Appreciably bent sp carbon chains : synthesis, structure and protonation of organometallic 1,3,5-triynes and 1,3,5,7-tetraynes of the formula (η^5-C_5Me_5)Re(NO)(PPh_3)((C=C)$_{n-}$ *p*-C_6H_4Me).

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Streszczenie

The diyne (η^5-C_5Me_5)Re(NO)(PPh_3)(C≡CC≡CSiMe_3) is elaborated to (η^5-C_5Me_5)Re(NO)(PPh_3)(C≡CC≡CC≡CSiR_3) (R=Me, **3a**; Et, **3b**) by sequences involving *n*-$Bu_4N^+F^-$ in aqueous THF to give (η^5-C_5Me_5)Re(NO)(PPh_3)(C≡CC≡CH) (91%), *n*-BuLi/CuI or *t*-BuOCu to give (η^5-C_5Me_5)Re(NO)(PPh_3)(C≡CC≡CCu) (**4**), and coupling with IC≡CSiMe_3 (48%) or BrC≡CSiEt_3 (84–65%). Complex **3b** is similarly converted to (η^5-C_5Me_5)Re(NO)(PPh_3)(C≡CC≡CC≡CH) (88%) and (η^5-C_5Me_5)Re(NO)(PPh_3)(C≡CC≡CC≡CCu) (**6**). Reactions of **4** and **6** with BrC≡C-*p*-C_6H_4Me give the title compounds (η^5-C_5Me_5)Re(NO)(PPh_3)((C≡C)$_n$-*p*-C_6H_4Me) (*n*= 3, **7**; 4, **8**; 77–66%). Optimized one flask conversions of **1a** and **3b** to **7** (81%) and **8** (71%) are described. The crystal structures of **7** (monoclinic, $P2_1/c$, *a*/*b*/*c*=17.951(8)/8.377(5)/22.160(9) Å, *β*= 103.63(5)°, *Z*=4), and **8** (monoclinic, $P2_1/n$, *a*/*b*/*c*=8.426(3)/16.400(6)/25.400(9) Å, *β*=97.51(3)°, *Z*=4) show markedly curved sp carbon chains—much more than hexatriynes or octatetraynes reported to date. The bond angles associated with the Re(C≡C)$_n$C moieties (min/max/avg) are 169.1(10)°/178.8(13)°/174.7° (**7**) and 170.0(9)°/178.8(10)°/175.7° (**8**). Other structural features are normal, and bending is provisionally ascribed to packing forces. Reaction of **7** and HBF_4·OEt_2 gives the cationic vinylidene complex [(η^5-C_5Me_5)Re(NO)(PPh_3)(C=C(H)C≡CC≡C-*p*-C_6H_4Me)]$^+BF_4^-$, the structure of which is established by extensive NMR analyses.

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