

Traditio et Innovatio

SYNTHESIS AND COORDINATION CHEMISTRY OF NEW α -SILICON ALKYNE COMPLEXES

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The Seidel group investigates α-donor substituted alkynes as valuable bridging unit between two metals in the μ - η^2 -C,C'- κ^2 -E,E'-binding mode. This system proofs to be very versatile, as a great variation of donor

Z 0 \bigcirc

atoms (C, N, O, P, S) could be introduced in various symmetric and asymmetric combinations, leading to a wide range of polynuclear complexes, that show strong electronic cooperativity of the metal centres.^[1-5]

NEW: Silicon functioning as donor centre



Fig. 1 Overview of possible second and third period donors on the alkyne of a tungsten precursor with variable ligand sphere and donor combinations that have been successfully isolated in polynuclear complexes (table).



S



N—

С /// О

Br

Br

O.

 Ph_2

 $-H^{\dagger}$

by CPh₃⁺



N O P S

С





 $\mathsf{E} = -\mathsf{CR}_{2}, -\mathsf{NR}_{2}, -\mathsf{NR}^{-}, -\mathsf{OR},$

 $-OR^{-}$, $-PR_{2}$, -SR, $-S^{-}$,

Fig. 2 Molecular structure of P,Si-alkyne complex [Tp*W(CO)Br(Ph₂PCCSiHPh₂)] (**1**) in the crystal with bend back angles at the alkyne (orange).

- High variability of donors and their substituents

Br

angle









1930

Fig. 6 IR spectra of 1 (black) and the reaction solution after addition of 1 eq. CPh_3BF_4 to **1** (blue) in CH_2CI_2 .

Fig. 7 Cyclic voltammogram of 2 without (black) and with addition of KOtBu (orange) in CH_2CI_2 (0.1 M Bu₄NPF₆, 0.1 V s⁻¹).

 $E \setminus V vs Fc/Fc^{\dagger}$

-0.5

0.0

0.5

1.0

-1.0

The platinum bound hydrogen in 2 can be removed by reaction with CPh_3BF_4 , proving the hydridic character. Accordingly, a protic behaviour by reaction with the *Brønsted* base KOtBu and abstraction of a hydrogen radical with TEMPO could not be observed. The cationic complex resulting from the hydride abstraction could not be isolated so far, but the reaction can be observed by IR and NMR spectroscopy.

Surprisingly, this reactivity can be modulated by the oxidation state of the tungsten as determined by cyclic voltammetry measurements. After addition of KOtBu, the oxidation of **2** is no longer reversible. This finding suggests that deprotonation at the Pt(II) centre is possible after oxidation of the complex. Subsequently, the oxidated species is no longer available for the reductive process.

 $-H^{+}$

by KOtBu

after oxidation

UMPOLUNG of Pt-H by OXIDATION <

Br

Ő

 Ph_2

References

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