Mn- and Cr-highly Electrophilic Carbenes: Calculated vs Experimental Parameters

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The experimental geometry obtained from single-crystal X-ray diffraction data for $[Mn(CO)_4(PH_2)_2C:]^+$ [1] is compared with the results of theoretical calculations made in the singlet ground state at the *ab initio* level by using HF and DFT methods, following similar procedures than those used for other organometallic complexes [2,3]. In addition to the structural computations, in order to theoretically quantify the highly electrophilic character showed experimentally by the carbene, further calculations were carried out involving the doublet ground state resulting from the addition of one electron to the cation. Electron affinities (EA) were found to be between 6.24 eV and 6.97 eV for the Mn complex, which confirmed the expectations.

The effect of the ligands on EAs has been analyzed by replacing P-bonded H atoms by NH_2 ligands, whereas the effect of the metal fragment has been studied by replacing Mn^+ by Cr and also comparing with our previous results with Ru^{2+} complexes, from which it seems clear that the effect of the positive charge on the metal dominates over the effect of changing the ligands to more π-accepting ones.

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