Highly electrophilic metalladiphosphanil carbenes: calculated vs experimental structural parameters.

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The experimental geometry obtained from single-crystal X-ray diffraction data for a couple of highly electrophilic metalladiphosphanil carbenes is compared to the results of theoretical calculations made at the *ab initio* level by using Density Functional Theory (DFT) methods.

Diffraction data for $[Ru(CN^tBu)_4(PPh_2)_2C:]^{2+}$ and $[Mn(CO)_4(PPh_2)_2C:]^+$ have been collected and the structures solved and refined using standard procedures [1]. Experimental geometries are in good agreement with results reported for similar compounds; for instance, the P-C-P bond angle has been found to be 101.3(4)° and 103.5(3)° in the first and second compounds, respectively, whereas C-P bond distances are, on average, 1.76(1) Å and 1.73(1) Å, respectively.

Theoretical geometry optimizations for the singlet ground state of both compounds have been performed using Hartree-Fock and DFT methods with several hybrid functionals (B3LYP, B3P86, etc) and basis sets (LanL2DZ, 6-31G*, 6-311++G**, etc). In order to achieve convergence in a reasonable time, phenyl and *terc*-butyl groups were replaced by hydrogen atoms in all calculations. The theoretically optimized geometries obtained showed a perfect C_{2v} symmetry in the highest levels of calculation and were somewhat relaxed when compared to the experimental ones; for instance, with the largest basis set, the P-C-P angle found was 137.9° for the first complex and 127.6° for the second complex, whereas the C-P bond distances were 1.66 Å and 1.67 Å, respectively. The absence of ligands attached to the C: atom in the calculated structures, which are present in the form of pyridine in the first experimental structure and in the form of iodine in the second, is probably responsible, to a certain degree, for the discrepancies.

In addition to the above structural computations, in order to theoretically quantify the highly electrophilic character showed experimentally by the two carbenes, further calculations were carried out involving the doublet ground state resulting from the addition of one electron to the cations. Electron affinities were found to be 8.99 eV for the Ru complex and 6.37 eV for the Mn complex, which confirmed the expectations.

[1] Ruiz, J., Mosquera, M. E. G., García, G., Patrón, E., Riera, V., García-Granda, S. & Van der Maelen, J. F. (2003). *Angew. Chem. Int. Ed*. **42**, 4767-4771.
[2] Van der Maelen, J. F., Ruiz, J. & García-Granda, S. (2003). *J. Appl. Cryst*. **36**, 1050-1055.