then provides intermediate B (Scheme I) from which Me_3Si^+ and Cl^- can easily eliminate[16b] to form **2**.

The mechanistic details of these reactions comprising particularly the crucial role of the R_2S coligand are investigated currently because, when understood,[18] this synthetic route may provide an interesting new entry into the synthesis of new types of μ-alkylidene–Pd compounds.

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Supplementary Material Available: Final values of refined positional and thermal parameters and an ORTEP view of **2** (40% probability) (2 pages). Ordering information is given on any current masthead page.

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(18) In intermediate B the SR_2 group must be present because of the influence this coligand exerts on the product formation (see Scheme I).

Formation of Fe–Os, Fe–Ru, and Fe–Co Bimetallic Particles by Thermal Decomposition of Heteropolynuclear Clusters Supported on a Partially Dehydroxylated Magnesia

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Bimetallic systems represent an important class of heterogeneous catalysts.[1,2] So far, most of the methods of preparation were mainly based on coimpregnation, ion-exchange, or coprecipitation techniques, which require high-temperature reduction of two metal salts adsorbed on an oxide support.

Recently, heteropolynuclear molecular clusters have been used as precursors of hypothetical bimetallic particles, which exhibited, in some cases, unusual catalytic properties in various kinds of reactions.[3-12] However, interpretation of the results was made difficult due to the lack of information regarding the real nature of the particles (size, surface, and bulk composition).

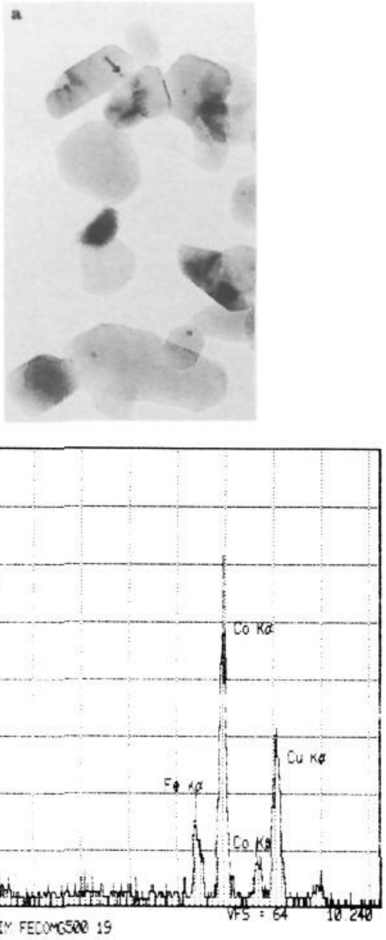

Figure 1. Fe–Co cluster issued from the decomposition of $HFeCo_3(CO)_{12}$/MgO at 500 °C under H_2: (a) TEM view of Fe–Co/MgO (500 000 magnification); (b) EDS spectrum of a 20-Å Fe–Co cluster (arrowed on (a)), taken with a 10 Å × 10 Å analysis window in the STEM VGHB 501 equipped with a Tracor EDX analyzer. The quantitative analysis from Fe Kα and Co Kα emission peak gives a ratio Co/Fe = 3.0 ± 0.4 (Cu Kα peak corresponds to the copper grid supporting the sample).

We wish to report here that with $H_2FeOs_3(CO)_{13}$, $H_2FeRu_3(CO)_{13}$, and $HFeCo_3(CO)_{12}$ supported on a partially hydroxylated magnesia, it is possible to obtain, after H_2 treatment at 400 °C, very small bimetallic particles, having the same bulk composition as that of the starting heteropolynuclear precursor cluster. This conclusion is based on high spatial resolution analytical microscopy.

The magnesia (100 m^2/g) was treated under O_2 for 10 h at 400 °C, evacuated at 400 °C under vacuum (10^{-5} torr), equilibrated with H_2O (25 torr) at 25 °C for 16 h, and then evacuated at 200 °C (16 h, 10^{-5} torr).

$H_2FeOs_3(CO)_{13}$, $H_2FeRu_3(CO)_{13}$, and $HFeCo_3(CO)_{12}$ were prepared according to known procedures.[13-15] The clusters were chemisorbed on magnesia from CH_2Cl_2 solutions. It has been

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Table I. Characterization of the Bimetallic Particles

precursor complexes	metal content/wt %	atomic ratio Fe/M cluster	atomic ratio Fe/M particle[a]	particle size/Å	comments
$H_2FeOs_3(CO)_{13}$	1,0	0.33	0.27 (0.05)	10-15	bimetallic particles only
$Fe_3(CO)_{12} + Os_3(CO)_{12}$	0,8	0.33	0	10-15	no Fe detected in all the particles
$H_2FeRu_3(CO)_{13}$	0,8	0.33	0.30 (0.15)	10-15	bimetallic particles only
$Fe_3(CO)_{12} + Ru_3(CO)_{12}$	1,1	0.33	0	10-50	no Fe detected in all the particles
$HFeCo_3(CO)_{12}$	0,9	0.33	0.33 (0.03)	20-40	bimetallic particles only

[a] Average ratios. The errors given in parentheses encompass all the values measured on at least 20 particles.

shown that, in the initial stage of the chemisorption, these clusters underwent proton abstraction by OH groups of the surface to give respectively $[HFeOs_3(CO)_{13}]^-$, $[HFeRu_3(CO)_{13}]^-$, and $[FeCo_3(CO)_{12}]^-$ (the cation being Mg^{2+} from the surface).[16] After removal of the solvent under vacuum, these supported anionic clusters were then treated under H_2 (400 torr) at 400 °C for 16 h. The final metal content was usually close to 1% (wt).

Coadsorption of two separate clusters ($Fe_3(CO)_{12} + M_3(CO)_{12}$ (M = Ru, Os); Fe/M = 1/3) was carried out under identical conditions. The two clusters were first adsorbed simultaneously on the magnesia support from a CH_2Cl_2 solution. $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$ were first strongly chemisorbed as $[HFe_3(CO)_{11}]^-$,[17] $[HRu_3(CO)_{11}]^-$,[18] and $[HOs_3(CO)_{11}]^-$.[19] Then, after removal of the solvent under vacuum, they were treated under H_2 (400 torr) at 400 °C for 16 h.

All these systems have been characterized by high-resolution analytical electron microscopy. Images were taken with a JEOL 100 C TEM and with a VGHB 501 field emission gun STEM. The latter, equipped with a Si-Li X-ray detector and TRACOR 5500 analyzer, was used to perform quantitative energy dispersive analysis (EDX) with a spatial resolution as small as 1 nm^2. Analysis has been carried out on large area of magnesia as well as on individual particles ranging from 1 to 5 nm. The atomic ratios between two elements were determined with an accuracy of 15%. Figure 1 gives a TEM view of a 2-nm FeCo bimetallic particle supported on magnesia.

The results of Table I indicate that for all the mixed-metal clusters studied, the particles are small and have a bimetallic composition. Besides, in two cases, the bulk composition of these particles is the same, within experimental error, as that of the starting clusters. Interestingly, the coimpregnation of $Fe_3(CO)_{12}$ + $Os_3(CO)_{12}$ or $Fe_3(CO)_{12}$ + $Ru_3(CO)_{12}$ does not result, after H_2 treatment, in the formation of bimetallic particles. In contrast, $H_2FeRu_3(CO)_{13}$ osmium or ruthenium particles are observed. Although iron was detected by EDX on large ensembles of MgO crystallites, the images did not show any contrast that could be attributed to Fe particles. This might indicate that iron is scattered all over the magnesia, probably in an oxidized form. With the $H_2FeRu_3(CO)_{13}$ precursor, the particles were found to be bimetallic but a reliable quantitative analysis of the Fe/Ru ratio could not be achieved. Although both Fe Kα and Ru Kα peaks were detected when the electron beam was scanned over the metal particles, the number of counts that could be accumulated under each peak was low, which leads to large statistical errors. Low counting rate was due to the instability of the Fe-Ru particles moving under the intense electron beam. In contrast Fe-Os particles were stable because of the low mobility of osmium (high melting point) and Fe-Co particles did not move because of their large size.

These results indicate that heteropolynuclear clusters supported on magnesia can be used to obtain small supported bimetallic particles of the same composition. Besides, coimpregnation of magnesia by two different monometallic clusters does not lead to the same results. The reasons why bimetallic molecular clusters exhibit such behavior is not clear. Indeed, the temperatures at which two different monometallic clusters start to decompose into metal particles are different,[18] and this may lead to separate metallic phases. In contrast, upon destruction of the heteropolynuclear clusters, the preexistence of metal-metal bonds might favor the formation of new metal-metal bonds between the two elements in the metal particles.

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Registry No. MgO, 1309-48-4; $H_2FeOs_3(CO)_{13}$, 12563-74-5; $H_2FeRu_3(CO)_{13}$, 12375-24-5; $HFeCo_3(CO)_{12}$, 21750-96-9; Fe, 7439-89-6; Os, 7440-04-2; Ru, 7440-18-8; Co, 7440-48-4.

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An Efficient Electrocatalytic Model Cytochrome P-450 Epoxidation Cycle

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We describe here an electrocatalytic cycle (Scheme I) in which molecular oxygen is activated toward olefin epoxidation by electrolytic reduction. This cycle is of special interest since it contains the essential elements of the cytochrome P-450 catalytic cycle:[1] dioxygen, reducing equivalents, metalloporphyrin catalyst, substrate, and activator.

The cycle has three major segments, each independently having literature precedent: (1) Initial reduction to Mn(II) with loss of chloride[2] followed by strong dioxygen binding[3] promotes a second reduction step to a Mn(II) superoxo complex.[4] (2) The latter, $(Mn^{II}Por)O_2^-$, complex has been shown to react with benzoyl chloride[5a] and with anhydrides[5b] to give metallo-acylperoxy complexes that undergo O-O bond heterolysis at room temperature to yield a high-valent manganese porphyrin complex capable of transferring one oxygen atom to a suitable substrate. (3) The reactivity of high-valent manganese with olefins has been extensively studied.[5a,6] Typically, the high-valent form is generated

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