

Pyridine and benzyltriethylammonium chloride *ate*-complexes of 2,2,2-trichlorobenzo[*d*]-1,3,2-dioxaphosphole in the reactions with alk-1-yne

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Selected spectral data

For **7**: ^1H NMR ($[\text{D}_6]\text{DMSO}$, 45 °C): 8.65 (very br. s, OH), 7.72 (d, H^5 , $^3J_{\text{H}6\text{CCH}5}$ 8.5 Hz), 7.40 (br. s, H^8), 7.33 (br. d, H^6 , $^3J_{\text{H}5\text{CCH}6}$ 8.5 Hz), 6.25 (d, H^3 , $^2J_{\text{PCH}3}$ 17.6 Hz), 2.71 (br. t, C^9H_2 , $^3J_{\text{H}10\text{CCH}9}$ 7.2 Hz), 1.51 (m, C^{10}H_2 , $^3J_{\text{H}9\text{CCH}10}$ 7.2 Hz, $^3J_{\text{H}11\text{CCH}10}$ 7.2 Hz), 1.43 (m, C^{11}H_2 , $^3J_{\text{H}11\text{CCH}10}$ 7.2 Hz, $^3J_{\text{H}12\text{CCH}10}$ 7.2 Hz), 0.98 (t, C^{12}H_3 , $^3J_{\text{H}12\text{CCH}10}$ 7.2 Hz). ^{13}C NMR ($[\text{D}_6]\text{DMSO}$) d: 115.18 [ddm (d), C^3 , $^1J_{\text{PC}3}$ 170.9 Hz, $^1J_{\text{HC}3}$ 164.3 Hz], 152.28 [m (s), C^4], 124.15 [m (d), C^{4a} , $^3J_{\text{PCCC}4a}$ 17.3 Hz], 126.10 [dd (s), C^5 , $^1J_{\text{HC}5}$ 162.3 Hz, $^3J_{\text{HC}7\text{CC}5}$ 8.1 Hz], 124.52 [d (s), C_6 , $^1J_{\text{HC}6}$ 165.81 Hz], 131.64 [dd (s), C^7 , $^1J_{\text{HC}7}$ 167.3 Hz, $^3J_{\text{HC}5\text{CC}7}$ 8.7 Hz], 123.6 [m (d), C^8 , $^3J_{\text{POCC}8}$ 6.6 Hz], 147.77 [ddd (d), C^{8a} , $^3J_{\text{HC}5\text{CC}8a}$ 7.6 Hz, $^3J_{\text{HC}7\text{CC}8a}$ 7.6 Hz, $^2J_{\text{POC}8a}$ 6.1 Hz], 34.60 [tdm (d), C^9 , $^1J_{\text{HC}9}$ 128.2 Hz, $^3J_{\text{PCCC}9}$ 17.8 Hz], 30.81 [tm (s), C^{10} , $^1J_{\text{HC}10}$ 126.1 Hz], 22.63 [tm (s), C^{11} , $^1J_{\text{HC}11}$ 126.1 Hz], 14.56 [qm (s), C^{12} , $^1J_{\text{HC}12}$ 124.6 Hz]. ^{31}P NMR ($[\text{D}_6]\text{DMSO}$) dp: 7.0 (br. s).

For **8**: ^1H NMR ($[\text{D}_6]\text{DMSO}$) d: 7.61 (d, H^7 , $^3J_{\text{H}6\text{CCH}7}$ 7.3 Hz), 7.58 (d, H^5 , $^3J_{\text{H}6\text{CCH}5}$ 7.7 Hz), 7.21 (dd, H^6 , $^3J_{\text{H}5\text{CCH}6}$ 7.7–8.1 Hz, $^3J_{\text{H}7\text{CCH}6}$ 7.7–8.1 Hz), 6.24 (d, H^3 , $^2J_{\text{PCH}3}$ 18.0 Hz), 2.66 (br. t, C^9H_2 , $^3J_{\text{H}10\text{CCH}9}$ 7.0 Hz), 1.50 (m, C^{10}H_2 , $^3J_{\text{H}9\text{CCH}10}$ 7.0 Hz, $^3J_{\text{H}11\text{CCH}10}$ 7.0 Hz), 1.36 (m, C^{11}H_2 , $^3J_{\text{H}11\text{CCH}10}$ 7.3 Hz, $^3J_{\text{H}12\text{CCH}10}$ 7.3 Hz), 0.90 (t, C^{12}H_3 , $^3J_{\text{H}12\text{CCH}10}$ 7.3 Hz). ^{13}C NMR ($[\text{D}_6]\text{DMSO}$) d: 115.12 [ddm (d), C^3 , $^1J_{\text{PC}3}$ 170.9 Hz, $^1J_{\text{HC}3}$ 163.7 Hz], 152.32 [m (s), C^4], 124.11 [m (d), C^{4a} , $^3J_{\text{PCCC}4a}$ 17.3 Hz],

126.11 [dd (s), C⁵, ¹J_{HC5} 162.8 Hz, ³J_{HC7CC5} 8.1 Hz], 124.53 [d (s), C⁶, ¹J_{HC6} 165.80 Hz], 131.65 [dd (s), C⁷, ¹J_{HC7} 167.9 Hz, ³J_{HC5CC7} 8.7 Hz], 123.6 [m (d), C⁸, ³J_{POCC8} 6.6 Hz], 147.73 [ddd (d), C^{8a}, ³J_{HC5CC8a} 7.1 Hz, ³J_{HC7CC8a} 7.1 Hz, ²J_{POC8a} 6.6 Hz], 34.61 [tdm (d), C⁹, ¹J_{HC9} 126.1 Hz, ³J_{PCCC9} 17.8 Hz], 30.79 [tm (s), C¹⁰, ¹J_{HC10} 125.6 Hz], 22.61 [tm (s), C¹¹, ¹J_{HC11} 125.6 Hz], 14.55 [qm (s), C¹², ¹J_{HC12} 124.6 Hz].
³¹P NMR ([²H₆]DMSO, 45 °C) d: 6.7 (d, 17.4 Hz).