalyst is characteristic of heavy elements and clearly shows that the neighbor atoms around Ru are also Ru, but its amplitude and consequently the peak intensity in the associated Fourier transform are much weaker than those of bulk Ru, indicating that Ru clusters are highly dispersed. A shoulder of the main peak in the Fourier transform may come from the oxygen atoms of the support. From the least-squares curve fitting[8] by the use of the theoretical scattering amplitude and phase factor by Teo and Lee,[9] the Ru–Ru interatomic distance in the cluster is determined to be 2.55 Å, which is shorter than the bulk value by as much as 0.13 Å, and the coordination number is about 4, which is significantly smaller than the bulk value of 12. Smaller coordination numbers[8,10] and shorter interatomic distances[11,12] have often been observed in very small metal clusters. Reduction in the coordination number is due to the surface effect and can be employed to estimate cluster sizes.[9] If three-dimensional hcp structure of the bulk metal is assumed, a cluster consisting of about 7 atoms has coordination number close to 4.

The adsorption of CO on the catalyst thoroughly changes the local structure around Ru atoms as evidenced in the EXAFS spectrum shown in Figure 1b. Compared with spectrum a, the oscillation decreases very rapidly with increasing *k* values, which means that now the neighboring atoms around Ru are not heavy elements but light ones. The associated Fourier transform shows two peaks which should be assigned to Ru–C and Ru–O of the adsorbed CO molecule. Due to the uncertainty of the electron mean free path in this system the coordination number of CO could not be determined, while the CO/Ru ratio of 1.2 was obtained from the chemisorption study. The spectrum does not change by vacuum pumping at room temperature, but the same spectrum as in Figure 1a is reproduced after heating the sample to 573 K while evacuating. The spectrum change between spectrum a and spectrum b is completely reversible by repeated adsorption/desorption cycles.

The following conclusions can be drawn from the present study. First, ultradispersed Ru clusters are formed on alumina support from $Ru_3(CO)_{12}$. Second, Ru–Ru bonds in the very tiny Ru clusters are disrupted by CO adsorption, leading to the formation of a new species like $Ru(CO)_n$. Third, the tiny Ru clusters are recovered by CO desorption.

These findings are closely related to those reported on Rh, and they suggest that the disruption of metal–metal bonds in tiny clusters upon adsorption of CO is a ubiquitous phenomenon. Since it is unlikely that decomposition takes place in large metal particles or single crystal, this might supply a clue to the understanding of dependences of selectivity and activity on particle size in catalytic reactions.[5]

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Chelation-Enhanced Fluorescence in 9,10-Bis(TMEDA)anthracene

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We wish to report that the fluorescence emission intensity of a structurally simple anthracene derivative, 9,10-bis(TMEDA)-anthracene[2] (**1**), increases over 1000-fold in the presence of zinc chloride. The mechanism by which this *chelation-enhanced fluorescence* (CHEF) occurs indicates that fluorescence detection of metal ions is possible by using structurally simple conjugates between fluorescent molecules and nitrogenous ligands.

In 1986, we reported the synthesis and characterization of anthracene **1** and its binuclear zinc chloride complex (**2**).[3] During the course of our work, we observed that acetonitrile solutions of compound **1** did not exhibit the high fluorescence characteristic of, for example, 9,10-dimethylanthracene; however, acetonitrile solutions of compound **2** were strongly fluorescent (blue) when irradiated with a long-wavelength UV light source. A survey of

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(1) Recipient of an Ohio State University graduate fellowship.

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