Group VI Metal Aminoborylene Complex-Catalyzed Demercuration Reactions of bis(Alkynyl)mercurials

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Electronic Supporting Information

1) Irradiation of [$(CO)_5Cr{=}BN(SiMe_3)_2$] (**1**) with [$Hg(C{\equiv}CPh)_2$] (**4a**) in C_6D_6 yielded a new boron-containing compound **5** as indicated e.g. by a $^{11}B\{^1H\}$-NMR signal at 25.0 ppm, a resonance for the $SiMe_3$-groups at 0.35 ppm in the ^1H-NMR spectrum (of the reaction mixture) and a EI-MS peak at *m/z* = 544 (M^+) (after GC-MS). As to verify the assumed bisborirene constitution of compound **5**, this species was prepared independently according to the known synthesis[1] of bisborirenes:

A pale yellow solution of 100 mg (0.25 mmol) **1** with 25.0 mg (0.13 mmol) 1,4-diphenylbuta-1,3-dyne in 1.5 ml benzene was irradiated for 6h at room temperature. The volatile components were removed under vacuum, and the brown residue was treated with 5 ml of hexane. The hexane solution was stored at -60° C over night. Precipitated [$Cr(CO)_6$] was removed and the solution was filtered over glass-fibre filter paper. The bisborirene **5** was isolated as a yellow solid in 80% yield (108mg). ^1H-NMR (500MHz, C_6D_6): δ = 7.84-7.83 (m, 4H, Ph), 7.20-6.88 (m, 6H, Ph), 0.35 (s, 36H, $SiMe_3$); $^{13}C\{^1H\}$-NMR (125 MHz, C_6D_6) : δ = 163.3 (bs, Ph-$\underline{C}$=), 149.3 (bs, =$\underline{C}$-$\underline{C}$=), 132.8 (s, Ph), 130.4 (s, Ph), 129.1 (s, Ph), 128.6 (s, Ph), 3.2 (s, N-$SiMe_3$); $^{11}B\{^1H\}$-NMR (160 MHz, C_6D_6): δ = 24.0 (s). EI-MS *m/z* = 544 (M^+).

2) Performance of catalytic experiments:

In a typical catalytic experiment solid **1** (0.0024 g, 0.0066 mmol) was added to a solution of [$Hg(C{\equiv}C\text{-}C_6H_4\text{-}p\text{-}Me)_2$] (0.066 mmol) in benzene (1.5 mL) and heated to 90ºC. The progress of the reaction was monitored by observation of the characteristic signals of the *para*-Me groups in the ^1H NMR spectra. At time = 0h, only the singlet for [$Hg(C{\equiv}C\text{-}C_6H_4\text{-}p\text{-}Me)_2$] at δ = 2.02 was observed. This resonance gradually disappeared after some hours, with appearance of a singlett at δ = 1.91 indicating the formation of the known diyne **7b**.[2] After 70h the starting material was fully consumed and only the signal at δ = 1.91 was detectable. The ^1H NMR spectra revealed no significant amount of any degradation product.

Crystalline **7b** (66% yield) was obtained upon extraction from the residue with hexane, filtration and storage of the filtrate at -60° C in. The ^1H-NMR (200MHz, C_6D_6) data were found to be identical to those reported earlier for this compound.[2]

References:

1) H. Braunschweig, T. Herbst, D. Rais, F. Seeler, *Angew. Chem.* 2005, **117**, 7627-7629; *Angew. Chem. Int. Ed.* 2005, 44, 7461-7463.

2) S. V. Damle, D. Seomoon, P. H. Lee, *J. Org. Chem.* 2003, **68**, 7085-7087.