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Characterisation by X-ray diffraction of Bidentate and Tridentate PCP and PCN NHC Core Pincer-Type Mn(I) Complexes

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Following the early generation of phosphines, N-heterocyclic carbenes (NHCs) have attracted much attention, leading to remarkable advances in different areas, such as organometallic chemistry, functional materials, and homogeneous catalysis. We turned our attention to the preparation, the coordinating properties, of novel NHC core tridentate ligands bearing phosphine and pyridine donor arms.

While only bidentate coordination was observed in all formed neutral Mn(I) complexes, a notable difference in the coordination mode was observed between two ligands bearing a pyridine extremity. When the pyridine is directly connected to the imidazole core, two isomeric complexes [1] and [2] were evidenced due to the possible formation of two thermodynamically favored five-membered metallacycles upon coordination of the phosphine or the pyridine arms. By contrast, when the pyridine is not directly connected, only bidentate complex [3] resulting from the concomitant coordination of NHC and PPh₂ donor units was observed, the coordination of pyridine would indeed have led to a less stable six-membered metallacycle.

On the other hand, cationic tridentate complexes [4](OTf), [5](OTf), and [6](OTf) were easily obtained as single isomers. These compounds are rare examples of NHC-containing manganese complexes pincer-type and constitute the first prototypes based on NHC core L₃-type ligand scaffolds.

The complete series of bi- and tridentate Mn(I) species have been fully characterized and systematically studied by single-crystal X ray diffraction. These studies allowed us to establish the solid-state structures of neutral bidentate Mn(I) complexes [1], [2], and [3] and their cationic tridentate congeners ([4](OTf), [5](OTf) and [6](OTf)). In all complexes, the hexacoordinate Mn(I) atom resides in a distorted octahedral environment. Three carbonyl coligands adopt a facial arrangement in all bidentate representatives. In the tridentate series, complexes [4](OTf) and [5](OTf) can be regarded as real pincers exhibiting the meridional coordination of the NHC core ligand with two CO coligands positioned in *trans* with respect to each other, while in [6](OTf) the PCN backbone acts as a tripodal ligand with the three CO coligands located *cis* to each other. Moreover, X-ray analyses reveal two different coordination modes for the nonsymmetrical PCN ligands in complexes mer-[Mn(CO)₃(κ³P,C,N)](OTf) ([5](OTf)) and fac-[Mn(CO)₃(κ³P,C,N)](OTf) ([6](OTf)) rationalized by the higher flexibility of ligand with CH₂Py extremity in the latter case.

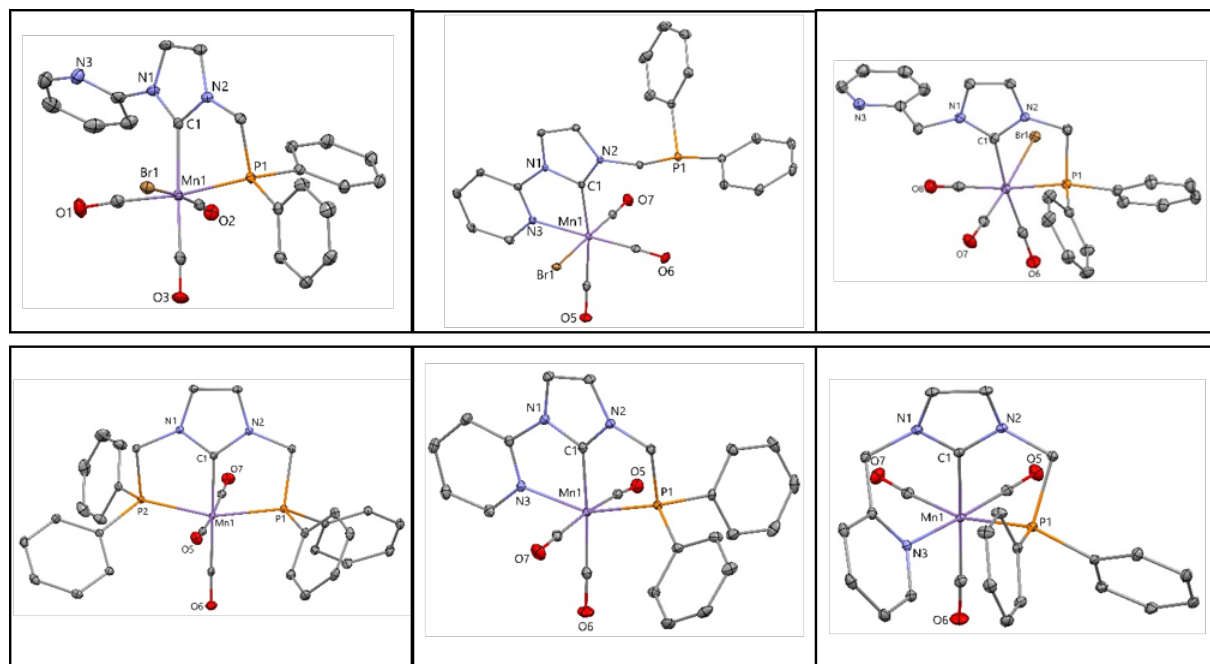


Figure 1. Perspective views of bidentate ([1], [2], and [3], *upper line*) and tridentate ([4](OTf), [5](OTf), and [6](OTf), *lower line*) Mn(I) NHC complexes with thermal ellipsoids drawn at the 30% probability level. The hydrogen atoms are omitted for clarity.

Reference:

Cationic PCP and PCN NHC Core Pincer-Type Mn(I) Complexes: From Synthesis to Catalysis

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