κ^3-(N^C^C)Gold(III) Carboxylates: Evidence for Decarbonylation Processes

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Metallocarboxylic acids (or hydroxycarbonyls M-C-(O)-OH) are key intermediates in various transition metal-mediated processes involving CO and H_2O, such as the water-gas shift reaction (WGSR).[1] In contrast to the numerous reports on their reactivity, their isolation has required tremendous efforts and only a few examples have been characterized.[2] Regarding their reactivity, most of them undergo decarboxylation as a decomposition pathway. However, alternatives can involve decarbonylation, for those bearing strong coordinating ligand.[2a] Using the κ^3-(N^C^C) pincer developed in our group,[3] we synthesized and characterized in situ the first gold(III)carboxylic acid, by ^13C NMR and IR spectra at -30°C.[4] Increasing the temperature up to 25 °C led to a spontaneous loss of CO, which was identified by ^13C NMR and GC-MS. In the context of the gold-catalyzed WGSR, we could demonstrate that the insertion of CO leads to the formation of a carboxylate intermediate, which undergoes decarbonylation. Further work is currently ongoing in our laboratory to elucidate the mechanism of this process.