Bull. Chem. Soc. Jpn., 72, 2357—2363 (1999)

Accounts

Reactions of Air-Polluting Gases (NO_x, SO_x) with Transition Metal Cluster Complexes

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(Received May 31, 1999)

As a molecular model for heterogeneous catalysis effected by fine metal particles, the reactions of NO, SO_2, and SO with hexanuclear ruthenium clusters have been investigated in detail. One typical reaction of gaseous NO with anionic cluster is a redox-type reaction to give an one-electron oxidation product in which the original cluster framework is retained. The other typical reaction is observed in the reaction of neutral clusters with NO leading to partially degraded products, to which not only NO, but also an NO_2 unit are coordinated. When a μ_2,η^3-allyl ligand is present in NO or SO_2 coordinated hexanuclear carbonyl clusters, variable temperature ^{1}H NMR spectra of the allyl terminal protons provide a good methodology to observe the fluxional behavior brought about by rapid migration of the NO and SO_2 ligands over the metal atoms in the cluster core. Stepwise reduction of cluster-bound SO_2 to SO and finally to S has been realized by the successive action of a Lewis acid and then CO or H_2.

One of the important topics in application of heterogeneous metal catalysis is removal of air polluting molecules from exhaust gases of combustion engines. A large number of studies have focused on reduction of nitrogen monoxide with hydrogen, carbon monoxide, and/or hydrocarbons by supported metal particles.[1,2] Removal of sulfur dioxide has attracted less attention but an important role of similar catalysts can also be expected. Naturally, efforts to elucidate the reaction procedure and thereby obtain a strategy for developing a better system have been made in the field of heterogeneous and surface sciences.[3,4] Although the recent spectroscopic and technological developments like scanning probe microscopy (SPM) have widened the scope of surface research[5] and enabled nanometer-order characterization of metal particles on a support,[6] it is still very difficult to trace net chemical reactions on metal surfaces, particularly those taking place on such small metal particles on a support.[7,8]

Organometallic cluster complexes have attracted substantial interest because of the often-referred analogies between cluster-coordinated molecules (ligands) and species bound to a heterogeneous metal surface,[9] but surprisingly few approaches have been taken in cluster chemistry toward understanding of the reaction of air polluting species. Several years ago, we initiated a project to investigate the reactions of gaseous NO_x and SO_x with high nuclearity ruthenium clusters hoping that they could provide molecular models of the reactions occurring on small metal particles. In this short article, we would like to summarize the results accumulated in our laboratory up to now, as well as their background and related reactions.

1. Hexaruthenium Carbide Carbonyl Clusters

Anionic and neutral hexanuclear ruthenium carbide carbonyl clusters, $[PPN]_2[Ru_6C(CO)_{16}]$ (**1**, PPN = $(Ph_3P)_2N^+$)[10] and $Ru_6C(CO)_{17}$ (**2**),[11] are the standard cluster complexes employed in the present work. The μ_6-carbido present in the center of the octahedral cluster framework appears to play an important role in some of the reactions described below, where drastic changes of the cluster skeleton can take place without entire decomposition.

Starting from a methyl derivative of **1**, $[Ru_6C(CO)_{16}(CH_3)]^-$ which was prepared in our laboratory, Izumi and Iwasawa have shown that the hexanuclear frame $[Ru_6C]$ is supportable on MgO and that this hexa-metal atom unit can reversibly take up eleven CO ligands (Eq. 1).[12,13]

$$[Ru_6C(\mu\text{-}OMg)_3]/MgO \underset{\text{evac. 523 K}}{\overset{CO+H_2}{\rightleftarrows}} [Ru_6C(CO)_{11}(\mu\text{-}OMg)_3]/MgO \qquad (1)$$

When neutral complex **2** was subjected to EI (electron-impact)/MS analysis at 543 K, 18 peaks were observed, which correspond to a parent peak and those due to successive losses of CO from it. The final peak at 617 was consistent with $[Ru_6C]^+$ and observed very strongly, while no peaks were present below it (Eq. 2).[14]

$$[Ru_6C(CO)_{17}]^+ \xrightarrow[-CO]{} [Ru_6C(CO)_{16}]^+ \xrightarrow[-CO]{} [Ru_6C(CO)_{15}]^+ \overset{\longrightarrow}{\underset{\longrightarrow}{\longrightarrow}} [Ru_6C]^+ \qquad (2)$$

Both of the observations suggest that these carbide carbonyl clusters may be regarded as a tiny metal particle consisting of six metal atoms and an interstitial carbide, outside of which is protected by chemisorption of an appropriate number of CO molecules.

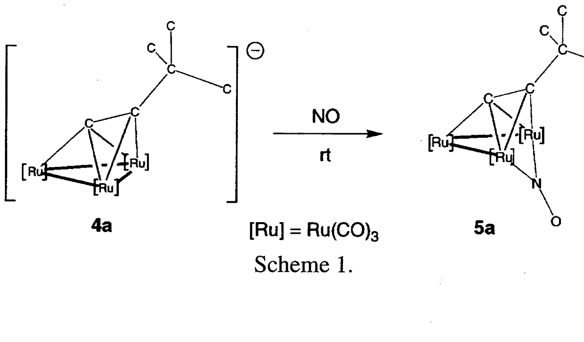
2. Trapping Gaseous NO on Cluster Complexes

When we started our project, there had already been known a number of cluster complexes with NO ligand.[15] Except for only one case, however, all of these complexes have been prepared by the reaction of NO^+ and NO_2^- on anionic and neutral carbonyl clusters, respectively, not by the direct reaction of gaseous NO. The neutral NO has been employed only in the reaction with $M_3(CO)_{12}$ to produce $M_3(CO)_{10}(NO)_2$ in 20 (M = Ru) and 14% (M = Os) yield, respectively.[16]

The basic problem in the reaction of gaseous NO with cluster complexes is facile cleavage of the metal–metal bond as well as substitution for a carbonyl ligand, which ends up with decomposition of the complex. This is because NO donates three electrons to the cluster and this third electron tends to function as a promoter to split M–M bonds.[15] In the successful preparation of $M_3(CO)_{10}(NO)_2$ mentioned above, a large amount of insoluble decomposition product is also concomitantly produced. We decided to examine a similar reaction of NO gas with the alkyne complex of triruthenium carbonyl $Ru_3(CO)_9(H)(C_2R)$ (**3a** R = ^{t}Bu, **3b** R = $SiMe_3$) expecting that the capping alkyne moiety would make the M–M bond stronger and prevent the cluster from decomposition on reacting with NO. Unlike the parent dodecacarbonyltriruthenium, **3** turned out to be very stable and did not react with NO even under forcing conditions. However, its anionic derivative $[PPN][Ru_3(CO)_9(C_2R)]$ (**4a** R = ^{t}Bu, **4b** R = $SiMe_3$), prepared by deprotonation of **3**, was found to react with NO gas smoothly at room temperature to give a neutral complex $Ru_3(CO)_9(C_2R)(NO)$ (**5**) in 40% isolated yield (Scheme 1).[17] X-Ray structural analysis revealed that a broken M–M bond is bridged by the NO ligand.

From this structural change, as well as the change of charge i.e. monoanionic reactant to give the neutral product, one may conclude that, of the three electrons which NO donates, two are used to cleave a Ru–Ru bond and the third is formally used to displace the anionic charge in **4**.

Having found that an anionic cluster can accommodate gaseous NO smoothly by a redox reaction, we turned to cluster complexes of higher nuclearity.[18] On bubbling of NO gas slowly through a CH_2Cl_2 solution of **1** at room temperature, red crystals of $[PPN][Ru_6C(CO)_{15}(NO)]$ (**6**) was isolated in 85% yield. The same complex has been prepared previously by the reaction of $Ru_6C(CO)_{17}$ with $[PPN][NO_2]$ and was proved to have a terminal NO ligand.[19] In our case of using **1**, neutral NO has replaced one carbonyl ligand and one negative charge. Since in complex **6** one negative charge is left, we tried further redox reaction with neutral NO, expecting to obtain a neutral bis(nitrosyl) complex. The reaction itself took place easily: the NO gas was bubbled slowly through a CH_2Cl_2 solution of **6** until characteristic IR absorption of **6** at 2022 cm^{-1} disappeared. Two complexes were isolated from the reaction mixture: a minor product obtained in about 13% yield was $[PPN][Ru_6C(CO)_{12}(NO)_3]$ (**7**) whose structure was determined by X-ray analysis (Fig. 1). The other complex isolated in about 23% yield was neutral and had composition $Ru_5C(CO)_{14}(NO)(NO_2)$ (**8**). The structure of its triphenylphosphine derivative (**8′**) was determined (Fig. 2) since the crystalinity of **8** was not good. The formation of complex **7** is simply replacement of three CO ligands (2-electron donor) with two NO ligands (3-electron donor) and therefore total valence electron number of the complex has been preserved. Complex **8** was a totally unexpected product. It has a distorted square-based pyramid structure with an interstitial carbide atom, but two of the edges have no direct metal–metal bond but are bridged by NO and NO_2 units. Whether the NO_2 ligand is derived by disproportionation of NO molecules ($3NO \rightarrow N_2O + NO_2$) on the cluster or it originates from a trace amount of NO_2, which may be present in the NO gas stream, is not clear yet. The reaction of gaseous



Scheme 1.

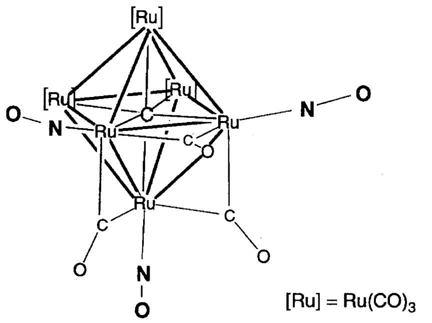


Fig. 1. Anionic part of complex **7**: $[Ru_6C(CO)_{12}(NO)_3]^-$.

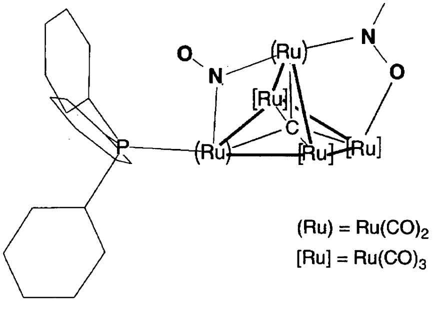


Fig. 2. Molecular structure of $Ru_5C(CO)_{13}(PPh_3)(NO)(NO_2)$ (**8′**).

NO_2 with either **1** or complex **6** in CH_2Cl_2 solution at room temperature also afforded a mixture of **7** and **8**. Apparently, reduction of neutral NO_2 to NO by a CO ligand on the cluster is a facile process.

The μ_2,η^3-allyl-coordinated cluster $[PPN][Ru_6C(CO)_{15}(C_3H_5)]$ prepared previously in this laboratory[20] exhibits a similar reaction pattern: On reacting with gaseous NO, it produced two neutral products smoothly. The first one was the "redox product" $Ru_6C(CO)_{14}(C_3H_5)(NO)$ (**9**) (Fig. 3) and the second complex was "degradation product" $Ru_5C(CO)_{11}(C_3H_5)(NO)_2(NO_2)$ (**10**) (Fig. 4) isolated in 30 and 11% yield, respectively. It is noteworthy that X-ray structural analysis of **9** has proved that the NO ligand is bonded to the Ru metal to which one of the allyl carbons coordinates.

Thus on trapping gaseous NO on carbonyl clusters, three different reaction types were observed: (1) two molecules of NO replace three CO ligands, (2) redox reaction where NO replaces one CO unit or cleaves one M–M bond while one negative charge is removed, and (3) coordination of NO accompanies fission of metal–metal bonds which lead to partial degradation of the cluster frame.

3. Trapping Gaseous SO_2 on Cluster Complexes

Since SO_2 is a two-electron donor, trapping it on a carbonyl cluster should be achieved simply by substitution for a CO ligand or cleavage of one metal–metal bond. The majority of SO_2 coordinated clusters reported so far are palladium and platinum complexes with or without CO ligands.[21] For the iron triad, several iron,[22—24] osmium,[25,26] and only one ruthenium cluster[27] with SO_2 ligand have been reported.

We have examined in detail the reaction of gaseous SO_2 with the hexanuclear ruthenium complexes.[28] Reaction of neutral carbide carbonyl cluster $Ru_6C(CO)_{17}$ (**2**) with SO_2 took place smoothly when the reactants were mixed at room temperature overnight in CH_2Cl_2 or in refluxing THF for 1 h, giving $Ru_6C(CO)_{16}(\mu\text{-}SO_2)$ (**11**) in good yield. Its IR spectra exhibited $\nu(SO_2)$ at 1246 and 1076 cm^{-1}. The $\nu(CO)$ which appeared at 2077 and 2057 cm^{-1} and the shift of the $\nu(CO)$ to higher energy by 9 cm^{-1} as compared to the parent carbonyl cluster indicate the strong electron-withdrawing nature of the SO_2 ligand. Coordination of SO_2 in **11**, however, is not very strong and gave starting $Ru_6C(CO)_{17}$ on stirring a THF solution under a CO atmosphere for 20 h.

The dianionic cluster $[PPN]_2[Ru_6C(CO)_{16}]$ (**1**) reacted in acetonitrile with gaseous SO_2 less easily and addition of Et_3NO was necessary to replace one CO ligand with SO_2 to give $[PPN]_2[Ru_6C(CO)_{15}(\mu\text{-}SO_2)]$ (**12**) in reasonable yield. X-ray structure analyses showed that the bonding parameters of the SO_2 were virtually the same in **11** and in **12**.

By changing the solvent to acetonitrile/methanol and thereby increasing the solubility of the amine oxide, a similar reaction afforded bis(sulfur dioxide) complex $[PPN]_2[Ru_6C(CO)_{14}(SO_2)_2]$ (**13**) (Fig. 5) but introduction of more than three SO_2 ligands was not successful. The IR $\nu(CO)$ shifts to higher energy are 15 and 16 cm^{-1} on going from **1** to **12** and further to **13**, indicating a steady decrease of electronic charge in the cluster core by the introduction of SO_2 ligand(s).

Complex **12** reacted with gaseous NO to produce a cluster complex bearing both SO_2 and NO ligands, $[PPN][Ru_6C(CO)_{14}(NO)(SO_2)]$ (**14**), following the redox type reaction. The relative position of these two ligands in the cluster has been found by X-ray analysis to be sharing the same metal atom (Fig. 6). Furthermore, the μ_2,η^3-allyl complex $[PPN][Ru_6C(CO)_{15}(C_3H_5)]$ underwent rapid reaction with SO_2 in CH_2Cl_2 at room temperature to give a 55% yield of $[PPN][Ru_6C(CO)_{14}(C_3H_5)(SO_2)]$ (**15**), whose structure was con-

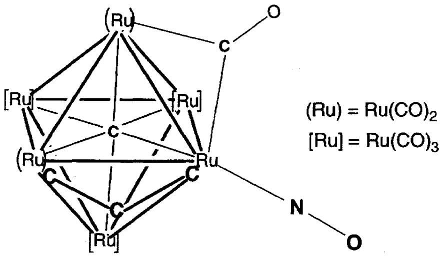


Fig. 3. Molecular structure of $Ru_6C(CO)_{14}(C_3H_5)(NO)$ (**9**).

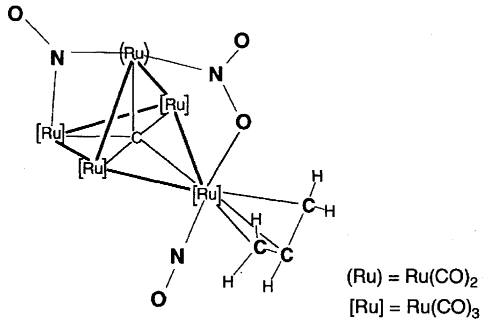


Fig. 4. Molecular structure of $Ru_5C(CO)_{11}(C_3H_5)(NO)_2(NO_2)$ (**10**).

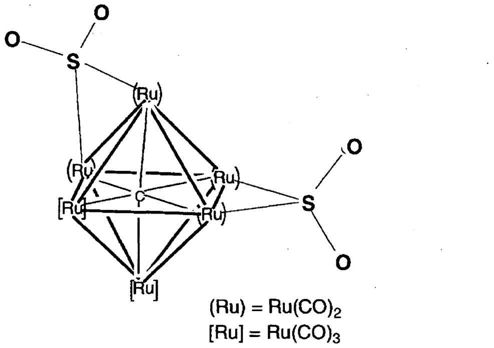


Fig. 5. Anionic part of complex **13**, $[Ru_6C(CO)_{14}(SO_2)_2]^{2-}$.

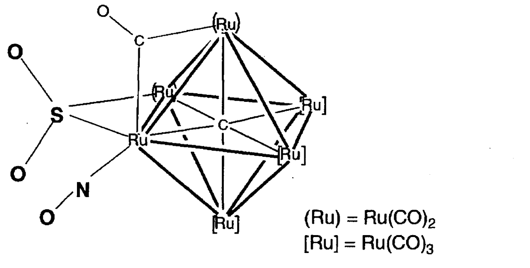


Fig. 6. Anionic part of complex **14**, $[Ru_6C(CO)_{14}(NO)(SO_2)]^{-}$.

firmed by X-ray single crystal analysis (Fig. 7).

4. Mobility of NO and SO_2 Ligands on the Cluster Core

The fluxional behavior of ligands in cluster complexes has attracted attention as a model for the movement of chemisorbed small molecules on metal surfaces. In this context, the mobility of ligands on a large cluster core appears particularly interesting and a number of reports have described the dynamics on clusters with five, six, and even higher nuclearities. Most of the fluxionality in these high-nuclearity clusters is concerned with carbonyl scrambling and/or hydride shift on the cluster cores[29] while mobility of NO or SO_2 has not been reported. We found that ^1H NMR spectra of coexisting μ_2,η^3-allyl ligand in complexes **9** and **15** is a convenient tool to monitor fluxional behavior of NO or SO_2 ligand.[30] This is based on the fact that signals due to protons at the allyl terminal carbons can easily provide information if the left and right halves of the cluster are magnetically equivalent.

Firstly, the mobility of carbonyl ligand was examined using ^{13}C NMR spectra of complex $Ru_6C(CO)_{16}(\mu\text{-}SO_2)$ (**11**). At room temperature, it is a sharp singlet; only below 183 K, did it separate into two broad peaks at $\delta = 211$ and 202.5, one of which was assignable to CO ligands coordinating to the two metals bridged by SO_2, while the other peak is due to the rest of the CO groups. The two peaks coalesce at 213 K, indicating facile scrambling of CO ligands even at −60 °C. As described below, the coordinated SO_2 should not migrate at this low temperature.[30]

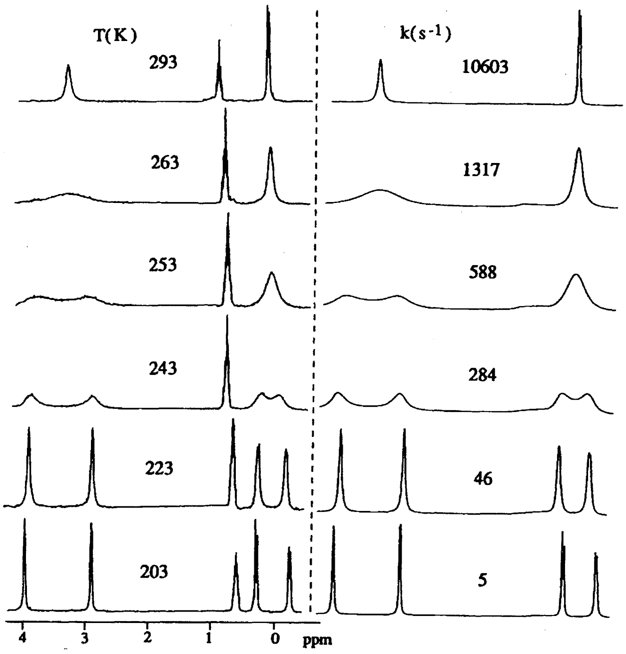


Fig. 8. Variable-temperature ^1H NMR spectra (400 MHz) of the C_3H_5 region of compound **9** in toluene-d_8. Left: observed spectra. Right: simulated spectra (*syn-* and *anti-*protons only) and rates.

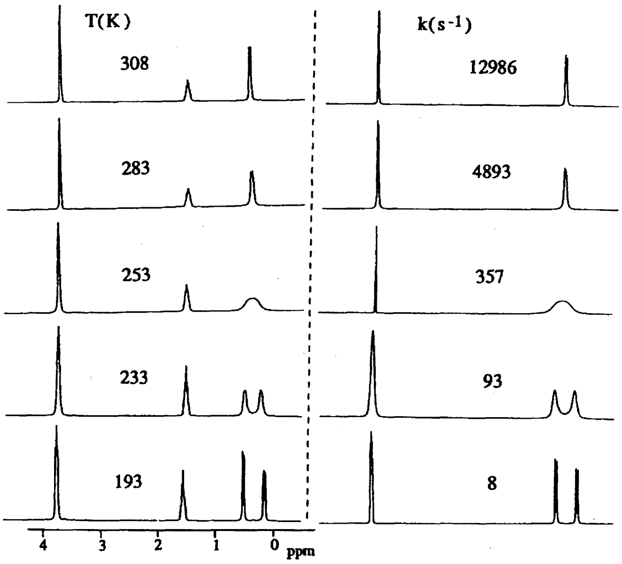


Fig. 9. Variable-temperature ^1H NMR spectra (400 MHz) of the C_3H_5 region of compound **15** in toluene-d_8. Left: observed spectra. Right: simulated spectra (*syn-* and *anti-*protons only) and rates.

A 400 MHz ^1H NMR spectra of **9** measured at various temperatures is shown on the left-hand side in Fig. 8. The spectrum at 203 K displayed two doublets due to non-equivalent *anti*-protons at $\delta = -0.23$ and 0.31, a multiplet for the central proton at $\delta = 0.63$, and a doublet and a singlet due to non-equivalent *syn*-protons at $\delta = 2.96$ and 4.04, respectively. The *anti* peaks coalesce at 253 K, the *syn* peaks at 263 K. The computer-simulated spectra (DNMR 5) depicted on the right-hand side of Fig. 8 afforded thermodynamic parameters $\Delta H^{\ddagger} = 9.5\pm0.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -7.8\pm0.5$ cal K^{-1} mol^{-1}. Likewise, variable-temperature NMR signals of complex **15** (Fig. 9) gave thermodynamic parameters: $\Delta H^{\ddagger} = 7.3\pm0.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = -16.6\pm3.2$ cal K^{-1} mol^{-1}. These fractional phenomena must be brought about by rapid migration of NO and SO_2 ligands over the cluster core skeleton. At the temperature NO and SO_2 migrate, mobility of the CO ligands must be even more facile. The other possibility, that the μ-allyl ligand rotates on the Ru–Ru edge, is unlikely: We prepared an analog of **9** where the allyl proton at the central carbon is replaced with an ester group, $Ru_6C(CO)_{14}(CH_2C(CO_2Me)CH_2)(NO)$ (**9′**), and found its fluxionality has parameters ($\Delta H^{\ddagger} = 9.2\pm0.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = -7.1\pm1.4$ cal K^{-1} mol^{-1}) virtually identical to those of **9**. If movement of allyl group is responsible in the temperature-dependent ^1H NMR change

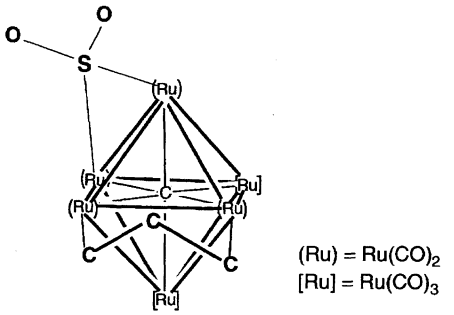


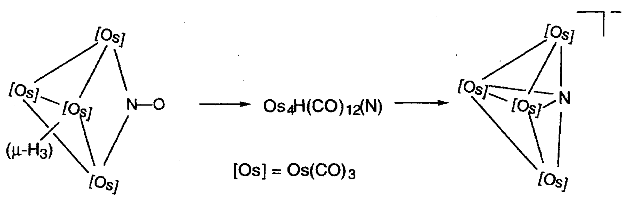
Fig. 7. Anionic part of complex **15**, $[Ru_6C(CO)_{14}(C_3H_5)(SO_2)]^-$.

of the cluster complex, steric and electronic effects of the carbomethoxy group should have given different thermodynamic parameters.

5. Reduction of Cluster-Bound NO

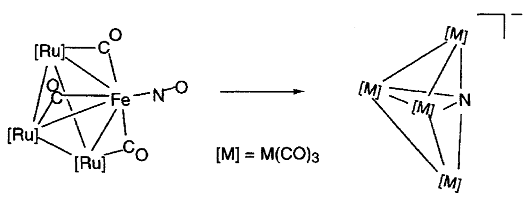
There are some cases known where a cluster-coordinated nitrosyl ligand undergoes deoxygenation reactions, although the NO ligand in these examples has not been introduced directly from gaseous NO.

Johnson et al. reported that on keeping CH_2Cl_2 or THF solutions of the tetranuclear nitrosyl complex $Os_4H_3(CO)_{12}(\mu_2\text{-}NO)$ for several days at room temperature, a nitride cluster, $Os_4(\mu\text{-}H)(CO)_{12}(\mu_4\text{-}N)$ was formed, which was further deprotonated into $[Os_4(CO)_{12}(\mu_4\text{-}N)]^-$ (Eq. 3).[31]



(3)

A somewhat similar reaction was found with Ru/Fe mixed-metal nitrosyl cluster; the reaction of $[FeRu_3(CO)_{12}(NO)]^-$ with CO gave in good yield a nitride complex as reported by Gladfelter (Eq. 4).[32]



(4)

Particularly interesting is the report by Martinengo and coworkers that gaseous NO itself can be utilized as the source of nitride in the reaction of NO/CO mixture with $[Rh_7(CO)_{16}]^{3-}$ to give directly $[Rh_6N(CO)_{15}]^-$.[33]

In all of these examples, the formation of interstitial nitride appears to be the driving force of the reactions. In the case of our NO-coordinated complexes, the presence of interstitial carbido presumably does not allow such driving force to operate.

6. Reduction of the Cluster-Bound SO_2

Removal of SO_2 from combustion gases by reduction to sulfur is of interest because harmless S_8 is often a more desirable product than oxidized form SO_4^{2-}.[34] The heterogeneous 0.5% $Ru/\gamma\text{-}Al_2O_3$ is one of the most active systems for the catalytic reduction of SO_2 with H_2 in the gas phase. The presence of Al_2O_3 appears crucial, since Ru metal alone has no catalytic activity.[35] It is likely that, aside from the role of Al_2O_3 as the carrier of fine metal particles, its Lewis acid character assists in the reduction.

Shriver and coworkers found that the $Fe_3(CO)_9$-bound SO_2 is transformed to μ_3-SO ligand on reduction with Na/Ph_2CO, but prior acetylation of the ligating SO_2 to an AcOSO ligand was necessary for its complete reduction to a sulfido ligand (Fig. 10). Although $[Fe_3(CO)_9(SO)]^{2-}$ represents the first example of a cluster-bound SO made by reductive cleavage of S–O bond in SO_2, addition of excess reducing agent resulted in decomposition of the cluster, and hence reactivity of the cluster-bound SO could not be studied.[23]

The reaction of **12** with a slight excess of methyl trifluoromethanesulfonate (MeOTf) in CH_2Cl_2 led to methylation of the SO_2 ligand to give a 70% isolated yield of $[PPN][Ru_6C(CO)_{15}(OSOMe)]$ (**16**). When an excess amount of MeOTf was reacted further with **16** at room temperature, a moisture-sensitive neutral cluster $Ru_6C(CO)_{15}(SO)$ (**17**) was isolated from the reaction mixture in 63% yield. The same complex was directly obtained by the reaction of **12** with an excess of MeOTf. A single-crystal X-ray analysis revealed that the SO ligand triply bridges the three Ru atoms. The presence of MeOMe liberated in the reaction mixture was detected by GLC. Thus the S–O bond cleavage of the cluster-coordinated SO_2 ligand is readily achieved by the action of Me^+ which acts as a Lewis acid. The same reaction was effected by the action of another Lewis acid, $BF_3\cdot OEt_2$, with **12** in CH_2Cl_2 solution (Scheme 2). In the reaction of **16** with $BF_3\cdot OEt_2$, **17** was obtained as expected, and the presumed BF_3-related product, $[PPN][MeOBF_3]$, was rationalized by hydrolysis of the reaction mixture and detection of methanol.

When a CH_2Cl_2 solution of **17** under one atmosphere of CO was heated at 70 °C for 6 h, a crystalline complex $Ru_6C(CO)_{16}S$ (**18**) could be isolated from the reaction mixture in 74% yield. As illustrated in Scheme 2, X-ray analysis showed that the reduction of the SO ligand to S in complex **18** is accompanied by incorporation of an additional CO into the cluster, cleavage of two metal–metal bonds, and swinging of the S-capped metal triangle to open the octahedral closed metal skeleton in **17**.[36]

The reduction of SO to S on the cluster was also effected by H_2. The reaction of **17** with H_2 (10 atm) and a small amount of CO (ca. 1.5 equiv) at 70 °C yielded four complexes isolated by column chromatography: The known trinuclear complex with a sulfido ligand, $Ru_3(CO)_9(\mu_2\text{-}H)(\mu_3\text{-}S)$ (12%),[37] new crystalline complexes $Ru_6C(CO)_{16}(H)_2S$ (**19**, 30%) and $Ru_6C(CO)_{16}(H)_4S$ (**20**, 9%), and a brown powder

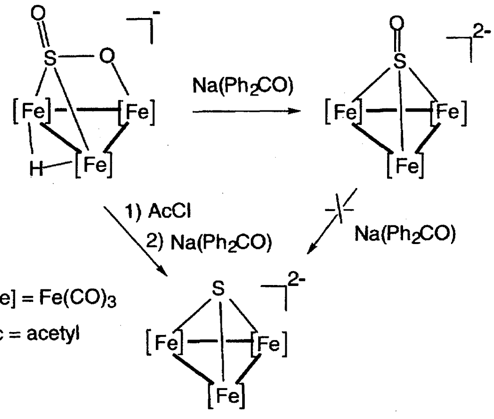
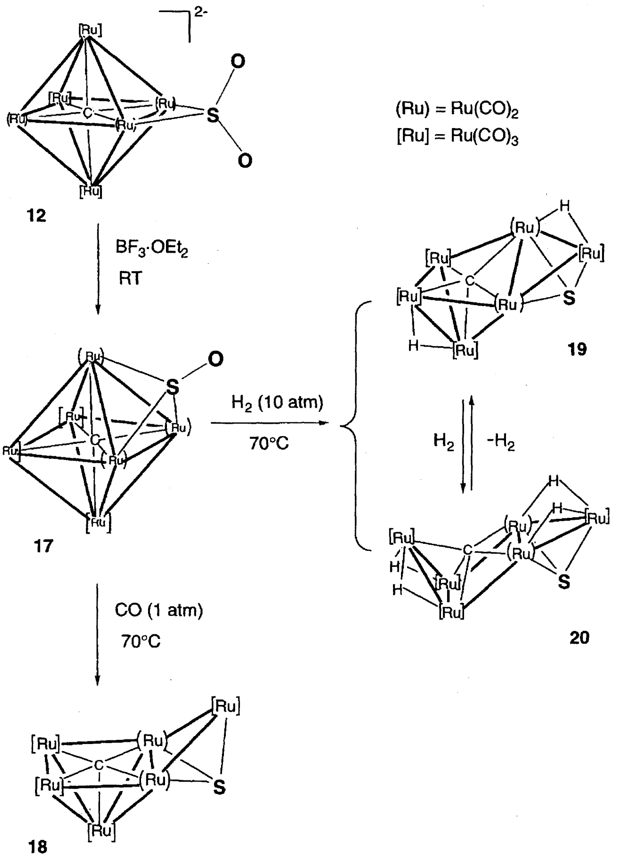


Fig. 10. Chemical reduction of SO_2 on trinuclear iron (Shriver, 1993).



Scheme 2.

(ca. 15%) which appeared to be a heptanuclear Ru complex with sulfur and CO ligands as supported by elemental analysis, IR, and ESMS. Structural characterization has shown that **19** has a shape analogous to that of **18** but, as a result of cleavage of additional metal–metal bond, the pentagonal unit is now very much distorted. Two more hydrogen atoms are present in **20**, and one more metal–metal bond has been broken, leading to an unique chair-like metal frame. The carbide atom is above the "chair" and well exposed: Such a carbon atom has attracted much interest as being relevant to carbon atoms bound to metal surfaces in heterogeneous catalysis.[38]

When a dichloromethane solution of **20** was allowed to stand under argon for 4 d, two hydrogen atoms were released to generate **19** almost quantitatively. But further release of dihydrogen from **19** to form **18** was not observed. Complex **19** in CH_2Cl_2 under 15 atm H_2 at room temperature very slowly but cleanly gave **20**. Complexes **19** and **20** are, therefore interconvertible, despite the large change in skeletal shape, by addition or removal of hydrogen atoms (Scheme 2).

Thus, reduction of sulfur oxide to S on highnuclearity ruthenium clusters takes place smoothly either by CO or H_2 once the cluster-bound SO_2 is transformed to SO. The first splitting of SO bond may be attained by the help of a Lewis acid.

7. Conclusion

Trapping of gaseous NO on ruthenium clusters takes place mainly in two ways: (1) with anionic cluster complexes, a redox-type reaction is the major process wherein one CO or one metal–metal bond is lost, as well as one negative charge, in order to accommodate three electrons which NO provides, and (2) with neutral cluster complexes, incorporation of neutral NO leads to degradation of the cluster frame. When the cluster has an interstitial atom which supports the cluster framework from inside, the degradation is often only partial and product complexes with smaller nuclearity may be isolated.

Reaction of SO_2 with carbonyl cluster is simply substitution of CO ligand for SO_2. The S–O bond cleavage of the cluster bound SO_2 was attained readily by the reaction with Lewis acids. Once a SO ligand is formed on the cluster, its reduction to S is easily done with CO or H_2. This reduction is accompanied by concomitant skeletal cluster rearrangement, where the resulting cluster shape depends on the amount of the reducing agent taken up by the cluster. The μ_2,η^3-allyl ligand on the NO or SO_2-coordinated cluster is a good probe to detect fluxional migration of these polluting molecules from one metal to the other. Variable temperature ^{1}H NMR spectra of *syn-* and *anti-*protons of the allyl group enable first determination of thermodynamic parameters for the mobility of these ligands on large metal clusters.

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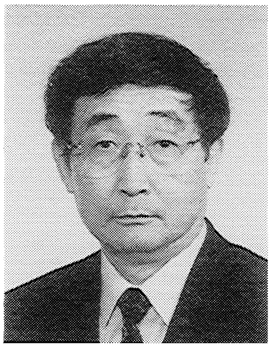

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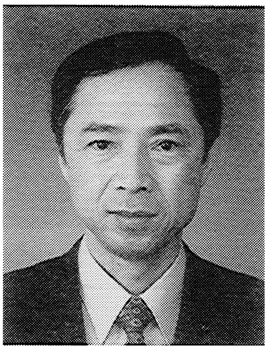

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