Oral presentation

Probing the Isolobal Relation between Cp‴NiP$_3$ and White Phosphorus using Multipolar Modelling and X-ray Restrained Wavefunction Fitting

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The isolobal principle [1] enables chemists to estimate the reactivity of larger and unknown fragments by comparing them to smaller, well-known fragments. Such a relationship exists between the organometallic fragment Cp´´´Ni (Cp´´´= 1,2,4-*tri*-tert-butylcyclopentadienyl, **1**, see Fig. 1 A [2]) and a single phosphorus atom. Thus, the compound Cp‴NiP3 is called an isolable analog to white phosphorus, P4.

In this work, we show how quantum crystallographical methods (multipolar modeling (MM) and X-ray restrained wavefunction (XRW) fitting) give deep insights into the nature of the bonding situation within **1**.[3,4,5] Especially the topological analysis (Figure 1 B) of the electron density as well as the wavefunction-based bonding analysis (Figure 1 C) contributed to a full picture of the complex bonding in this organometallic transition metal complex.

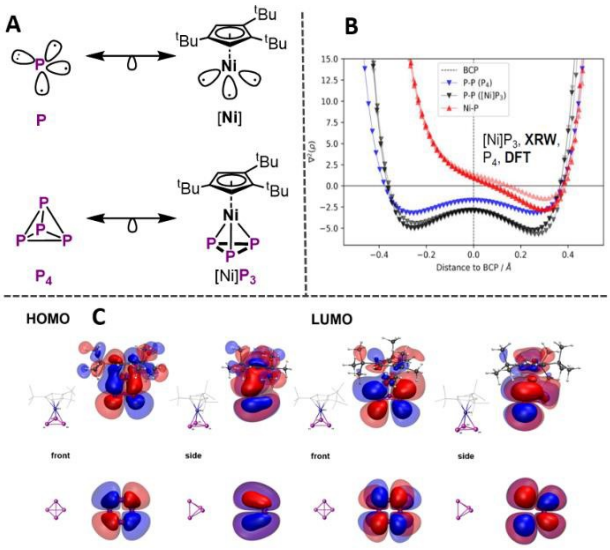

Figure 1. Isolobal relationship between **1** and P_4 (**A**)**.** Distribution of the Laplacian of the total electron density along various bonds in **1** and P4 (**B**). Comparison between the HOMO/LUMO shapes of **1** and P4 (**C**).

We found the isolobale principle to be valid in every aspect of our analysis and described **1** as a *metallatetrahedrane*. The Ni-P bonds were described as dative, covalent bonds. The differences in reactivity between **1** and P4 could be well explained by the results of the complementary bonding analysis, combined from both quantum crystallographic methods.

Furthermore, we present the first example of the copper wavelength Cu Kβ (λ = 1.392 Å) being employed in quantum crystallographic modeling. We describe the advantages and drawbacks compared to the established Mo Kα radiation (λ = 0.7107 Å).

[1] Elian, M., Chen, M. M.-L., Mingos, D. M. P., Hoffmann, R. (1976). *Inorg. Chem.* **15,** 1148–1155.

[2] Hansen, N. K., Coppens, N. (1978). *Acta Cryst A***34**, 909–921.

[3] Jayatilaka, D., Dittrich, B. (2008). *Acta Crystallogr. A***64**, 383–393.

[4] Meurer, F., Kleemiss, F.,Riesinger, C., Balázs, G., Vukociv, V., Shenderovich, I. G., Jelsch, C. , Bodensteiner M. (2024). *Chem. Eur. J.* e202303762

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