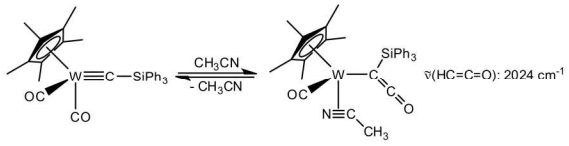
Universität Rostock

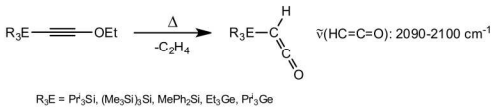
# Migratory Insertion at a Ketenyl Complex


**Christopher Timmermann**, Alexander Villinger and Wolfram W. Seidel*

## Literature survery about ketenyl complexes



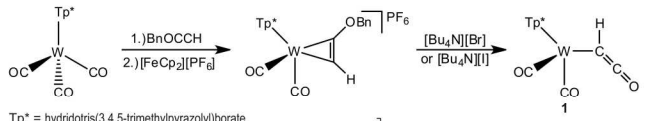

Wadepohl et al.[1]




$R_3E$ = $Pr^i_3Si$, $(Me_3Si)_3Si$, $MePh_2Si$, $Et_3Ge$, $Pr^i_3Ge$

Ponomarev et al.[2]

## Coordination of an α-oxygen alkyne and cleavage of the O-C bond




Tp* = hydridotris(3,4,5-trimethylpyrazolyl)borate

- In situ synthesis of the free alkyne according to known reaction instructions[3] (alkyne not stable above –80 °C)
- coordination at the tungsten precursor after oxidation from W(I) to W(II) with ferrocenium hexafluorophosphate
- cleavage of the benzyl group by bromide or iodide to generate the prototype of a ketenyl-ligand (in $^1$H-NMR: *H*CCO at 14.43 ppm)

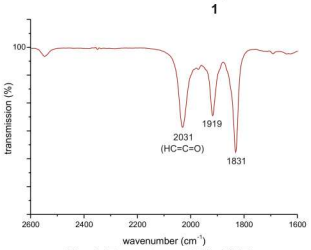
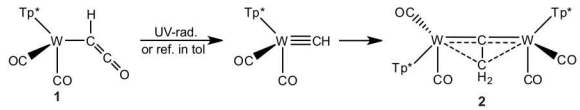



***Fig. 1*** IR spectrum of **1** in THF.

## Stability of the ketenyl complex



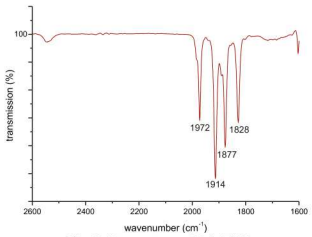




***Fig. 2*** IR spectrum of **2** in THF.

- 16 VE $\eta^1$-ketenyl complex unusually stable in air (over serveral weeks)
- under light release of a CO and formation of a carbin complex
- the carbin complex is not stable and dimerizes to form a $\eta^2$-bridged dinuclear compound[4]

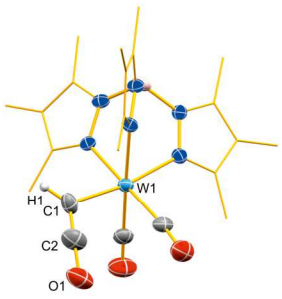
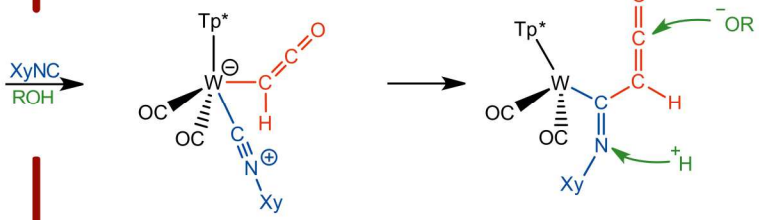
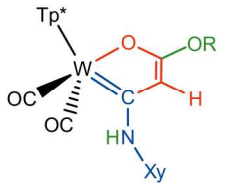



***Fig. 3*** Molecular structure of **1** in the crystal.

## Mechanism of the migratory insertion




## Formation of an oxametallacyclic complex (3):



R = Et = **3a**
Me = **3b**
H = **3c**

## Reactions with other protic nucleophiles

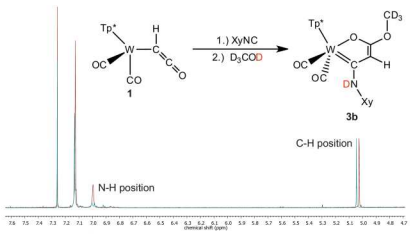



***Fig. 7*** $^1$H-NMR spectra of **3a** (red) and **3b** (teal) in $CDCl_3$.

- synthesis with deuterated MeOH shows that the nitrogen from the isocyanide is protonated by the alcohol (**3b**)
- instead of **3c** a dimer is formed by the addition of water (**4**)

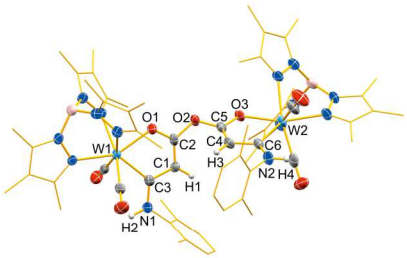
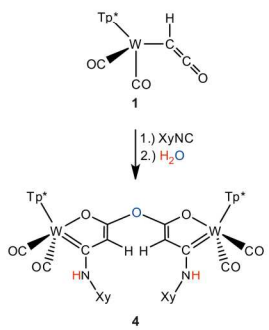



***Fig. 8*** Molecular structure of **4** in the crystal.




## Properties of 3a in comparsion to the ketenyl complex (1)

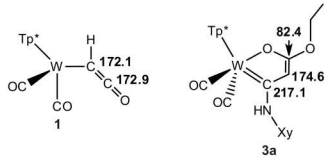



***Fig. 4*** $^{13}$C-NMR references from certain carbon atoms of **1** and **3a** in $CDCl_3$ (ppm).

| Selected bond lenghts [Å] | | |
|---|---|---|
| compound | 1 | 3a |
| W1-C1 | 2.036(9) | |
| C1-C2 | 1.248(7) | 1.371(5) |
| C2-O1 | 1.183(9) | 1.283(5) |
| C1-C3 | | 1.398(5) |
| W1-C3 | | 2.189(4) |
| W1-O1 | | 2.110(3) |
| C2-O2 | | 1.348(5) |
| C3-N1 | | 1.366(5) |

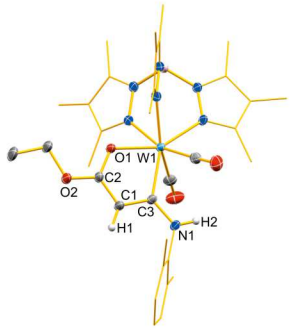



***Fig. 5*** Molecular structure of **3a** in the crystal.

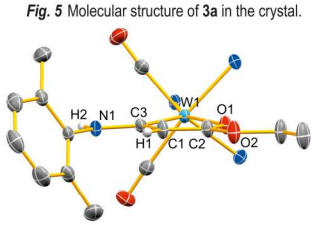



***Fig. 6*** Side view **3a**.


[1] H. Wadephol, U. Arnold, H. Pritzkow, M. Calhorda, L. F. Veiros, *J. Organomet. Chem.* **1999**, *587*, 233-243.
[2] S. V. Ponomarev, A. S. Zolotareva, R. N. Ezhov, Y. V. Kuznetsov, V. S. Petrosyan, *Russ. Chem. Bull., Int. Ed.* **2001**, *50*, 1093-1096.
[3] G. B. Dudley, K. S. Takaki, D. D. Cha, R. L. Danheiser, *Org. Lett.* **2000**, *2*, 3407-3410.
[4] G. M. Jamison, A. E. Bruce, P. S. White, J. L. Templeton, *J. Am. Chem. Soc.* **1991**, *133*, 5057-5059.


INSTITUT FÜR CHEMIE| **Universität Rostock,** Albert-Einstein-Straße 3a | 18059 Rostock | Germany