



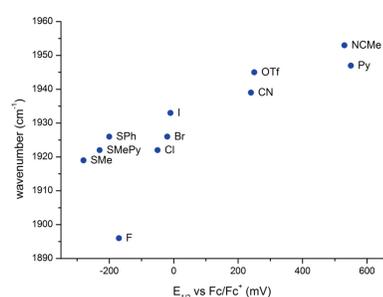
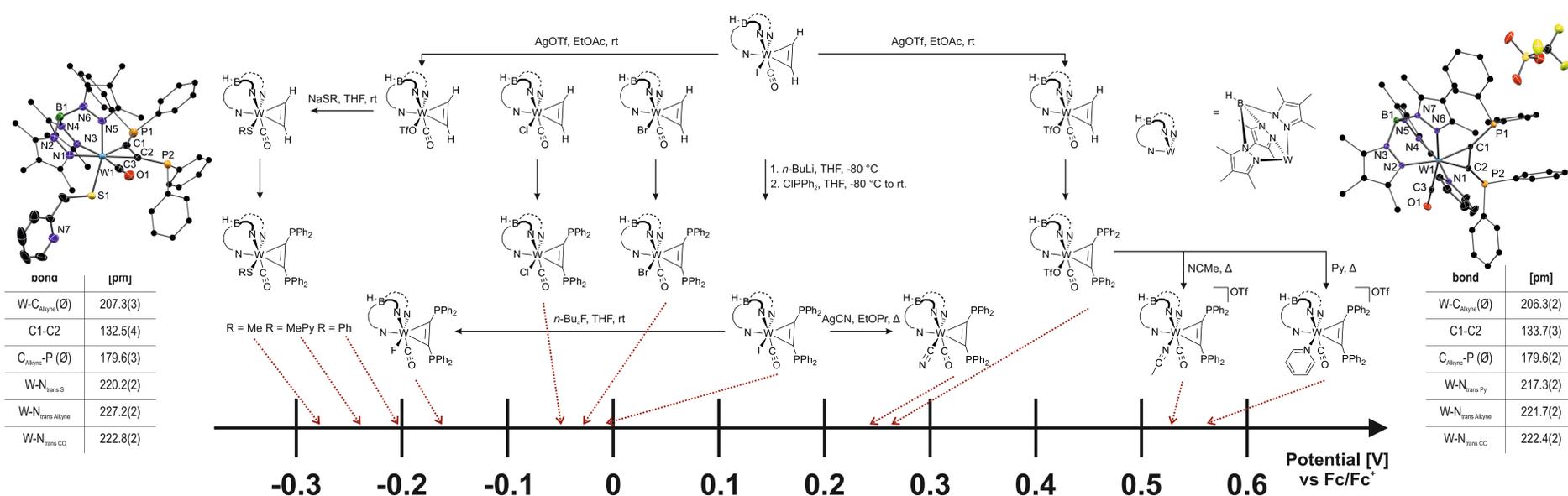
# Highly Tunable Side-On dppa Complexes of Tungsten: Synthesis, Properties and Preliminary Catalytical Studies

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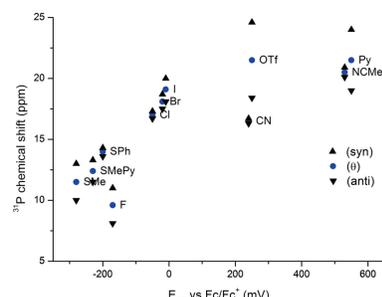
## Introduction

While phosphine ligands have been in use in homogeneous catalysis for many decades,<sup>1</sup> their tunability renders them subjects of research to this day.<sup>2</sup> Among the adjustable properties, intrinsic redox activity of the backbone has been achieved for some organic substituents,<sup>3</sup> but mostly through the use of ferrocene-containing species like 1,1'-bis(diphenylphosphino)ferrocene (dppf) and its chiral derivatives of the *Josiphos* type.<sup>4</sup> To broaden the scope of redox active metal centres, we set out to generate complexes of bis(diphenylphosphino)acetylene (dppa) which usually serves as a bridging ligand in an  $\mu_2$ -end-on coordination mode.<sup>5</sup> A preceding side-on coordination of the triple bond to W causes the substituents to bend back, thus enabling a  $\kappa^2$ -P,P chelating coordination of a second metal centre. Given the affinity of W towards the P-donor functions of dppa, we had to develop a synthetic protocol of prior coordination of acetylene gas, which in turn is converted into dppa by  $S_E$  after deprotonation.<sup>6</sup> The air- and water stable ligands of the type  $[(Tp^*)W(CO)(X)(dppa)]$  are obtainable on a multigram-scale and have been tuned in their properties by systematic substitution of the X-ligand. While some synthetic pathways have been adopted from the literature,<sup>7</sup> others have been newly developed for this research.

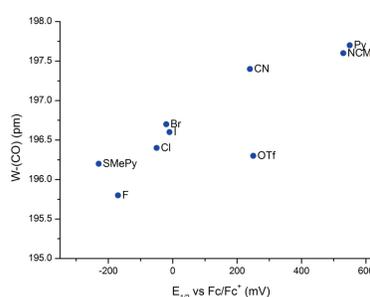
## Synthesis and Properties



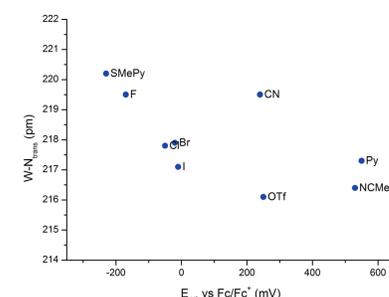
A linear dependence of the energy required for C-O stretching and redox potential could be established. Only the fluoride ligand shows exceptional behaviour which is unsurprising given the peculiar interaction of this ligand with metal centres.<sup>8</sup>



Comparably small differences in the <sup>31</sup>P resonances of the dppa-phosphines are present. Chemical shifts increase with the redox potential but level out for the cationic compounds. The more striking difference can be found in the anisotropy of both alkyne positions, which seems to be mostly dependent on steric demand and flexibility of the X-ligand in question.



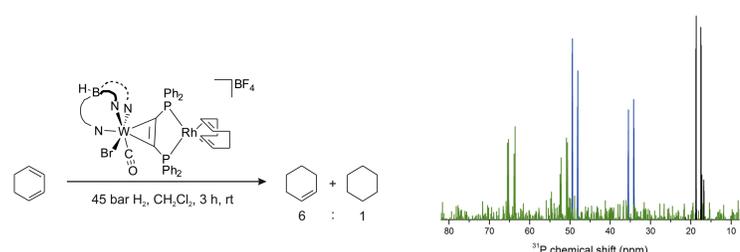
Metal-carbon bonds are clearer indicators of the electronic situation than the C-O bond in a carbonyl.<sup>9</sup> The effects observed follow a clear trend and indicate the decreased  $\pi$ -backbonding capability of W in the electronically depleted and, especially, cationic dppa complexes.



The N atom in trans-position to X follows a textbook-like behaviour of elongation when stronger donors are present. Merely cyanide does not fit the trend and thereby proves its identity as a strong  $\sigma$ -donor, leaving the high W<sup>VI</sup> potential to be caused by its  $\pi$ -acceptor capability. For the cations, the charge causes shorter bonds than would be otherwise expected from the strong N-donors acetonitrile and pyridine.

## Catalytical Studies

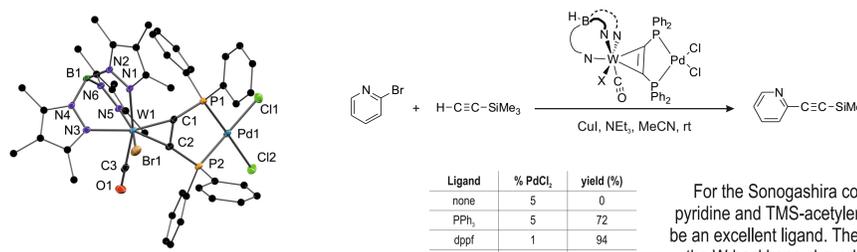
### Hydrogenation



The Rhodium complex of complex ligand  $[(Tp^*)W(CO)Br(dppa)]$  exhibits the identical behaviour as found for simpler ligands in early investigations.<sup>10</sup> With 1% catalyst, 1,3-cyclohexadiene is fully converted into cyclohexene before further hydrogenation to cyclohexane can be observed, indicating a high affinity of Rh to the diene.

Upon exposure to  $[Rh(COD)_2]_2BF_4$ , the <sup>31</sup>P chemical shift of coordinated dppa (black) experiences a shift to higher resonances and the typical coupling to <sup>103</sup>Rh (blue). After the hydrogenation reaction, a single set of signals remains (green), albeit with another high-field shift, which could represent a solvent-, H<sub>2</sub>- or substrate-complex.

### Sonogashira-Coupling



Upon coordination of PdCl<sub>2</sub>, the P-functions of the alkyne experience a further bend-back from the tungsten centre to accommodate a square-planar coordination sphere around Pd ( $\Sigma$  of angles = 360.0°).

Ligand	% PdCl <sub>2</sub>	yield (%)
none	5	0
PPh <sub>3</sub>	5	72
dppf	1	94
dppf	2.5	94
dppf	5	93
X = Br	2.5	14
X = Br	5	40
X = Br	7.5	46
X = SMe	5	2
X = SPh	5	21
X = Cl	5	19
X = I	5	29
X = CN	5	45

For the Sonogashira coupling of 2-bromopyridine and TMS-acetylene, dppf turned out to be an excellent ligand. The complex-ligands with the W-backbone show differences in activity indeed, however, a linear dependency on the redox potential could not be observed. The overall yields range from low to moderate while the halide complexes show lower consistency of results than their thiolate- and cyanide analogues. After the reaction, substantial amounts of  $[WPd]$  moieties could be regenerated.

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