Synthese und Reaktionsverhalten von $\{[Hf](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CR)_2\}Ni(CO)$; die Röntgenstrukturanalyse von $[(\eta^5\text{-}C_5H_4SiMe_3)_2Hf(C{\equiv}C^tBu)]_2O$

Synthesis and Reaction Behaviour of $\{[Hf](\mu-\sigma,\pi\text{-}C{\equiv}CR)_2\}Ni(CO)$; the Solid-State Structure of $[(\eta^5\text{–}C_5H_4SiMe_3)_2Hf(C{\equiv}C^tBu)]_2O$

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The synthesis of the heterobimetallic hafnium(IV)-nickel(0) complexes $\{[Hf](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CR)_2\}Ni(CO)$ (**3a**, [Hf] = $(\eta^5\text{-}C_5H_5)_2Hf$, R = Ph; **3b**, [Hf] = $(\eta^5\text{-}C_5H_4SiMe_3)_2Hf$, R = ^{t}Bu) in which an early (Hf) and a late (Ni) transition metal atom are bridged by σ- and π-bound alkynyl groups succeeds by treatment of $[Hf](C{\equiv}CR)_2$ (**1a**, [Hf] = $(\eta^5\text{-}C_5H_5)_2Hf$, R = Ph; **1b**, [Hf] = $(\eta^5\text{-}C_5H_4SiMe_3)_2Hf$, R = ^{t}Bu) with equimolar amounts of $Ni(CO)_4$ (**2**).

The reaction chemistry of **1** and **3** towards different substrates is discussed. Treatment of **3b** with $P(OMe)_3$ (**4a**) affords the mononuclear nickel monocarbonyl complex $Ni(CO)[P(OMe)_3]_3$ (**5**), while the reaction of **1a** or **1b** with MCl_2 (**6a**, M = Fe; **6b**, M = Ni; **6c**, M = Co) produces by an cyclopentadienyl transfer from hafnium to M the sandwich compounds $(\eta^5\text{-}C_5H_4R')_2M$ (M = Fe: **7a**, R' = H; **7b**, R' = $SiMe_3$; M = Ni: **7c**, R' = H; **7d**, R' = $SiMe_3$; M = Co: **7e**, R' = H). Addition of KOH to **1b** or **3b**, respectively, affords the homobimetallic hafnium complex $\{[Hf](C{\equiv}CR)\}_2O$ (**8**) in which two [Hf](C≡CR) fragments are bridged by an oxygen atom.

Possible reaction mechanisms for the formation of **5**, **7** and **8** by starting from **1** or **3** will be given.

The result of the X-ray structure analysis of **8** is reported. Complex **8** crystallises in the monoclinic space group $C2/c$ with the cell parameters $a = 24.437(8)$, $b = 14.655(5)$, $c = 14.123(4)$ Å, $\beta = 101.67(2)^\circ$, $V = 4953(3)$ Å^3, $Z = 4$ and $D = 1.454$ g cm^{-3}. Complex **8** contains a linear Hf-O-Hf unit with pseudo-tetrahedral coordinated hafnium atoms.

Key words: Hafnocene, Nickel, Iron, Cobalt, Alkynyl