Ionic and Covalent Copper(II)-Based Catalysts for Michael Additions. The Mechanism[¶]

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[¶] Dedicated to prof. José Luis Soto on occasion of his retirement.

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General: Electrospray mass spectrometry analyses were recorded on a Navigator quadrupole mass spectrometer (Finnigan AQA ThermoQuest) equipped with an electrospray ion source. The instrument was operated in the positive (ESI+) ion mode at a probe tip voltage of 3 kV. The samples were introduced into the mass spectrometer ion source directly through a Rheodyne injector with a 20 μ L sample loop. The mobile phase flow (100 μ L/min of 70:30 v/v CH₃CN/H₂O) was delivered by a P2000 HPLC pump (ThermoQuest) to the vaporization nozzle of the electrospray ion source at 165 °C and nitrogen was employed as both a drying and a nebulizing gas. Skimmer cone voltages were varied between 10 and 100 eV. Spectra were typically an average of 15-20 scans. Theoretical isotope patterns were calculated by use of the *Isoform* program and used to aid assignment.

ESI-MS experimental parameters were previously optimized: the temperature of the electrospray ion source (165 °C) and the skimmer cone voltage (30 eV). The mobile phase used was CH₃CN/H₂O 70:30. No significant changes in the ESI mass spectra could be observed either by using pure CH₃CN as the mobile phase or by direct sample (in CH₂Cl₂) infusion to the vaporization nozzle of the electrospray ion source. However, since the relative intensities of the peaks vary depending on the experimental conditions, it is clear that the ESI-MS technique provides only qualitative information on the species present and not quantitative data on the concentrations present.

Table 2. Electrospray mass spectral data for various mixtures in CH₃CN/H₂O, 70:30.

Entry	Compounds and Mixtures	Identified species ^a
1 ^b	3a	$m/z = 157 [M + H]^+$
2 ^b	Adam-Box	$m/z = 451 [M + H]^+$
3 ^b	5a	$m/z = 227 [M + H]^+$ $m/z = 244 [M + NH_4]^+$ $m/z = 249 [M + Na]^+$ $m/z = 290 [M + Na + CH_3CN]^+$
4 ^{b,c}	Adam-Box + Cu(SbF ₆) ₂	$m/z = 451 [Adam-Box + H]^+$ $m/z = 554-558 (544) [(Adam-Box)Cu(CH_3CN)]^+$ $m/z = 598-602 (600) [(Adam-Box)Ag(CH_3CN)]^+$ $m/z = 789-794 (791) [(Adam-Box)Cu(CH_3CN)SbF_6]^+$, 10-CH₃CNSbF₆ $m/z = 963-967 (963) [(Adam-Box)_2Cu]^+$ $m/z = 1007-1011 (1009) [(Adam-Box)_2Ag]^+$
5 ^c	3a + Cu(SbF ₆) ₂	$m/z = 300-303 (300) [(enolate-3a)Cu(CH_3CN)_2]^+$, 16 . $m/z = 536-541 (538) [(3a)Cu(CH_3CN)_2SbF_6]^+$ $m/z = 610-614 (612) [(3a)_2CuSbF_6]^+$ $m/z = 628-632 (630) [(3a)_2Cu(H_2O)SbF_6]^+$
6 ^{b,c}	Adam-Box + Cu(SbF ₆) ₂ + 3a	$m/z = 668-672 (668) [(Adam-Box)Cu-enolate-3a]^+$, 17 .
7 ^c	Adam-Box + Cu(SbF ₆) ₂ + 5a	$m/z = 974-979 (976) [(Adam-Box)Cu(5a)SbF_6]^+$
8 ^c	Adam-Box + Cu(SbF ₆) ₂ + 3a + 4a	0 min, 1 hour, 2 hours, 5 hours: $m/z = 668-672 (668) [(Adam-Box)Cu(enolate-3a)]^+$, 17 . 1 day: $m/z = 963-967 (963) [(Adam-Box)_2Cu]^+$

^a Reported m/z values are from the lowest to the highest mass in the isotope envelope of the clusters; values in parentheses correspond to the most abundant peak. Unidentified ions in the spectra have not been included.

^b Samples dissolved in CH₃CN and diluted in CH₃CN/H₂O, 70:30.

^c Samples dissolved in CH₂Cl₂ and diluted in CH₃CN/H₂O, 70:30.

Table 2. Entry 1: ESI(+) mass spectrum of a solution of **3a** in CH₃CN/H₂O, 70:30. The inset shows the calculated isotope distribution pattern for the detected species.

Table 2. Entry 2: ESI(+) mass spectrum of a solution of Adam-Box in CH₃CN/H₂O, 70:30. The inset shows the calculated isotope distribution pattern for the detected species.

Table 2. Entry 3: ESI(+) mass spectrum of a solution of **5a** in CH₃CN/H₂O, 70:30. The inset shows the calculated isotope distribution pattern for the detected species.

Table 2. Entry 4: ESI(+) mass spectrum of a solution of Adam-Box + Cu(SbF₆)₂ in CH₃CN/H₂O, 70:30. The inset shows the calculated isotope distribution pattern for the detected species.

040122PEP21#83-116 RT: 1.51-2.09 AV: 34 NL: 4.01E6
T: [0,0] + p ESI sid=30.00 Full ms [600.00-1100.00]

040120PEP12#88 RT: 1.45 AV: 1 NL: 2.80E7
T: [0,0] + p ESI sid=30.00 Full ms [200.00-650.00]

040120PEP12#88 RT: 1.45 AV: 1 NL: 2.41E7
T: [0,0] + p ESI sid=30.00 Full ms [200.00-650.00]

Table 2. Entry 5: ESI(+) mass spectrum of a solution of **3a** + Cu(SbF₆)₂ in CH₃CN/H₂O, 70:30. The inset shows the calculated isotope distribution pattern for the detected species.

040122PEP02#138 RT: 1.80 AV: 1 NL: 9.18E5
T: {0,0} + p ESI sid=30.00 Full ms [550.00-900.00]

040122PEP01#110 RT: 1.81 AV: 1 NL: 3.90E6
T: {0,0} + p ESI sid=30.00 Full ms [150.00-600.00]

Table 2. Entry 6: ESI(+) mass spectrum of a solution of Adam-Box + Cu(SbF₆)₂ + **3a** in CH₃CN/H₂O, 70:30. The inset shows the calculated isotope distribution pattern for the detected species.

Table 2. Entry 7: ESI(+) mass spectrum of a solution of Adam-Box + $\text{Cu}(\text{SbF}_6)_2$ + **5a** in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$, 70:30. The inset shows the calculated isotope distribution pattern for the detected species.