Ion-Pairing Thermodynamics for (η^5-pentadienyl)$Fe(CO)_2^-$ (Pentadienyl = MeCp, C_5Me_5, C_5Ph_5, C_9H_7) and X-ray Crystal Structure of [(η^5-C_5Ph_5)$Fe(CO)_2$][PPN]

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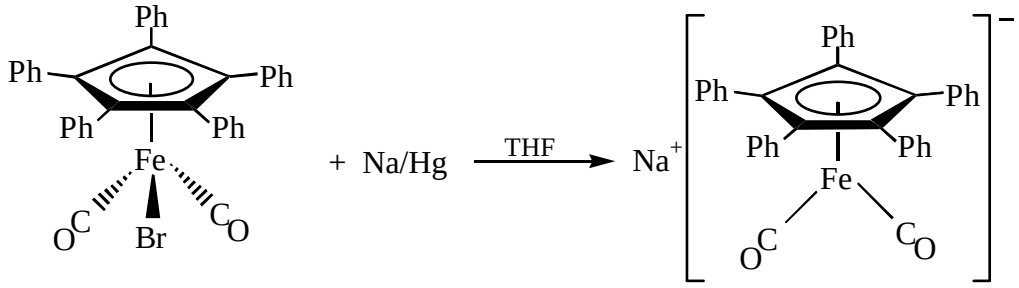
Abstract

The pentadienyl complexes [(η^5-pentadienyl)$Fe(CO)_2$][Na] (pentadienyl) MeCp, C_5Me_5, C_5Ph_5, C_9H_7) have been prepared in THF from the corresponding dimers [(η^5-pentadienyl)$Fe(CO)_2]_2$ and (η^5-C_5Ph_5)$Fe(CO)_2$Br. The exact composition of the ion pairs that exist in THF solution was explored as a function of temperature by FT-IR spectroscopy. The sodium metalates bearing the pentadienyl ligands MeCp, C_5Me_5, and C_9H_7 show the presence of two species that involve carbonyl oxygen-sodium and iron-sodium contact ion pairs in THF. In contrast, the pentaphenylcyclopentadienyl complex [(η^5-C_5Ph_5)$Fe(CO)_2$][Na] reveals the existence of solvent-separated ion pairs and carbonyl oxygen-sodium contact ion pairs. The absence of iron-sodium contact ion pairs in [(η^5-C_5Ph_5)$Fe(CO)_2$][Na] is attributed to a steric shielding of the iron center by the ancillary phenyl groups. The temperature-dependent behavior of these sodium metalates was explored by variable-temperature FT-IR measurements, and the equilibrium constants for the observed ion-pairing equilibria have been used to determine values for ΔH and ΔS. The X-ray structure of [(η^5-C_5Ph_5)$Fe(CO)_2$][PPN] is reported. The reactivity of [(η^5-C_5Ph_5)$Fe(CO)_2]^-$ with CO_2 was investigated, and only in the case of the lithium salt was the carboxylate complex [(η^5-C_5Ph_5)$Fe(CO)_2(CO_2)]^-$ observed by IR spectroscopy.



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