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Modified synthesis for Ru–Rh heterobimetallic metallacarboranes based on ruthenium *exo-nido* complexes and not accompanied by *exo–nido* → *closo* rearrangement

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NMR spectra of mixtures of the isomers are given in accordance with literature descriptions of such mixtures containing inseparable isomers of *exo-nido* carborane clusters.[S1,S2] The symmetric and asymmetric isomers are hereinafter denoted as **S** and **AS**, respectively.

Compound 3: ^{1}H NMR (CD_2Cl_2, 400.13 MHz), δ: 7.40–6.94 (set of overlapping m, ~38H, Ph, **A** + **AS**), 4.56 (m, 4H, CH=CH_{COD}, **S**), 4.22 (m, CH=CH_{COD}, **AS**), 3.96 (m, CH=CH_{COD}, **AS**), 2.87 (br.s, 2H, CH_{carb}, **S**), 2.42 (br.s, CH_{carb}, **AS**), 2.53 and 2.12 (m, $CH_{2(COD)}$, **AS**), –3.52 (m, H(12), **AS**), –3.96 (m, 2H, H(9,12), **S**), –5.25 (m, H(8), **AS**), –13.92 (m, 1H, H(8), **S**), –16.52 (m, H(9), **AS**). ^{31}P{^{1}H} (CD_2Cl_2, 161.98 MHz), δ: 56.32 and 44.98 (both br.s (1 : 1), P, **AS**), 54.92 (br.s, P, **S**). ^{13}C{^{1}H} (CD_2Cl_2, *J*(Hz) *J** = *J*(^{103}Rh–^{13}C) Ph groups signals of asymmetric isomer are not specified), δ: 135.2, 130.8, 128.4, (*o*-, *p*-, *m*-C(Ph)) 134.8 (d, $J_{C\text{-}P}$ 9.8 Hz *ipso*-C(Ph)), 95.6 (br.s, C_{carb}, **S**), 76.6 (d, *J** 11.8 Hz, *C*H=*C*H_{COD}, **AS**), 76.3 (d, *J** 11.8 Hz, *C*H=CH_{COD}, **S**), 75.8 (d, *J** 11.8 Hz, CH=*C*H_{COD}, **AS**), 36.8 (s, CH_2, **AS**), 33.0 (s, CH_2, **S**), 32.17 (s, CH_2, **AS**). ^{11}B{^{1}H} (CD_2Cl_2, 192.57 MHz), δ: –5.21 (br.s), –7.13 (br.s), –11.01 (br.s), –16.87 (br.s), –21.88 (s), –23.41 (br.s). Found (%): C, 54.57; H, 5.41; P, 6.10. Calc. for $C_{46}H_{53}B_9ClP_2RhRu$ (%): C, 54.99; H, 5.41; P 6.17.

Compound 4: ^{1}H NMR (CD_2Cl_2, 600.22 MHz), δ: 7.32, 7.26 and 7.16 (all m, ~36H, Ph, **S** + **AS**), 3.88 (dd, J_1 4.7 Hz, J_2 2.3 Hz, 4H, CH=CH_{NBD}, **S**), 3.67 (m, 2H, CH_{NBD}, **S**), 3.53 and 3.63(both m (1 : 1), CH=CH_{NBD}, **AS**), 3.45 (m, CH_{NBD}, **AS**), 2.74 (br.s, 2H, CH_{carb}, **S**), 2.65 and 2.26 (both br.s (1 : 1), CH_{carb}, **AS**), 1.35 (t, *J* 1.4 Hz, 2H, $(CH_2)_{NBD}$, **S**), 1.19 (t, *J* 1.5 Hz, $(CH_2)_{NBD}$, **AS**), –3.82 (m, H(12), **AS**), –4.26 (m, 2H, H(9,12), **S**), –4.69 (m, H(8), **AS**), –14.22 (m, 1H, H(8), **S**), –16.61 (m, H(9), **AS**). ^{1}H{^{11}B} NMR (CD_2Cl_2, 600.22 MHz), δ: 7.32, 7.26 and 7.16 (all m, ~36H, Ph, **S** + **AS**), 3.88 (dd, J_1 4.7 Hz, J_2 2.3 Hz, 4H, CH=CH_{NBD}, **S**), 3.67 (m, 2H, CH_{NBD}, **S**), 3.53 and 3.63 (both m (1 : 1), CH=CH_{NBD}, **AS**), 3.45 (m, CH_{NBD}, **AS**), 2.74 (br.s, 2H, CH_{carb}, **S**), 2.65 and 2.26 (both br.s (1 : 1), CH_{carb}, **AS**), 2.54 (br.s, 1H, BH_{carb}, **S**), 2.50 and 2.29

(both br.s (1 : 1), BH_{carb}, **AS**), 1.73 (br.s, 1H, BH_{carb}, **AS**), 1.35 (t, *J* 1.4 Hz, 2H, $(CH_2)_{NBD}$, **S**), 1.19 (t, *J* 1.5 Hz, $(CH_2)_{NBD}$, **AS**), 0.64 (br.s, 2H, BH_{carb}, **S**), –3.82 (m, H(12), **AS**), –4.26 (m, 2H, H(9,12), **S**), –4.69 (d-like, *J* 49.2 Hz, H(8), **AS**), –14.22 (t, *J* 9.9 Hz, 1H, H(8), **S**), –16.61 (t-like, *J* 8.4 Hz, H(9), **AS**). $^{31}P\{^1H\}$ (CD_2Cl_2, 242.97 MHz), δ: 56.53 and 44.72 (br.s and d-like (1 : 1), **AS**), 54.36 (br.s, **S**). $^{13}C\{^1H\}$ (CD_2Cl_2, 150.93 MHz): 134.82 (t-like), 134.45 (dd, J_1 16.2 Hz, J_2 10 Hz), 130.35 (br.s), 130.11 (d-like), 128.20 (d-like), and 128.05(t-like) (Ph, **S** + **AS**), 58.92 (d, J_{Rh-C} 5.6 Hz, $(CH_2)_{NBD}$, **S**), 47.11 (d-like, CH_{NBD}, **S** + **AS**), 43.18(d, J_{Rh-C} 9.0 Hz, $CH{=}CH_{NBD}$, **S**), 34.32 (br.s, C_{carb}, **S**), 31.15 and 33.34 (br.s, C_{carb}, **AS**). $^{11}B\{^1H\}$ (CD_2Cl_2, 192.57 MHz), δ: –8.18 (br.s), –11.61 (br.s), –14.46 (br.s), –18.93 (br.s), –23.86 (br.s), –25.30 (br.s). Found (%): C, 53.25; H, 5.19; B, 9.48. Calc. for $C_{45}H_{49}B_9ClP_2RhRu0.5CH_2Cl_2$ (%): C, 53.01; H, 4.89; B, 9.44.

Compound 5: ^1H NMR (CD_2Cl_2, 400.13 MHz), δ: 7.45, 7.32, 7.16, and 6.99 (all m, ~38H, Ph, **S** + **AS**), 4.19 (br.s, 4H, $CH{=}CH_{COD}$, **S**), 4.13 (t-like,$CH{=}CH_{COD}$, **AS**), 3.81 (m, $CH{=}CH_{COD}$, **AS**), 2.44 (m, $CH_{2(COD)}$, **S** + **AS**), 2.14–2.22 (s and q-like, 10H, Me, s + $CH_{2(COD)}$, **S**), 2.10 and 2.07 (1 : 1) (both br.s, Me, **AS**), –3.25 (m, H(12), **AS**), –4.19 (m, 2H, H(9,12), **S**), –13.34 (m, 1H, H(8), **S**), –16.62 (m, H(9), **AS**).$^{31}P\{^1H\}$ (CD_2Cl_2, 161.98 MHz), δ: 58.09 and 40.97 (br.s and d-like (1 : 1), P, **AS**), 54.43 (br.s, P, **S**). $^{13}C\{^1H\}$ (CD_2Cl_2, 100.51 MHz), δ: 135.08 (br.s), 134.88 (t-like), 134.69 (br.s), 134.49 (dd, *J* 26.9 Hz, *J* 10 Hz), 130.39 (br.s), 129.97 (d, *J* 2.3 Hz), and 128.07 (t-like) (Ph, **S** + **AS**), 80.34 (d, J_{Rh-C} 11.5 Hz, $CH{=}CH_{COD}$, **S**), 79.99 and 79.75 (both d, J_{Rh-C} 11.6 and 11.8 Hz, $CH{=}CH_{COD}$, **AS**), 58.97(br.s, C_{carb}, **S**), 33.01 (s, $CH_{2(COD)}$, **AS**), 32.23 (s, $CH_{2(COD)}$, **S**), 31.17 (s, $CH_{2(COD)}$, **AS**), 27.89 (s, Me, **S**), 27.55 and 27.29 (both s, Me, **AS**). $^{11}B\{^1H\}$ (CD_2Cl_2, 161.98 MHz), δ: –4.30 (br.s), –8.79 (br.s), –12.54 (br.s), –18.45 (br.s), –21.60 (s), –23.44 (br.s). Found (%): C, 56.04; H, 5.45; B, 9.41. Calc. for $C_{48}H_{57}B_9ClP_2RhRu$ (%): C, 55.83; H, 5.56; B 9.42.

Compound 6: ^1H NMR (CD_2Cl_2, 400.13 MHz), δ: 7.33, 7.24, 7.17, and 7.12 (all m, ~36H, Ph-**S** + **AS**), 3.66 (br.s, 2H, NBD(CH), **S**), 3.64 (t-like, 4H, *J* 2.1 Hz, $CH{=}CH_{NBD}$, **S**), 3.45, 3.35, and 3.26 (all br.s (1 : 1 : 1), CH_{NBD}, $CH{=}CH_{NBD}$, **AS**), 2.07 (br.s, 6H, Me, **S**), 1.83 (br.s, 3H, Me, **AS**), 1.29 (br.s, 2H, $CH_{2(NBD)}$, **S**), 1.26 (br.s, 3H, Me, **AS**), 1.13 (br.s, $CH_{2(NBD)}$, **AS**), –3.53 (m, H(12), **AS**), –4.25 (m, H(9,12), **S** and H(8), **AS**), –14.04 (m, 1H, H(8), **S**), –16.59 (m, H(9), **AS**). $^{31}P\{^1H\}$ (CD_2Cl_2, 161.98 MHz), δ: 56.90 and 44.89 (br.s and d-like (1 : 1), P, **AS**), 54.54 (br.s, P, **S**). $^{13}C\{^1H\}$ (CD_2Cl_2, 100.51 MHz): 135.03 (br.s), 134.84 (t-like, *J* 4.9 Hz), 134.64 (br.s), 134.47 (dd, *J* 21.5, 10 Hz), 130.36 (br.s), 130.07 (d-like), 128.22 (d-like, *J* 10.3 Hz), 128.04 (t-like), and 127.94(br.s) (Ph, **S** + **AS**), 58.63 (d, *J* 5.6 Hz, $CH_{2(NBD)}$, **S**), 48.43 (d, J_{Rh-C} 8.8 Hz, $CH{=}CH_{NBD}$, **AS**), 48.48 and 48.17 (both d, both J_{Rh-C} 8.8 Hz, $CH{=}CH_{NBD}$, **AS**), 47.08 (d-like, *J* 2.0, CH_{NBD}, **S** + **AS**), 30.09 and 30.05 (both br.s, C_{carb}, **S** + **AS**), 28.46 (br.s, Me, **S**) and 27.18

(br.s, Me, **AS**). $^{11}B\{^{1}H\}$ (CD_2Cl_2, 161.98 MHz): –7.00 (br.s), –13.89 (br.s), –17.41 (br.s), –20.58 (br.s), –23.74 (s), –25.31 (br.s). Found (%): C, 55.21; H, 5.37; B, 9.71. Calc. for $C_{47}H_{53}B_9ClP_2RhRu$ (%): C, 55.53; H, 5.25; B 9.57.

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