

**A Strategy for Generating Naked-Metal Clusters for Gas-Phase Reactivity Studies by FTICR–MS\*\***

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Cluster reactivity in the gas phase has been probed extensively with clusters generated by using a variety of custom-built sources. These include pulsed-laser vaporisation, continuous-operation ovens, fast-atom and secondary-ion sputtering, dc discharge, and pulsed-arc cluster-ion sources.<sup>[1]</sup> All generate an assortment of clusters of different nuclearities, and MS<sup>n</sup> techniques make selection of a particular sized cluster relatively straightforward. Both homo- and heteronuclear clusters are known.<sup>[2]</sup> All of these techniques employ a similar strategy to cluster synthesis; that is, the target is vaporised, the gas-phase metal atoms condensed, and the resulting clusters examined by mass spectrometry. We report herein an entirely different approach for the production of bare-metal gas-phase clusters, in which presynthesised transition-metal–carbonyl-cluster anions are delivered into the gas phase by a standard electrospray ionisation (ESI) source and stripped free of ligands by using collision-induced dissociation (CID) at the skimmer cone. The benefits of this approach are high yields of a specific cluster, no requirement for a special source, easy access to heteronuclear clusters and/or those with interstitial atoms, and a vast library of known clusters to draw from.

Because mixed-metal–carbonyl clusters are currently extensively used as precursors for metal nanoparticle catalysts (the clusters are absorbed inside mesoporous silica and calcined to remove the ligands),<sup>[3]</sup> examination of their gas-phase reactivity may provide insight into their action as

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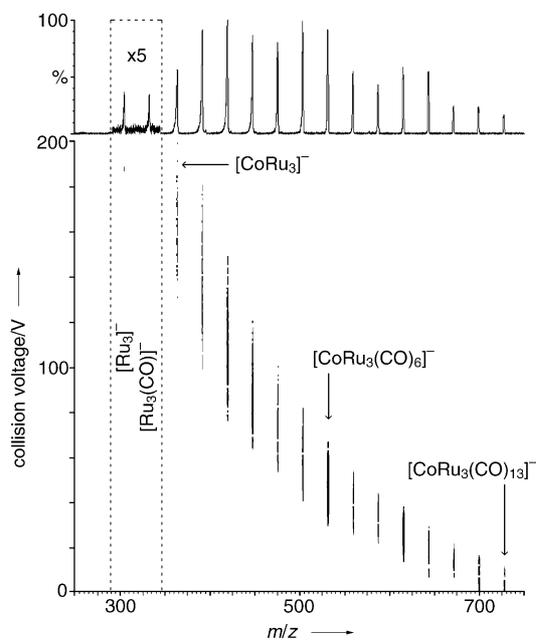
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catalysts in the solid state and represent a means of high throughput screening of potential catalysts for activity. Clusters used as catalysts are usually bimetallic, with well defined nuclearities and metal ratios (e.g.  $[\text{Pd}_6\text{Ru}_6]$ ,  $[\text{Ru}_{12}\text{Cu}_4\text{C}_2]$ ,  $[\text{Ru}_5\text{PtC}]$ ,  $[\text{Ru}_{10}\text{Pt}_2\text{C}_2]$ )<sup>[4]</sup> and often have interstitial atoms that confer extra structural stability. Generating such naked nanoparticles in the gas phase in useable yield presents what would appear to be an insurmountable challenge for conventional cluster sources, but is essentially trivial by using our approach. Most cluster syntheses form a number of products, and this is an advantage with a mass-spectrometric approach. The reaction mixture may be analysed directly, and separation, ligand stripping, and reactivity studies may be carried out on the various clusters in the gas phase. We have previously demonstrated the efficiency of the stripping process for a wide range of anionic clusters, with nuclearities up to 20 metal atoms and with up to 40 carbonyl ligands.<sup>[5]</sup> Neutral clusters may also be readily chemically derivatized and stripped in the same manner.<sup>[6]</sup> A report of a related strategy concerns stripping the cluster  $[\text{Pt}_4(\text{PF}_3)_8]$  by electron ionisation to provide the clusters  $[\text{Pt}_n]^+$  ( $n=1-4$ ),<sup>[7]</sup> but this approach relies on the precursor cluster being able to be transferred into the gas phase from the solid by heating under vacuum, thus the size and type of cluster that can be studied is limited (in particular, the anionic clusters of interest as catalyst precursors).

The high efficiency of the ligand-stripping process is illustrated in Figure 1, the energy dependent ESIMS/MS<sup>[8]</sup> of  $[\text{CoRu}_3(\text{CO})_{13}]^-$ .<sup>[9]</sup> Carbonyl ligands are removed from the core as free CO by collision-induced dissociation (CID) of the cluster ions with an inert target gas (e.g. Ar). The energy of the ion-molecule collisions is represented by the collision voltage, which may be smoothly increased from 0 to 200 V (other instruments alter different parameters to achieve CID,

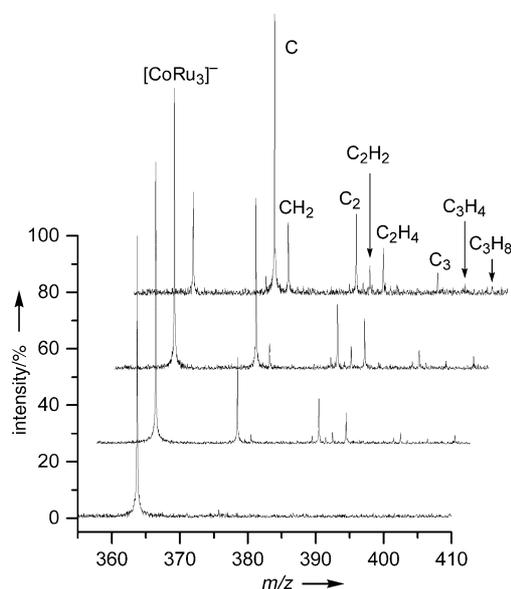


**Figure 1.** EDESIMS/MS of  $[\text{CoRu}_3(\text{CO})_{13}]^-$ . The highlighted area has been enhanced in intensity ( $\times 5$ ).

but the principle remains the same). The cross-peak in the bottom right-hand corner of the contour map represents the intact parent ion; the remainder are fragment ions. In addition to the carbonyl loss ions  $[\text{CoRu}_3(\text{CO})_n]^-$  ( $n=0-12$ ), all present in high intensity, at the highest collision voltages the metal core itself may be fragmented, and the ions  $[\text{Ru}_3]^-$ ,  $[\text{CoRu}_2]^-$ ,  $[\text{Ru}_2]^-$  and  $[\text{Ru}]^-$  generated (see Supporting Information).

Any of the fragment ions may be selected for reaction with neutral molecules using an FTICR mass spectrometer.<sup>[10]</sup> The reactivity of clusters in the gas phase has been investigated by many groups, often with the intention of developing gas-phase models for heterogenous catalysis.<sup>[11]</sup> We have taken a similar approach and, as a preliminary study, have investigated the reactivity of the naked cluster  $[\text{CoRu}_3]^-$  with  $\text{CH}_4$  and  $\text{H}_2$ .

The  $[\text{CoRu}_3]^-$  cluster reacts with methane after activation by SORI (sustained off-resonance irradiation). In Figure 2 are



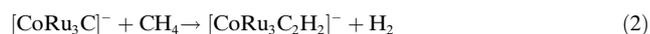
**Figure 2.** FTICRMS<sup>n</sup> of  $[\text{CoRu}_3]^- + \text{CH}_4$  after SORI activation for 0 s (bottom), 1 s, 5 s, and 15 s (top).

shown the spectra collected by reaction of  $[\text{CoRu}_3]^-$  with  $10^{-7}$  Torr of  $\text{CH}_4$  after SORI for 0, 1, 5 and 15 seconds. The primary process is dehydrogenation of methane molecules by the naked anionic metal cluster to produce carbide species [Eq. (1)].



Additionally, the partially hydrogenated species  $[\text{CoRu}_3\text{CH}_2]^-$ ,  $[\text{CoRu}_3\text{C}_2\text{H}_2]^-$  and  $[\text{CoRu}_3\text{C}_2\text{H}_4]^-$ ,  $[\text{CoRu}_3\text{C}_3\text{H}_4]^-$  and  $[\text{CoRu}_3\text{C}_3\text{H}_8]^-$  are observed. Long periods of activation do not lead preferentially to higher carbide species, nor to a significant change in the ratio of carbide species to the hydrogenated species. Rather, the main effect is enhancement of the C and  $\text{CH}_2$  species at the expense of the

bare-metal core. Formation of the higher hydrocarbon species necessarily proceeds sequentially [e.g. Eq. (2), (3)].



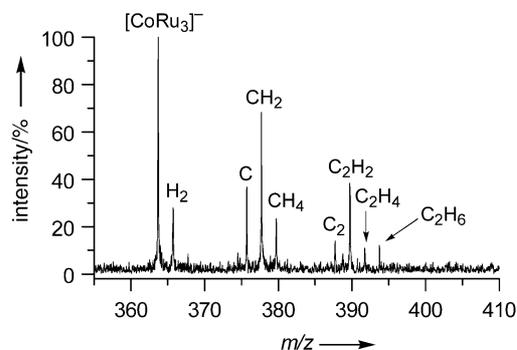
Similar reaction of the above products with methane will yield  $[\text{CoRu}_3\text{C}_3\text{H}_4]^-$  and  $[\text{CoRu}_3\text{C}_3\text{H}_8]^-$ . However, there is a limit to this process, as the intensity of the  $\text{C}_2$  and  $\text{C}_3$  species do not increase upon prolonged activation. Further reaction of these species may lead to hydrocarbon elimination [e.g. Eq. (4)].



These reactions are consistent with the observation that for the monocarbide species signal intensity increases significantly, mostly at the expense of the naked-metal core. Higher levels of C/H addition could be obtained by the selection of the  $[\text{CoRu}_3\text{C}]^-$  core followed by further reaction with  $\text{CH}_4$  (without additional activation), thus allowing observation of  $[\text{CoRu}_3\text{C} + n\text{CH}_4]^-$  ( $n=1, 2, 3$ ; see Supporting Information). We plan experiments with larger clusters to determine whether the extent of reactivity can be increased further.

The oligomerization of hydrocarbons on a metal surface is important, especially for the Fischer–Tropsch synthesis of hydrocarbons from CO and  $\text{H}_2$ .<sup>[12]</sup> Many features of the synthesis indicate that the mechanism is complicated and leads to a range and distribution of products, the appearance of different functional groups and variations with catalysts and conditions.<sup>[13]</sup> Experimental information on the various elementary reactions that make up the Fischer–Tropsch synthesis is important to overall understanding, and we consider that our strategy will provide fundamental data on certain steps in this process.

To extend the analogy to the Fischer–Tropsch synthesis, pulsed-in hydrogen gas was used to hydrogenate the mixture of clusters prepared from the reactions with methane. Figure 3 shows the results of this process, and the preferential hydrogenation of the carbides suggests that it is the carbon atom rather than the metal atoms that preferentially react with hydrogen. However, the presence of  $[\text{CoRu}_3\text{H}_2]^-$ ,



**Figure 3.** FTICRMS<sup>n</sup> of  $[\text{CoRu}_3]^- + \text{CH}_4$  after SORI activation for 5 s, followed by pulsed-in hydrogen gas.

$[\text{CoRu}_3\text{CH}_4]^-$ , and  $[\text{CoRu}_3\text{C}_2\text{H}_6]^-$  indicate that at least some of the hydrogen is adsorbed on the metal atoms, consistent with mechanisms in which  $\text{M}_n\text{--H}$  and  $\text{M}_n\text{--C}_x\text{H}_y$  species coexist on the metal surface.

In summary, transition-metal carbonyl clusters are a potentially rich source of naked (or partially ligated) clusters for gas-phase reactivity studies. Advantages of this approach include the direct analogy that can be drawn with supported nanocatalysts prepared from identical precursors, the potential of using the technique as a means of rapidly screening new clusters for catalytic activity,<sup>[14]</sup> and the fact that a conventional electrospray source can be used for the preparation of naked clusters. Work is underway to evaluate other clusters and their reactions with various gases, including CO,  $\text{H}_2$ ,  $\text{C}_x\text{H}_y$ ,  $\text{O}_2$ , and NO.

### Experimental Section

EDESI mass spectra were collected on a Micromass Quattro LC triple-quadrupole instrument, and reactivity studies were carried out by using a Bruker Daltonics 3 T APEX II FTICR mass spectrometer. See supporting information for further details.

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