Supplemental Material

Synthesis, Characterization and Structures of Cyclic Organorhodium Complexes of the Type [Rh{CH(SO_2Ph)$CH_2CH_2YR_2$-κ*C*,κ*Y*}L_2] (YR_2 = PPh_2, NMe_2; L_2 = Diphosphine, Cyclooctadiene)

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1. Preparation of Starting Materials

$PhSO_2CH_2CH_2CH_2PPh_2$ (**1**) was synthesized by conversion of $NaPPh_2$ with $PhSO_2CH_2CH_2$-CH_2Br[1] which was prepared according to a conventional method from KSPh and $BrCH_2CH_2$-CH_2Br[2] followed by oxidation with acetic acid/H_2O_2.[3] The amino compound $PhSO_2CH_2CH_2$-CH_2NMe_2 (**2**) was obtained by oxidation of $PhSCH_2CH_2CH_2NMe_2$[4] with acetic acid/H_2O_2. [{Rh(cod)}$_2$(μ-Cl)$_2$] (**5**) and [{Rh(C_2H_4)$_2$}$_2$(μ-Cl)$_2$] (**6**) were obtained according to established procedures.[5] The dimeric Rh(I) complexes of the type of [{Rh(P$\frown$P)}$_2$(μ-Cl)$_2$] (P$\frown$P = dmpe, **7a**; dppm **7b**; dppe **7c**; dppp, **7d**) were received by reaction of either [{Rh(cod)}$_2$(*μ*-Cl)$_2$] (**5**) or [{Rh(C_2H_4)$_2$}$_2$(*μ*-Cl) $_2$] (**6**) with the respective diphosphine in toluene.[6,7] To avoid a predominant formation of the cationic bis(diphosphine)rhodium(I) complexes [Rh(P$\frown$P)$_2$]-Cl the addition of the diphosphine has to be performed slowely. Best results were obtained using complex **5** for synthesis of the dppe complex **7c** and using complex **6** for complexes **7a**, **7b** and **7d**. Whereas the dinuclear olefin complexes **5** and **6** are relatively air stable, the respective diphosphine complexes [{Rh(P$\frown$P)}$_2$(*μ*-Cl)$_2$] (**7a**–**d**) are highly air and moisture sensitive and have to be stored under argon.

2. NMR Spectroscopic Data of Starting Materials

2.1. $PhSO_2CHCH_2CH_2PPh_2$ (**1**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.83 (m, 2H, $CH_2CH_2CH_2$), 2.11 (m, 2H, CH_2PPh_2), 3.20 (m, 2H, CH_2SO_2Ph), 7.28–7.35 (m, 10H, P*Ph*$_2$), 7.48–7.52 (m, 2H, *m-H*, SO_2Ph), 7.56–7.62 (m, 1H, *p-H*, SO_2Ph), 7.81–7.82 (m, 2H, *o-H*, SO_2Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.5 (d, $^2J(^{13}C,^{31}P)$ = 18.8 Hz, $CH_2CH_2CH_2$), 26.7 (d, $^1J(^{13}C,^{31}P)$ = 12.5 Hz CH_2PPh_2), 56.7 (d, $^3J(^{13}C,^{31}P)$ = 13.6 Hz, CH_2SO_2Ph), 127.9–138.9 (m, C_{Ar}). ^{31}P NMR (81 MHz, $CDCl_3$): δ –16.4 (s, *P*Ph$_2$).

2.2. $\mathrm{PhSO_2CHCH_2CH_2NMe_2}$ (**3**)

^{1}H-NMR (400 MHz, $\mathrm{CDCl_3}$): δ 1.77–1.85 (m, 2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_2}$), 2.07 (s, 6H, $\mathrm{N(C}\mathit{H}_3)_2$), 2.24 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{NMe_2}$), 3.09–3.13 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{SO_2Ph}$), 7.48–7.52 (m, 1H, *m-H*, $\mathrm{SO_2Ph}$), 7.56–7.61 (m, 1H, *p*-H, $\mathrm{SO_2Ph}$), 7.84–7.86 (m, 2H, *o*-H, $\mathrm{SO_2Ph}$). ^{13}C-NMR (125 MHz, $\mathrm{CDCl_3}$): δ 20.7 (s, $\mathrm{CH_2}\mathit{C}\mathrm{H_2CH_2}$), 45.0 (s, $\mathrm{N(}\mathit{C}\mathrm{H_3)_2}$), 54.0 (s, $\mathit{C}\mathrm{H_2SO_2Ph}$), 57.2 (s, $\mathit{C}\mathrm{H_2NMe_2}$), 127.9 (s, *o-C*, $\mathrm{SO_2Ph}$), 129.2 (s, *m-C*, $\mathrm{SO_2Ph}$), 133.6 (s, *p-C*, $\mathrm{SO_2Ph}$), 139.2 (s, *i-C*, $\mathrm{SO_2Ph}$).

2.3. $[\{\mathrm{Rh(cod)}\}_2(\mu\text{-}\mathrm{Cl})_2]$ (**5**)

^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 1.71/2.46 (m/m, 8H/8H, $\mathrm{C}\mathit{H}_2$), 4.18 (s, br, 8H, $\mathrm{C}\mathit{H}$). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 31.0 (s, $\mathit{C}\mathrm{H_2}$), 78.7 (d, $^1J(^{13}\mathrm{C},^{103}\mathrm{Rh})$ = 13.8 Hz, CH).

2.4. $[\{\mathrm{Rh(C_2H_4)_2}\}_2(\mu\text{-}\mathrm{Cl})_2]$ (**6**).

^{1}H NMR (200 MHz, THF-d_8): δ 3.10 (s, br, 16H, $\mathrm{C}\mathit{H}_2$). ^{13}C NMR (50 MHz, THF-d_8): δ 60.7 (s, br, $\mathit{C}\mathrm{H_2}$).

2.5. $[\{\mathrm{Rh(P}\frown\mathrm{P)}\}_2(\mu\text{-}\mathrm{Cl})_2]$ (**7a–d**)

$\mathrm{P}\frown\mathrm{P}$ = dmpe (**7a**): ^{1}H NMR (400 MHz, $\mathrm{CD_3NO_2}$): δ 1.41 (m, 24H, $\mathrm{PC}\mathit{H}_3$), 1.51 ('d', N = 17.0 Hz, 8H, $\mathrm{C}\mathit{H}_2\mathrm{P}$). ^{13}C NMR (50 MHz, $\mathrm{CD_3NO_2}$): δ 16.2 ('t', N = 26.6 Hz, $\mathrm{P(}\mathit{C}\mathrm{H_3)_2}$), 29.2 ('t''d', N = 51.2/6.1Hz, $\mathrm{CH_2PMe_2}$). ^{31}P NMR (81 MHz, $\mathrm{CD_3NO_2}$): δ 55.8 (d, $^1J(^{31}\mathrm{P},^{103}\mathrm{Rh})$ = 196.6 Hz, $\mathit{P}\mathrm{Me_2}$).

$\mathrm{P}\frown\mathrm{P}$ = dppm (**7b**): ^{1}H NMR (400 MHz, THF-d_8): δ 3.92 (td, $^2J(^1\mathrm{H},^{31}\mathrm{P})$ = 10.6 Hz, $^3J(^1\mathrm{H},^{103}\mathrm{Rh})$ = 2.5 Hz, 4H, $\mathrm{C}\mathit{H}_2\mathrm{P}$), 7.15–7.30 (m, 24H, *m-H/p-H* $\mathrm{PPh_2}$), 7.91–8.02 (m, 16H, *o-H* $\mathrm{PPh_2}$). ^{13}C NMR (100 MHz, THF-d_8): 51.2 (t, $^1J(^{13}\mathrm{C},^{31}\mathrm{P})$ = 23.7 Hz, $\mathit{C}\mathrm{H_2P}$), 131.3 ('t', N = 10.0 Hz, *o-C*, $\mathrm{PPh_2}$), 132.4 (s, *p-C*, $\mathrm{PPh_2}$), 135.9 ('t', N = 11.8 Hz, *m-C*, $\mathrm{PPh_2}$), 139.6 ('t', N = 38.4 Hz, *i-C*, $\mathrm{PPh_2}$). ^{31}P NMR (81 MHz, THF-d_8): δ –27.4 (d, $^1J(^{31}\mathrm{P},^{103}\mathrm{Rh})$ = 169.0 Hz, $\mathit{P}\mathrm{Ph_2}$).

$\mathrm{P}\frown\mathrm{P}$ = dppe (**7c**): ^{1}H NMR (400 MHz, THF-d_8): δ 2.00 ('d', N = 19.2 Hz, 8H, $\mathrm{C}\mathit{H}_2\mathrm{P}$), 7.19–7.43 (m, 24H, *m-H*/*p-H* $\mathrm{PPh_2}$), 7.80–7.89 (m, 16H, *o-H* $\mathrm{PPh_2}$). ^{13}C NMR (100 MHz, THF-d_8): δ 28.9 ('t''d', N = 57.2/3.8 Hz, $\mathit{C}\mathrm{H_2PPh_2}$), 128.3 (m, *m-C*, $\mathrm{PPh_2}$), 129.6 (s, *p-C*, $\mathrm{PPh_2}$), 134.1 (m, *o-C*, $\mathrm{PPh_2}$), 137.6 (m, *i-C*, $\mathrm{PPh_2}$). ^{31}P NMR (81 MHz, THF-d_8): δ 73.6 (d, $^1J(^{31}\mathrm{P},^{103}\mathrm{Rh})$ = 197.8 Hz, $\mathit{P}\mathrm{Ph_2}$).

$\mathrm{P}\frown\mathrm{P}$ = dppp (**7d**): ^{1}H NMR (400 MHz, THF-d_8): δ 1.73 (s, br, 4H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_2}$), 2.14 (s, br, 8H, $\mathrm{C}\mathit{H}_2\mathrm{PPh_2}$), 7.00–7.10 (m, 16H, *m-H*, $\mathrm{PPh_2}$), 7.13–7.18 (m, 8H, *p-H* $\mathrm{PPh_2}$), 7.65–7.69 (m, 16H, *o-H* $\mathrm{PPh_2}$). ^{13}C NMR (100 MHz, THF-d_8): 20.7 (s, br, $\mathrm{CH_2CH_2CH_2}$), 29.3 (t, $^2J(^{13}\mathrm{C},^{31}\mathrm{P})$ = 19.6 Hz, $\mathit{C}\mathrm{H_2PPh}$), 127.8 (s, br, *m-C*, $\mathrm{PPh_2}$), 129.0 (s, *p-C*, $\mathrm{PPh_2}$), 134.4 (s, br, *m-C*, $\mathrm{PPh_2}$), 138.3 ('t', N = 42.0 Hz, *i*-*C*, PPh_2). ^{31}P NMR (81 MHz, THF-d_8): δ 32.5 (d, $^{1}J(^{31}P,^{103}Rh)$ = 212.8 Hz, $\mathit{P}Ph_2$).

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