

Formation of η^1 -P-(2-Phosphinophenol)Ni(0)(PMe₃)₃ and Oxidation to *cis/trans*-Bis(2-phosphinophenolato)nickel(II) Complexes

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Dedicated to Prof. Dr. Dr. h. c. Wilhelm Keim on the occasion of his 65th birthday

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o-Phosphinophenols **1** (P[∧]OH) react with equimolar amounts of Ni(PMe₃)₄ at low temperatures to give yellow Ni(0) complexes such as [(HO~P)Ni(PMe₃)₃] **2a** with only P coordination of the P[∧]OH ligand. Oxidation of solutions of **1** and Ni(PMe₃)₄ by dioxygen leads to brown bis(*o*-phosphinophenolato-P[∧]O)nickel chelate complexes **3a-d**. Structure elucidation by NMR is consistent with a *cis*-square planar geometry for **3a-c** and a *trans*-square planar solution structure of the *tert*-butylphenylphosphino derivative **3d**. The geometric isomers were distinguished by different ranges of phosphorus coordination shifts and ³¹P-¹³C-2 and ³¹P-¹³C-1 coupling constants. In the solid state, **3d** adopts also a *cis*-square planar geometry. The steric stress of the substituents causes *anti*-orientation of the *tert*-butyl groups at phosphorus (*R,R* and *S,S* diastereoisomers) and a significant distortion (22°) of the planes of the two five-membered rings. With less bulky substituents the *R,S* and *S,R* diastereoisomers are preferred as in the *cis*-square planar complex **3c** with *syn*-orientation of the two isopropyl and phenyl groups, respectively.