

Bond Activation in Iron(II) and Nickel(II) Complexes of Polypodal Phosphanes

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Z. Naturforsch. **2010**, *65b*, 238–250; received January 3, 2010

Dedicated to Professor Rolf W. Saalfrank on the occasion of his 70th birthday

A pyridine-derived tetraphosphane ligand (donor set: NP₄) has been found to undergo remarkably specific C–P bond cleavage reactions, thereby producing a ligand with an NP₃ donor set. The reaction may be reversed under suitable conditions, with regeneration of the original NP₄ ligand. In order to investigate the mechanism of this reaction, the NP₃ donor ligand C₅H₃N[CMe(CH₂PMe₂)₂][CMe₂(CH₂PMe₂)] (**11**) was prepared, and its iron(II) complex **4** generated from Fe(BF₄)₂ · 6 H₂O, with methyl diethylphosphinite (**7**) as an additional monodentate ligand. Ligand **11** has, in addition to the NP₃ donor set, one methyl group in close contact with the iron center, reminiscent of an agostic M ··· H–C interaction. Depending on the stoichiometric amount of iron(II) salt, a side product **15** is formed, which has a diethylphosphane ligand instead of the phosphinite **7** coordinated to iron(II). While attempts to deprotonate the metal-coordinated methyl group in **4** were unsuccessful, the reaction was shown to occur in an alternative complex (**18**), which is similar to **4** but has a trimethylphosphane ligand instead of the phosphinite **7**. The reaction of complex **15** with CO gave two different products, which were both characterized by single-crystal X-ray diffraction. One (**19**) is the dicarbonyl iron(II) complex of the triphosphane ligand **11**, the other (**3**) is the carbonyl iron(II) complex of the tetraphosphane C₅H₃N[CMe(CH₂PMe₂)₂]₂ (**1**). This suggests an *intermolecular* mechanism for the C–P bond formation in question.

Key words: Bond Activation, N/P Ligands, Polypodal Ligands, Agostic Interaction, Iron, Nickel