

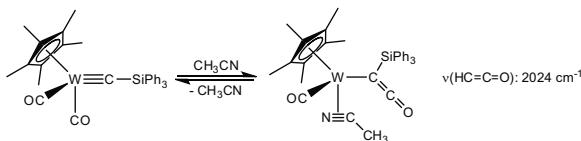


Properties and Reactivity of a Ketenyl-Tungsten Complex

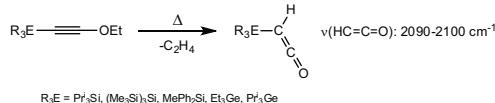


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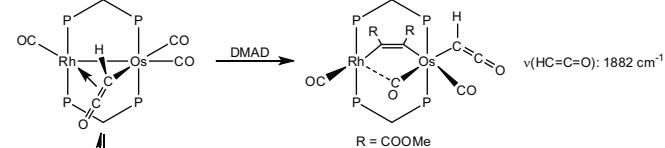
Wadephohl et al.^[1]:



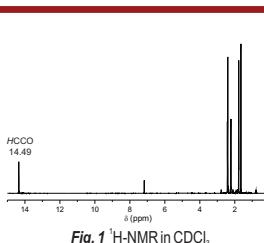
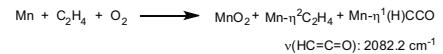
Ponomarev et al.^[3]:



Cowie et al.^[2]:



Zhou et al.^[4]:



Selected bond lengths [Å]

W1-C1	2.036(9)
C1-C2	1.248(7)
C2-O1	1.183(9)
W1-C3	1.972(5)
W1-C4	1.955(7)
C3-O2	1.128(5)
C4-O3	1.142(8)

MS (ESI-TOF/MS, m/z): 621,19 [$\text{M}+\text{H}^+$]

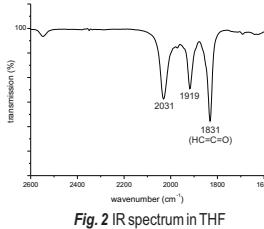
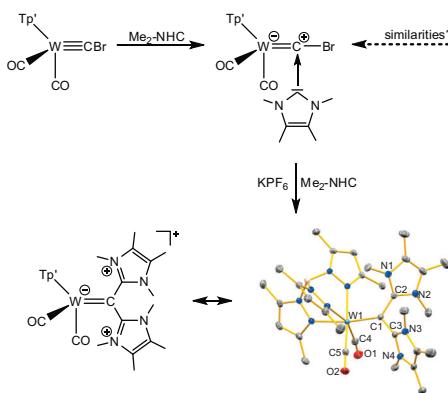
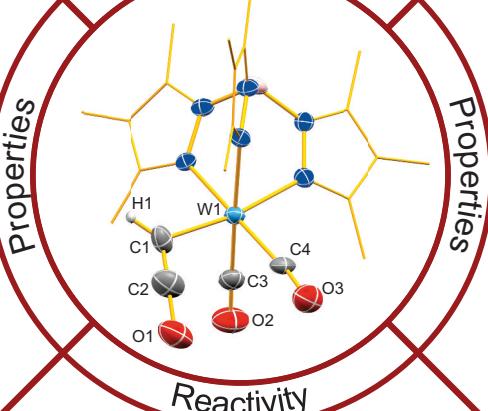


Fig. 2 IR spectrum in THF



Similar Examples



Reactivity

- reversible signal at -1.56 V (WII/WI)
- two irreversible signals at 0.25 V and 0.33 V

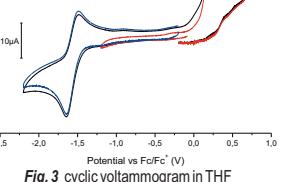


Fig. 3 cyclic voltammogram in THF

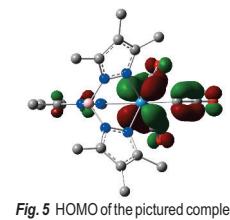
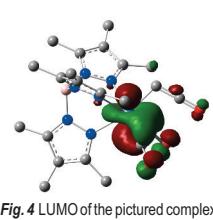


Fig. 4 LUMO of the pictured complex

Fig. 5 HOMO of the pictured complex

- possible to cleave a hydride from the ketenyl ligand? the left example of a carbyne complex shows the nucleophilic attack of a NHC at the α -C atom
- hydride abstraction at the ketenyl ligand led to a new complex with two carbonyl ligands (2061 cm^{-1} ; 1977 cm^{-1}) but the α -C hydrogen persists → reactivity different from the bromo-derivate (left)
- formation of a carbyne complex via UV radiation and after time dimerization to a η^2 -bridded dinuclear tungsten complex^[5]

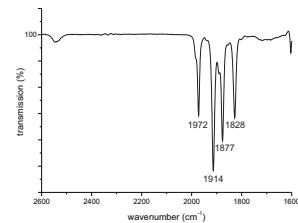
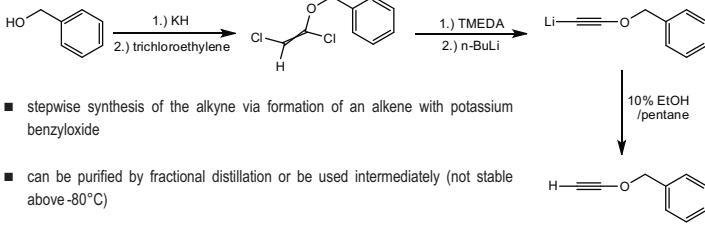
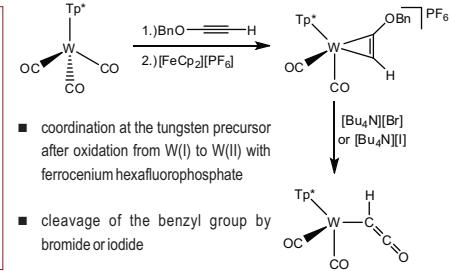
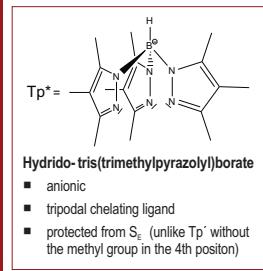


Fig. 6 IR spectrum of the dinuclear complex in THF

Synthesis of the free alkyne^[6]



Coordination of the alkyne and cleavage of the O-benzyl bond



[1] H. Wadephohl, U. Arnold, H. Pritzkow, M. Calhorda, L. F. Veiro, *J. Organomet. Chem.* **1999**, *587*, 233-243.

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[3] S. V. Ponomarev, A. S. Zolotareva, R. N. Ezhov, Y. V. Kuznetsov, V. S. Petrosyan, *Russ. Chem. Bull., Int. Ed.* **2001**, *50*, 1093-1096.

[4] M. Zhou, J. Dong, L. Miao, *J. Phys. Chem. A* **2004**, *108*, 2431-2435.

[5] G. M. Jamison, A. E. Bruce, P. S. White, J. L. Templeton, *J. Am. Chem. Soc.* **1991**, *113*, 5057-5059.

[6] G. B. Dudley, K. S. Takaki, D. D. Cha, R. L. Danheiser, *Org. Lett.* **2000**, *2*, 3407-3410.