Supplementary Material (ESI) for Dalton Transactions

Supporting Information for

Reactivity of the Zwitterionic Ligand $EtNHC(S)Ph_2P{=}NPPh_2C(S)NEt$ towards $Ru_3(CO)_{12}$. Ligand Fragmentation Leading to the Methideylamide [-N(Et)-CH-] μ_3-Bridging Moiety.

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The masses observed for cluster **6** and the intensity ratio of the different isotope peaks are in excellent agreement with the calculated pattern for the expected protonated molecule $\{Ru_3(CO)_7)(\mu_3\text{-}S)[(\mu_2\text{-}N{:}\eta\text{-}C{:}\kappa\text{-}P)Ph_2PN{=}PPh_2CHNEt](H)\}^+$ ([M+H]$^+$-CO). Furthermore, other signals were present at m/z = 1041, 1025, 1003, 947, 919 and 891 Da attributed respectively to [M+K]$^+$, [M+Na]$^+$, [M+H]$^+$, ([M+H]$^+$-2CO), ([M+H]$^+$-3CO), ([M+H]$^+$-4CO) (Figure S1).

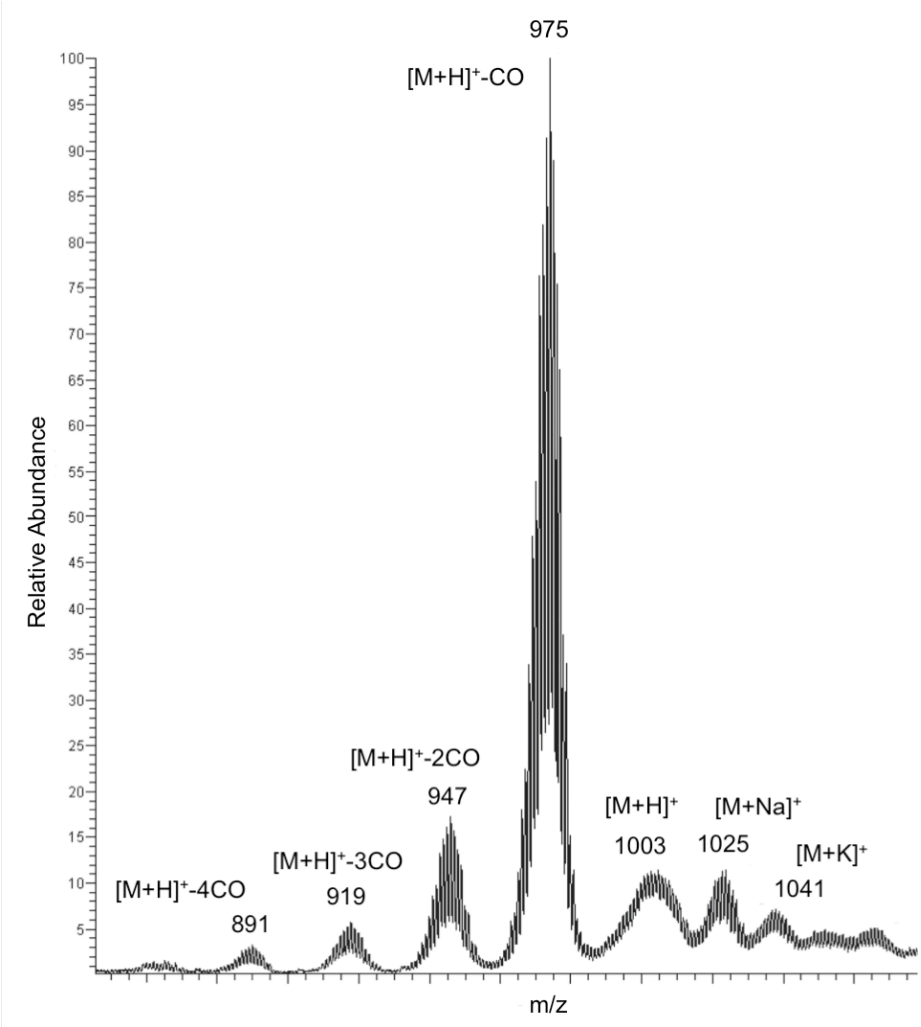

Figure S1 Positive ion ESI-MS of cluster **6** in CH_3OH.

These mass-to-charge ratios were interpreted as spectral fragments derived from the cluster in the LIT experiment, due to the desolvation temperature (250°C) and intrinsic instability of the CO molecule as ligand in gas phase. For refined tandem mass spectrum structural characterization, the gaseous $\{Ru_3(CO)_8)(\mu_3\text{-}S)[(\mu_2\text{-}N{:}\eta\text{-}C{:}\kappa\text{-}P)Ph_2PN{=}PPh_2CHNEt](H)\}^+$ ([M+H]$^+$) protonated cluster centered at *m/z* = 1003 Da was mass-selected for collision-induced dissociation (CID). The product ion mass spectrum (figure S2) shows the loss of one, two, three and four molecules of CO at *m/z* = 975, 947, 919 and 891 Da respectively.

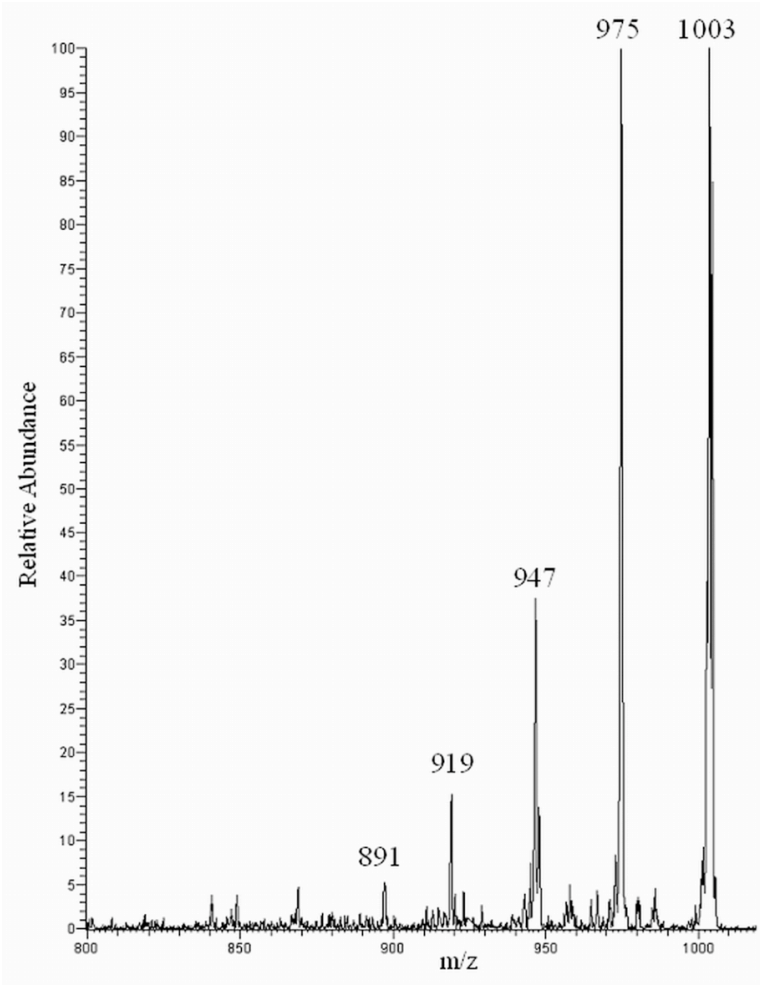

Figure S2 Positive ion ESI-MS-MS spectrum of *m/z* = 1003 $[M+H]^+$ of cluster **6** in CH_3OH.