

s13.m38.p15 **Highly Electrophilic Metalladiphosphanil Carbenes: Calculated vs Experimental Structural Parameters.** Juan F. Van der Maelen Uría^a, Santiago García-Granda^a, and Javier Ruiz^b, ^aDpt. Química Física y Analítica, ^bDpt. Química Orgánica e Inorgánica, Facultad de Química, Universidad de Oviedo, E-33006 Oviedo, Spain. E-mail: fvu@fq.uniovi.es

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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 $[\text{Ru}(\text{CN}^t\text{Bu})_4(\text{PPh}_2)_2\text{C}:]^{2+}$ and $[\text{Mn}(\text{CO})_4(\text{PPh}_2)_2\text{C}:]^+$ 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 *tert*-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.

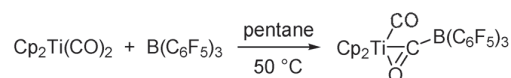
In addition to the above structural computations, in order to theoretically quantify the highly electrophilic character showed experimentally by the two carbenes, further calculations were carried out involving the doublet ground state resulting from the addition of one electron to the cations. Electron 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.

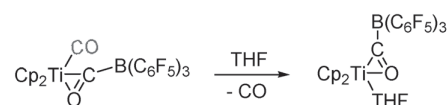
s13.m38.p16 **Reactivity of $[\text{Cp}_2\text{Ti}(\text{CO})_2]$ and $[\text{Cp}_2\text{VCO}]$ with $\text{B}(\text{C}_6\text{F}_5)_3$: Formation and X-Ray Characterisation of the Acylborane Titanium Complexes and Zwitterionic Ring-Borylated Vanadium(III) Complexes.** L. Vendier, C. Guyard-Duhayon, R. Choukroun, C. Lorber, B. Donnadieu, Laboratoire de Chimie de Coordination, CNRS, 205 Route de Narbonne, 31077 Toulouse Cedex, France. E-mail: vendier@lcc-toulouse.fr

Keywords: X-ray diffraction; Boranes; Titanium and Vanadium

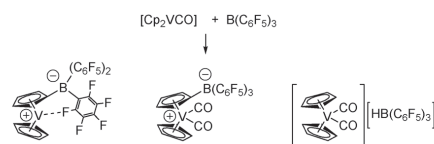
The reactivity of the borane $\text{B}(\text{C}_6\text{F}_5)_3$ towards organic and organometallic substrates is of current interest. New organic reactions, new catalytic processes and new reactivity pathways have been observed for this borane. In our studies of the reactivity of $\text{B}(\text{C}_6\text{F}_5)_3$ with organometallic complexes of the groups 4 and 5 elements, in which catalytic application in olefin polymerization is well known, we first have explored its reactivity with $[\text{Cp}_2\text{Ti}(\text{CO})_2]$. The product of this reaction was the acylborane derivative $[\text{Cp}_2\text{Ti}(\text{CO})(\eta^2\text{-OCB}(\text{C}_6\text{F}_5)_3)]$. The preferential attack of borane at the carbon atom of a carbonyl ligand is puzzling if we consider that attack at the more nucleophilic oxygen atom of the carbonyl ligand should be favored [1].



When the product is treated in toluene with THF, CO evolution occurred. The resulting yellow solution gives, crystalline $[\text{Cp}_2\text{Ti}(\text{THF})(\eta^2\text{-OCB}(\text{C}_6\text{F}_5)_3)]$.



Thus we decided to extend our investigation of the reactivity of the borane toward the readily available vanadium(II) carbonyl $[\text{Cp}_2\text{V}(\text{CO})]$. The reaction resulted in formation of zwitterionic, ring-borylated vanadium(III) complexes $[(\text{Cp})(\text{C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3)\text{V}]$ and $[(\text{Cp})(\text{C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3\text{V}(\text{CO})_2)]$ and of the salt $[\text{Cp}_2\text{V}(\text{CO})_2][\text{HB}(\text{C}_6\text{F}_5)_3]$ [2].



All these complexes were characterized by single-crystals X-ray diffraction. The technique is very useful since it allows to confirm the nature of the paramagnetic formed species and to yield other structural information necessary to a better knowledge of the mechanism of the chemical reactions.

- [1] R. Choukroun *et al.* *Organometallics* 2003, **22**, 1995-1997
 [2] R. Choukroun *et al.* *Organometallics*, 2004, in Press