DETAILED CHARACTERIZATION OF SELECTED FIRST ROW TRANSITION METAL PINCER COMPLEXES AS WELL AS THEIR PURE LIGANDS BY ELECTROSPRAY-MS AND MS/MS

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Mass spectrometry, particularly electrospray ionization (ESI) and for some special applications also matrix-assisted laser desorption/ionization (MALDI) mass spectrometry coupled to various tandem mass spectrometric analyzers, constitutes nowadays an important tool for the characterization of newly synthesized organometallic compounds [1]. This includes not only high resolution/accurate mass determination for the confirmation of the elemental composition of the intact compound, but also tandem mass spectrometry with accurate mass determination of all product ions for structural confirmation as many of these analytes exhibit paramagnetic properties, thus making NMR-experiments rather difficult.

Initially, we investigated the fragmentation behavior of selected diisopropyl-phosphine-based bidentate and tridentate ligands with variations in the aromatic backbone (benzene, pyridine, 4-methyl-S-triazine) as well as in the spacer group(s) by ESI-low-energy collision-induced dissociation (LE-CID) in combination with MS/MS. Among the bidentate compounds most fragmentations yield clear-cut even-electron product ions, except for two isomeric compounds, where abundant low-mass radical cations are formed due to homolytic C–P and N–P bond cleavage, respectively. Interestingly, the tridentate ligands investigated only yield radical cations as product ions for the corresponding C–P-based compound. PNP pincer complexes with either cobalt (II) chloride and nickel (II) chloride show as first fragmentation step loss of an isopropyl radical (–43 Da, typically for Ni > Co) leading to radical product ions, not seen for pure ligands (–42 Da, loss of propene) [2]. Further fragmentations include either loss of a second isopropyl radical or HCl. All other fragmentations include bond cleavage at the remaining isopropyl-substituents with bond fissions at the C–P- and the N–P-bond with only minor abundance. All product ion assignments were carried out with the aid of accurate mass determinations. Differences in the fragmentation pattern for corresponding Ni- and Co-derivatives are not only varying intensities between analogous product ions, but also the high tendency for the Ni-compounds to form radical cation/cation pairs (spaced by 1 Da), which is not the case for the Co-compound.

In the investigation of transition metal-catalyzed reactions by ESI-MS, potential components of the catalytic cycle can be detected and identified based on their fragmentation behavior by performing tandem mass spectrometry. In this context, fragmentation of the substrate initially bound to the metal complex can be observed and thus assigned.

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[1] Fleissner, S., Pittenauer, E., Pecak, J., Kirchner , K., *Rapid Commun. Mass Spectrom.* **2022**, *36*, https://doi.org/10.1002/rcm.9281.

[2] Fleissner, S., Pittenauer, E., Kirchner, K., *J. Am. Soc. Mass Spectrom.*, submitted (2023).