Low-coordinate 3d transition metal complexes with a bulky carbazolyl ligand

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Since the early 1960s the understanding of organometallic coordination chemistry has evolved. Sterically demanding ligands showed that the coordination number of a metal does not only depend on its own preference but even more on the properties of the used ligands, so the rise of such low-coordinate complexes started. Accordingly, the term “low-coordinate” nowadays describes complexes with a coordination number of 3 or less. As our group developed a bulky carbazolyl ligand R (1,8-bis(3,5-ditertbutylphenyl)-3,6-ditertbutylcarbazole), which showed its utility in low coordinate main group chemistry, especially with silicon[1], and in the stabilisation towards dicoordinate copper(II) complexes[2] we aimed to extend its scope to other 3d transition metals. Through a metathesis approach with the corresponding potassium carbazolide we were able to generate a row of novel transition metal complexes of the type “RMX” (M = Cr, Mn, Fe, Co, Ni) with additional THF molecules. The complexes appear either in monomeric ($RM(THF)_2(Cl)$) or in dimeric ($[RM(THF)(\mu\text{-}Cl)]_2$) form, dependent on the used metal. Treatment of these complexes with the stronger Lewis donor PMe_3 lead to the formation of the phosphine analogous. Reaction with BCF (Tris(pentafluorophenyl)-borane) of the dimeric species instead allows the abstraction of the THF molecules and forces the metal centers in an extremely unsaturated environment. This creation of low-coordinate, highly reactive species should be used for various subsequent reactions.

References:

[1] A. Hinz, *Angew. Chem. Int. Ed.* **2020**, *59*, 19065-19069.
[2] M. Kaiser, J. Göttlicher, T. Vitova, A. Hinz, *Chem. Eur. J.* **2021**, *27*, 7998-8002.