Investigation of the effect of solvation on ^{1}J(Metal-P) spin-spin coupling

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The solvent effect on the indirect 1J(M-P) spin-spin coupling constant in phosphine selenoether peri-substituted acenaphthene complexes LMCl2 (see Fig. 1) is studied at the BP86 level of nonrelativistic and four-component relativistic density functional theory. [1] Depending on the metal, the solvent effect can amount to as much as 50% or more of the total J-value. This explains the previously found disagreement between the 1J(Hg-P) coupling in LHgCl2, observed experimentally and calculated without considering solvent effects. To address the solvent effect, we have used polarizable continuum and microsolvated models. The solvent effect can be separated into indirect (structural changes) and direct (changes in the electronic structure). These effects are additive, each brings roughly about 50% of the total effect. Pilot calculations of 1J(M-P) couplings in analogous systems with other metals indicate that for metals preferring square planar structures the solvent is insignificant because these structures are fairly rigid. Tetrahedral structures are less constrained and can respond more easily to external effects such as solvation.

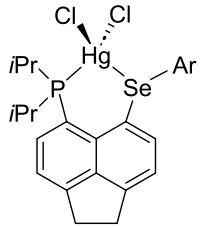

Figure 1. $LHgCl_2$ (Ar = Ph)

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