Synthesis and spectroscopic (^{1}H NMR, ESR) characterization of new aryloxy-Mn(II) complexes: steric control over O-vs. phenyl-pi-coordination of ArO$^-$ ligands ArO$^-$=$C_6H_5O^-$, 4-methyl-$C_6H_4O^-$, 3,5-dimethyl-$C_6H_3O^-$, 2,6-di-*tert*-butyl-$C_6H_3O^-$, 2,6-dimethyl-$C_6H_3O^-$) to the "Mn(II)Cp" moiety, and their reactivity with carbon dioxide.

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The coordination chemistry of phenoxide ligands, such as $C_6H_5O^-$, 4-(CH_3)-$C_6H_4O^-$, 3,5-$(CH_3)_2$-$C_6H_3O^-$, 2,6-(*tert*-butyl)$_2$-$C_6H_3O^-$, 2,6-$(CH_3)_2$-$C_6H_3O^-$, to Mn(II) has been investigated because of the possible implication of Mn(II)–phenoxide complexes as intermediates in the phenylphosphate carboxylase enzyme, a protein which catalyses the selective carboxylation of phenylphosphate to 4-OH-benzoic acid using CO_2. We report here the synthesis and characterization of $[CpMn(\mu\text{-}OAr)(THF)]_2$ (ArO = $C_6H_5O^-$, 4-(CH_3)-$C_6H_4O^-$, 3,5-$(CH_3)_2$-$C_6H_3O^-$, 2,6-$(CH_3)_2$-$C_6H_3O^-$) and [CpMn(η^5-ArO)] (ArO = 2,6-(*tert*-butyl)$_2$-$C_6H_3O^-$ and 2,6-$(CH_3)_2$-$C_6H_3O^-$) complexes, the first examples of mixed-sandwich complexes with Cp and phenate as π-ligands. The latter bear the 2,6-substituted phenoxide π-coordinated to the $[Mn(Cp)]^+$ moiety. The different mode of bonding of the phenoxide ligands to Mn(II), substantiated by ^{1}H NMR and electron spin resonance (ESR) spectroscopy, is controlled by the steric hindrance of substituents at the 2- and 6-position. The reactivity of the π-bonded ligand towards CO_2 is also reported as a quite rare example of nucleophilic attack at the cumulene by the ring-carbon of the phenoxide, which is driven by electron density localization at the 4-position generated upon π-coordination to Mn(II).*Key words*: Mn(II)-complexes, phenoxide ligands, ^{1}H NMR spectroscopy, ESR spectroscopy, reaction with carbon dioxide.

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