

Mononuclear Ruthenium Catalysts for the Direct Propargylation of Heterocycles with Propargyl Alcohols

Emilio Bustelo,^[a] and Pierre H. Dixneuf*^[a]

^[a] Institut de Chimie de Rennes, UMR 6509 Université de Rennes 1 - CNRS, Organométalliques et Catalyse, Campus de Beaulieu, 35042 Rennes, France.

Fax: +33 223236939

E-mail: pierre.dixneuf@univ-rennes1.fr

Supporting Information

Spectroscopic data for complexes 9 and 12:

[(*p*-cymene)RuCl(PCy₃){C(OH)CH=CHPh}][B(Ar_F)₄] (**9**): ¹H NMR (300 MHz, CD₂Cl₂, 233 K): δ 1.27 – 1.94 (m, 6 H + 30 H, CH(CH₃)₂ + PCy₃), 2.21 (d, 3 H, ²J_{HP} = 9.5 Hz, PCy₃), 2.92 (m, 1 H, CH(CH₃)₂), 6.12 and 6.50 (both bs, 4 H, C₆H₄), 7.57 – 7.70 (m, 2 H + 4 H, CH=CH + B(Ar_F)₄), 14.18 (bs, 1 H, Ru=C(OH)-). ³¹P{¹H} NMR (121.4 MHz, CD₂Cl₂, 233 K): δ 39.0 (s). ¹³C{¹H} NMR (75.4 MHz, CD₂Cl₂, 233 K): δ 18.5 (s, CH₃), 23.0 – 29.7 (m, PCy₃ + CH₃), 97.46, 100.5, 101.4 and 101.9 (s, C₆H₄), 129.9 and 136.3 (s, CH=CH), 287.5 (d, ²J_{CP} = 16.0 Hz, Ru=C(OH)-). COSY: 7.77? 7.65. HMQC: 14.2? nothing; 7.77? 136.3; 7.65? 129.9. HMBC: 14.18? 287.5, 136.3; 7.77? 287.5; 7.65? 287.5.

[(*p*-cymene)RuCl(PPh₃){C(OH)CH=CHPh}][B(Ar_F)₄] (**12**): ¹H NMR (300 MHz, CD₂Cl₂, 233 K): δ 1.25 (m, 6 H, CH(CH₃)₂), 1.84 (s, 3 H, CH₃), 2.76 (m, 1 H, CH(CH₃)₂), 5.19 and 5.73 (both d, 2 H, C₆H₄), 5.96 (bs, 2 H, C₆H₄), 7.36 – 7.60 (m, 17 H, CH=CH + PPh₃), 13.80 (bs, 1 H, Ru=C(OH)-). ³¹P{¹H} NMR (121.4 MHz, CD₂Cl₂, 233 K): δ 36.8 ppm. ¹³C{¹H} NMR (75.4 MHz, CD₂Cl₂, 233 K): δ 18.25 (s, CH₃), 20.90 and 22.98 (s, CH₃), 33.80 (s, CH), 91.53, 91.92, 97.05 and 98.73 (s, C₆H₄), 115 – 135 (s, C₆H₄ + PPh₃), 122.5 and 128.4 (s, CH=CH), 289.1 (d, ²J_{CP} = 15.7 Hz, Ru=CH(OH)-). COSY: 7.22? 7.58. HMQC: 13.80? nothing; 7.22? 122.5; 7.58? 128.4. HMBC: 13.80? 289.1, 122.5; 7.22? 289.1, 128.4; 7.58? 289.1, 122.5.

Spectroscopic data for complexes 10 and 13:

[(*p*-cymene)RuCl(PCy₃)(CO)][OTf] (10): IR (Nujol, cm⁻¹): 1974 ν(CO). ¹H NMR (300 MHz, CD₂Cl₂, 298 K): δ 1.30 - 1.50, 1.81, 1.91, 2.12 and 2.37 (m, 6 H + 33 H, CH(CH₃)₂ + PCy₃), 2.31 (s, 3 H, CH₃), 2.71 (m, 1 H, CH(CH₃)₂), 6.40, 6.79, 6.76 and 6.82 (all d, 4 H, ³J_{HH} = 6.7 Hz, C₆H₄). ¹³C{¹H} NMR (75.4 MHz, CD₂Cl₂, 298 K): δ 196.2 (d, ²J_{CP} = 25.0 Hz, CO), 96.93, 100.0, 103.8, 105.3, 119.9 and 123.8 (s, C₆H₄), 32.55 (s, CH), 20.0 – 30.0 (br, CH₃ + PCy₃). ³¹P{¹H} NMR (121.4 MHz, CD₂Cl₂, 298 K): δ 58.4 ppm (s).

[(*p*-cymene)RuCl(PPh₃)(CO)][OTf] (13): IR (Nujol, cm⁻¹): 2027 ν(CO). ¹H NMR (300 MHz, CD₂Cl₂, 298 K): δ 1.29 and 1.35 (d, 6 H, ³J_{HH} = 6.9 Hz, CH(CH₃)₂), 2.04 (s, 3 H, CH₃), 2.80 (m, 1 H, CH(CH₃)₂), 5.90, 6.22, 6.24 and 6.64 (all d, 4 H, ³J_{HH} = 6.0 Hz, C₆H₄), 7.55 – 7.66 (m, P-C₆H₅). ¹³C{¹H} NMR (75.4 MHz, CD₂Cl₂, 298 K): δ 193.7 (d, ²J_{CP} = 24.8 Hz, CO), 134.1, 129.6, 132.8 and 130.1 (all d, P(C₆H₅)₃), 97.65, 100.1, 104.5, 105.5, 121.7 and 124.3 (s, C₆H₄), 32.42 (s, CH), 23.42, 22.06 and 19.17 (s, CH₃). ³¹P{¹H} NMR (121.4 MHz, CD₂Cl₂, 298 K): δ 39.3 ppm (s).