Ruthenium-mediated Insertion of an Unsaturated C4 Unit into the P-N Bond of an Aminophosphine Ligand

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Supporting Information

General Techniques. All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures.[1] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. $[RuCp(MeCN)_3]PF_6$ was prepared according to the literature.[2] ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AVANCE-250 spectrometer operating at 250.13, 62.86, and 101.26 MHz, respectively, and were referenced to $SiMe_4$ and H_3PO_4 (85%). ^1H and $^{13}C\{^1H\}$ NMR signal assignments were confirmed by ^1H-COSY, 135-DEPT, and HSQC(^1H-^{13}C) experiments.

$[RuCp(PPh_2NEt_2)(CH_3CN)_2]PF_6$ (1). To a solution of $[RuCp(CH_3CN)_3]PF_6$ (300 mg, 0.69 mmol) in CH_2Cl_2 (5 mL) PPh_2NEt_2 (179 mg, 0.69 mmol) was added and the mixture was stirred for 2 h at room temperature. After removal of the solvent, a yellow powder was obtained which was collected on a glass frit, washed with Et_2O (3 x 10 mL), and dried under vacuum. Yield: 416 mg (93 %). Anal. Calcd. for $C_{25}H_{31}F_6N_3P_2Ru$: C, 46.16; H, 4.80; N, 6.46. Found: C, 46.10; H, 4.72; N, 6.55. ^1H NMR (δ, CD_2Cl_2, 20°C): 7.61 - 7.30 (m, 10H, Ph), 4.26 (s, 5H, Cp), 3.42 – 3.20 (m, 4H, Et), 2.22 (6H, CH_3CN), 0.96 (t, J_{HH} = 7.1 Hz, 3H, Et). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20°C): 137.4 (d, $^1J_{CP}$ = 46.0 Hz, Ph^1), 131.4 (d, $^2J_{CP}$ = 11.5 Hz, $Ph^{2,6}$), 129.7 (d, $^4J_{CP}$ = 1.9 Hz, Ph^4), 128.0 (d, $^3J_{CP}$ = 9.6 Hz, $Ph^{3,5}$), 127.3 (CH_3CN), 77.4 (d, J_{CP} = 2.3 Hz, Cp), 42.4 (d, J_{CP} = 6.5 Hz, CH_2), 13.6 (d, J_{CP} = 2.3 Hz, CH_3), 3.7 (CH_3CN). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 20°C): 102.1 (PPh_2), -143.0 ($^1J_{FP}$ = 711.8 Hz, PF_6).

$[RuCp(\eta^3\text{-}(P,C,C)\text{-}PPh_2CHC\text{-}(CH_2)_3\text{-}\eta^2\text{-}(C,C)\text{-}CCHNEt_2)]PF_6$ (2a). To a solution of **1** (100 mg, 0.15 mmol) in CH_2Cl_2 (10 mL) 1.1 equiv of 1,6-heptadiyne (19.5 μL, 0.17 mmol) was added and the mixture was stirred for 2 h at room temperature. After removal of the solvent under reduced pressure, an orange solid was obtained which was washed with Et_2O (5mL), and dried under vacuum. Yield: 75 mg (52 %). Anal. Calcd. for $C_{28}H_{33}F_6NP_2Ru$: C, 50.91; H, 5.09; N, 2.12. Found: C, 50.83; H, 5.11; N,

2.19. ^{1}H NMR (δ, CD_2Cl_2, 20°C): 7.68 – 7.41 (m, 10 H, Ph), 5.09 (s, 5H, Cp), 4.01 (d, $^{2}J_{HP}$ = 4.7 Hz, 1H, H^{1}), 3.58 (d, J_{HP} = 5.7 Hz, 1H, H^{4}), 3.01 – 2.86 (m, 2H), 2.82 – 2.51 (m, 6H), 2.39 – 2.27 (m, 2H), 0.96 (t, J_{HH} = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (δ, CD_2Cl_2, 20°C): 133.2 (d, $^{2}J_{CP}$ = 11.9 Hz, $Ph^{2,6}$), 132.4 (d, $^{2}J_{CP}$ = 12.3 Hz, $Ph^{2',6'}$), 132.1 (d, $^{4}J_{CP}$ = 3.5 Hz, Ph^{4}), 131.6 (d, $^{4}J_{CP}$ = 2.3 Hz, $Ph^{4'}$), 129.8 (d, $^{3}J_{CP}$ = 11.5 Hz, $Ph^{3,5}$), 129.0 (d, $^{3}J_{CP}$ = 11.9 Hz, $Ph^{3',5'}$), 125.9 (d, $^{1}J_{CP}$ = 47.9 Hz, Ph^{1}), 117.8 (d, J_{CP} = 6.9 Hz, C^{4}), 117.4 (d, J_{CP} = 4.6 Hz, C^{3}), 79.1 (d, J_{CP} = 1.5 Hz, Cp), 75.8 (C^{2}), 46.8 (CH_2), 40.8 (d, J_{CP} = 24.2 Hz, C^{1}), 36.0 (d, J_{CP} = 7.3 Hz, CH_2), 33.2 (CH_2), 23.1 (CH_2), 12.1 (CH_3). $^{31}P\{^{1}H\}$ NMR (δ, CD_2Cl_2, 20°C): 4.2 (PPh_2), -143.0 ($^{1}J_{FP}$ = 710.8 Hz, PF_6).

Reaction of 1 with 1,7-octadiyne in CD_2Cl_2. Formation of [RuCp(η^{3}-(P,C,C-PPh_2-CH-$C(CH_2)_4$-η^{2}-(C,C)-CCHNEt_2]PF_6 (2b) and [RuCp(η^{1}-(P)-PPh_2-CH=$C(CH_2)_4$-η^{3}-(C,C,N)-CCHNEt_2]PF_6 (3b). A 5 mm NMR tube was charged with **1** (30 mg, 0.05 mmol) in CD_2Cl_2 (0.5 mL) and 1,7-octadiyne (6,1 µL, 0.05 mmol) was added via syringe. The reaction was then monitored by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy. After 20 min both **2b** and **3b** are formed in an approximately 3:1 ratio. After 5 h this ratio already changed to ca. 1:6. Due to spectral overlap with **3b** only the most characteristic signals of **2b** could be unequivocally assigned. ^{1}H NMR (δ, CD_2Cl_2, 20°C): 5.10 (s, 5H, Cp), 3.53 (d, $^{2}J_{HP}$ = 4.7 Hz, 1H, H^{1}), 2.90 (d, J_{HP} = 7.6 Hz, 1H, H^{4}), 0.83 (t, J_{HH} = 7.1 Hz, 6H, Et). $^{31}P\{^{1}H\}$ NMR (δ, CD_2Cl_2, 20°C): 3.3 (PPh_2), -143.0 ($^{1}J_{FP}$ = 710.8 Hz, PF_6). After heating at 40°C for 8 h, **2b** is completely converted to **3b**.

[RuCp(η^{1}-(P)-PPh_2CH=C-$(CH_2)_3$-η^{3}-(C,C,N)-CCHNEt_2)]PF_6 (3a). A stirred solution of **2a** (50 mg, 0,08 mmol) in CH_3NO_2 (5 mL) was kept overnight at 80°C. After removal of the solvent under reduced pressure, an orange solid was obtained which was washed with Et_2O (5 mL), and dried under vacuum. Yield: 45 mg (85 %). Anal. Calcd. for $C_{28}H_{33}F_6NP_2Ru$: C, 50.91; H, 5.04; N, 2.12. Found: C, 50.87; H, 5.11; N, 2.08. ^{1}H NMR (δ, CD_3NO_2, 20°C): 8.08 – 7.88 (m, 2H, Ph), 7.73 – 7.34 (m, 6H, Ph), 7.33 – 7.16 (m, 2H, Ph), 6.35 (d, J_{HP} = 9.8 Hz, 1H, H^{1}), 6.03 (s, 1H, H^{4}), 4.76 (s, 5H, Cp), 3.72 – 3.51 (m, 1H), 3.03 – 2.44 (m, 4H), 2.27 – 1.84 (m, 5H), 1.21 (t, J_{HH} = 7.1 Hz, 3H), 0.81 (t, J_{HH} = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (δ, CD_3NO_2, 20°C): 172.0 (d, J_{CP} = 27.2 Hz, C^{3}), 137.5 (d, $^{1}J_{CP}$ = 54.4 Hz, Ph^{1}), 134.0 (d, $^{2}J_{CP}$ = 12.3 Hz, $Ph^{2,6}$), 131.6 (d, $^{1}J_{CP}$ = 47.2 Hz, $Ph^{1'}$), 131.3 (d, $^{4}J_{CP}$ = 2.3 Hz, Ph^{4}), 130.4 (d, $^{2}J_{CP}$ = 10.7 Hz, $Ph^{2',6'}$), 129.9 (d, $^{4}J_{CP}$ = 2.3 Hz, $Ph^{4'}$), 128.7 (d, $^{3}J_{CP}$ = 10.0 Hz, $Ph^{3,5}$), 128.6 (d, $^{3}J_{CP}$ = 10.7 Hz, $Ph^{3',5'}$), 117.4 (d, J_{CP} = 47.9 Hz, C^{1}), 91.3 (d, J_{CP} = 3.1 Hz, C^{2}), 82.2 (d, J_{CP} = 1.9 Hz, Cp), 79.1 (d, J_{CP} = 1.5 Hz, C^{4}), 58.3 (CH_2), 44.1 (d, J_{CP} = 8.8 Hz, CH_2), 38.4 (CH_2), 28.8 (d, J_{CP} = 19.6 Hz, CH_2),

25.1 (CH_2), 13.8 (CH_3), 12.1 (CH_3). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 20°C): 74.1 (PPh_2), -143.3 ($^1J_{FP}$ = 707.1 Hz, PF_6).

[RuCp(η^1-(P)-PPh$_2$-CH=C(CH$_2$)$_4$-η^3-(C,C,N)-CH-NEt$_2$]PF$_6$ (3b). To a solution of **1** (100 mg, 0.15 mmol) in CH_2Cl_2 (10 mL) 1.1 equiv of 1,7-octadiyne (20.8 μL, 0.15 mmol) was added and the mixture was heated for 8 h at 40°C. After removal of the solvent under reduced pressure, an orange solid was obtained which was washed with Et_2O (5mL), and dried under vacuum. Yield: 56 mg (55 %). Anal. Calcd. for $C_{29}H_{35}F_6NP_2Ru$: C, 51.63; H, 5.23; N, 2.08. Found: C, 51.55; H, 5.27; N, 2.17.^{1}H NMR (δ, CD_2Cl_2, 20°C): 7.96 – 7.79 (m, 2H, Ph), 7.66 – 7.39 (m, 6H, Ph), 7.34 – 7.18 (m, 2H, Ph), 6.21 (d, J_{HP} = 9.8 Hz, 1H, H^1), 6.06 (s, 1H, H^4), 4.69 (s, 5H, Cp), 3.78 – 3.57 (m, 1H), 3.28 – 3.12 (m, 1H), 2.72 – 2.40 (m, 2H), 2.34 – 1.68 (m, 8H), 1.22 (t, J_{HH} = 7.0 Hz, 3H), 0.89 (t, J_{HH} = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20°C): 169.5 (d, J_{CP} = 25.3 Hz, C^3), 137.8 (d, $^1J_{CP}$ = 54.1 Hz, Ph^1), 134.1 (d, $^2J_{CP}$ = 12.3 Hz, $Ph^{2,6}$), 131.8 (d, $^4J_{CP}$ = 2.3 Hz, Ph^4), 131.1 (d, $^1J_{CP}$ = 45.6 Hz, $Ph^{1'}$), 130.3 (d, $^4J_{CP}$ = 2.3 Hz, $Ph^{4'}$), 130.3 (d, $^2J_{CP}$ = 10.7 Hz, $Ph^{2',6'}$), 129.0 (d, $^3J_{CP}$ = 10.3 Hz, $Ph^{3,5}$), 122.5 (d, J_{CP} = 48.0 Hz, C^1), 90.8 (d, J_{CP} = 2.7 Hz, C^2), 82.7 (d, J_{CP} = 1.9 Hz, Cp), 79.8 (C^4), 58.4 (CH_2), 44.9 (CH_2), 43.8 (d, J_{CP} = 6.5 Hz, CH_2), 36.2 (d, J_{CP} = 21.5 Hz, CH_2), 29.9 (CH_2), 28.3 (CH_2), 14.2 (CH_3), 12.9 (CH_3). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2, 20°C): 76.3 (PPh_2), -142.9 ($^1J_{FP}$ = 710.8 Hz, PF_6).

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1 Perrin, D. D.; Armarego, W. L. F.*Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: New York, **1988**.

2 Gill; T. P.; Mann, K. R.*Organometallics* **1982**, *1*, 485.