Electronic Supplementary Information

Early-Late Heterobimetallic Rh-Ti and Rh-Zr Complexes via Addition of Early Metal Chlorides to Mono- and Divalent Rhodium

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Experimental

General Considerations. Unless specified otherwise, all manipulations were performed under an argon atmosphere using standard Schlenk line or glove box techniques. Toluene, diethyl ether, C_6D_6, THF and pentane were dried over and distilled from NaK/Ph_2CO/18-crown-6 and stored over molecular sieves in an Ar-filled glove box. Fluorobenzene and $CDCl_3$ were dried with and then distilled from CaH_2 and stored over molecular sieves in an argon-filled glove box. The following compounds were prepared according to literature procedures: $[Rh(COD)Cl]_2$,[1] (PNP)Rh(CH_2=CH^tBu) (**1**),[2] (PNP)Rh(H)(Cl)[3] and (PNP)$TiCl_3$.[4] All other chemicals were purchased from either Aldrich or Acros and used as received unless otherwise noted. NMR spectra were recorded on a Varian Inova 300, Varian Mercury 300 or Varian NMRS 500 spectrometer. For ^1H and ^{13}C NMR spectra, the residual solvent peak was used as an internal reference. ^{31}P NMR spectra were referenced externally using 85% H_3PO_4 at 0 ppm and ^{19}F NMR spectra were referenced externally using neat trifluoroacetic acid at -78.5 ppm. Chemical shifts are reported in ppm and coupling constants in Hz Elemental analyses were performed by CALI Labs, Inc. (Parsippany, NJ)**.**

Synthesis of (PNP)Rh($TiCl_3$)(Cl), 2. To a solution of **1** (30 mg, 0.049 mmol) in fluorobenzene was added a solution $TiCl_4$ (5.4 µL, 0.049 mmol) in fluorobenzene (108 µL) with stirring. A rapid colour change from orange to dark green was observed and the mixture was stirred for 5 min. Filtration, layering of the solution with pentane and cooling to -30 °C gave rise to a green crystalline solid. Isolation of the solid, washing with pentane and drying in vacuo gave a dark green solid (27 mg, 77%). Single crystals suitable for an X-ray diffraction study were grown by layering a fluorobenzene solution with pentane. ^1H NMR (300 MHz, C_6D_6) δ: 7.74 (2H, dt, J = 8, J = 1.5, $C_{Ar}H$), 7.22 (2H, s, $C_{Ar}H$), 6.79 (2H, d, J = 8, $C_{Ar}H$), 3.43 (2H, m, C*H*CH$_3$), 2.37 (2H, m, C*H*CH$_3$), 2.07 (6H, s, CC*H*$_3$), 1.81 (6H, dvt, J = 8, J = 8, CHC*H*$_3$), 1.48 (6H, dvt, J= 8, J = 7, CHC*H*$_3$), 0.96 (6H, dvt, J = 8, J = 8, CHC*H*$_3$), 0.79 (6H, dvt, J = 7, J = 7, CHC*H*$_3$). (CD$_2$Cl$_2$) δ: 7.71 (2H, d, J = 8, C$_{Ar}$*H*), 7.51 (2H, s, C$_{Ar}$*H*), 7.25 (2H, d, J = 8, C$_{Ar}$*H*), 3.42 (2H, m, C*H*CH$_3$), 2.65 (2H, m, C*H*CH$_3$), 2.44 (6H, s, CC*H*$_3$), 1.86-1.63 (12H, m, CHC*H*$_3$), 1.13-0.90 (12H, m, CHC*H*$_3$). ^{13}C{^{1}H} NMR (75 Hz, CD$_2$Cl$_2$) δ: 156.4 (vt, J = 7, *C*N), 137.4 (vt, J = 3, *C*$_{Ar}$), 133.7 (s, *C*$_{Ar}$), 132.2 (s, *C*$_{Ar}$), 130.1 (vt, J = 17, *C*$_{Ar}$), 123.0 (vt, J = 4, *C*$_{Ar}$), 28.5 (vt, J = 11.4, *C*HCH$_3$), 27.6 (vt, J = 11.4, *C*HCH$_3$), 21.1 (s, *C*H$_3$), 20.6 (s, *C*H$_3$), 20.0 (s, *C*H$_3$), 19.6 (s, *C*H$_3$), 19.1 (s, *C*H$_3$). ^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$) δ: 40.1 (d, J = 124). (CD$_2$Cl$_2$) δ: 42.3 (d, J = 122). Anal. Calcd: C, 43.30; H, 5.59. Found: C, 43.34; H, 5.63.

Synthesis of (PNP)RhCl. To a solution of (PNP)Rh(H)(Cl) (59 mg, 0.10 mmol) in toluene (5 mL) was added a solution of TEMPO (16 mg, 0.10 mmol) in toluene (2 mL). After 16 h the volatiles were removed and the residue recrystallised as small green blocks from toluene at -30 °C (39 mg, 66 %). ^{1}H NMR (300 MHz, C$_6$D$_6$) δ: 46.26, 39.39 (2H, br, overlapping), 8.06 (overlaps with protio-solvent), 3.51 (24H, br). Anal. Calcd: C, 55.08; H, 7.11. Found: C, 54.97; H, 7.03. μ_{eff} (Evans NMR method) = 1.9 $\mu_{B.}$.

Synthesis of 2 by reaction of (PNP)Rh(Cl) with TiCl$_3$. To a Young's NMR tube was added a solution of (PNP)RhCl (15 mg, 0.026 mmol) in C$_6$D$_6$ (1 mL) and TiCl$_3$ (4.1 mg, 0.026 mmol) and it was sonicated briefly. The mixture was heated for 48 h at 90 °C, after which time ^{1}H and ^{31}P NMR spectroscopy revealed the formation of **2** in approximately 70% yield.

Synthesis of 2 by reaction of (PNP)TiCl$_3$ with [(cod)RhCl]$_2$. To a Young's NMR tube was added a solution of (PNP)TiCl$_3$ (20 mg, 0.34 mmol) in toluene (1 mL) and [(cod)RhCl]$_2$ (8.5 mg, 0.17 mmol) and the resultant mixture was heated at 55 °C. After 41 h, examination of the reaction by ^{1}H and ^{31}P NMR spectroscopy revealed the formation of **2** in approximately 75%

yield.

Synthesis of (PNP)Rh(ZrCl$_3$)(Cl), 3. To a solution of **1** (60 mg, 0.098 mmol) in fluorobenzene (3 mL) was added ZrCl$_4$ (22.8 mg, 0.098 mmol) and the mixture was stirred for 5 min. A colour change from orange to red was observed and the solution was filtered. Layering with pentane and cooling (-30 °C) gave an orange crystalline material (56 mg, 75%). Single crystals suitable for an X-ray diffraction study were grown by layering a deuterated benzene solution with pentane. ^{1}H NMR (300 MHz, C_6D_6) δ: 7.61 (2H, d, J = 8, $C_{Ar}H$), 7.42 (2H, s, $C_{Ar}H$), 7.24 (2H, d, J = 8, $C_{Ar}H$), 3.16-2.99 (2H, m, $CHCH_3$), 2.78-2.59 (2H, m, $CHCH_3$), 2.42 (6H, s, CCH_3), 1.72-1.53 (12H, m, $CHCH_3$), 1.24-1.07 (12H, m, $CHCH_3$). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2) δ: 152.2 (vt, J = 11, CN), 137.0 (s, C_{Ar}), 134.1 (s, C_{Ar}), 133.1 (s, C_{Ar}), 130.6 (vt, J = 16, C_{Ar}), 123.0 (s, C_{Ar}), 28.1 (vt, J = 12, $CHCH_3$), 27.3 (vt, J = 12, $CHCH_3$), 21.1 (s, CH_3), 20.4 (s, CH_3), 20.0 (s, CH_3), 19.3 (s, CH_3), 18.7 (s, CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6) δ: 39.7 (d, J = 122). Anal. Calcd: C, 40.85; H, 5.27. Found: C, 40.76; H, 5.40.

Decomposition of 3 in DCM to give S1. The dissolution of **3** in CH_2Cl_2 led to over a period of 3 d a color change from orange to dark purple and was concurrent with the disappearance of signals attributable to **3**, and the appearance of a new pair of signals in 1:1 ratio by ^{31}P NMR spectroscopy ($^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2) δ: 89.2 (1P, d, J = 143), 41.3 (1P, s) ppm). Although we have not pursued full characterization, upon layering with pentane a small crop of purple crystals of complex **S1** (Figure S1) suitable for an X-ray diffraction study was obtained. Complex **S1** resulted from a formal addition of a molecule of dichloromethane to complex **3** with the CH_2 group inserting into one of the Rh-P bonds and the two Cl complementing the original four in **S1** to give a $ZrCl_6$ near-octahedron that shares three of the chlorides with Rh. A reaction of a phosphine ligated rhodium(I) complex with CH_2Cl_2 to give an R_3PCH_2Rh species is not without precedent with Marder et al. reporting the conversion of $[RhCl(PMe_3)_3]$ into fac-$[RhCl_2(CH_2PMe_3)(PMe_3)_3]Cl$.[5] Evidently from the X-ray molecular structure of complex **5** there no longer exists a metal-metal single bond with a Zr-Rh distance of 3.27 Å.

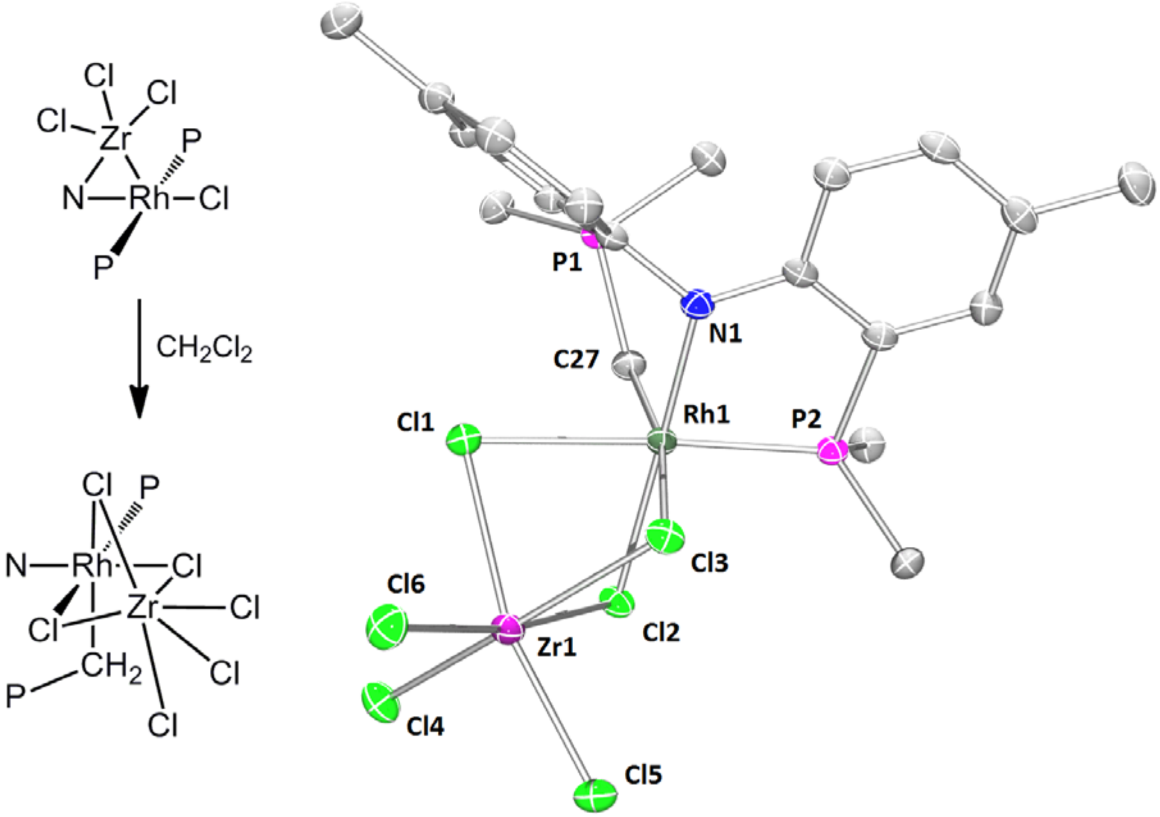

Figure S1. Synthesis, structural formula (left) and a POV-Ray[6] rendition of the ORTEP[7] drawing (right, ellipsoids set to 50%) of **S1** showing selected atom labeling. The hydrogen atoms, methyl groups of the isopropyl moieties and molecule of co-solvent are omitted for clarity. Selected bond distances (Å) and angles (°): Rh1-N1 1.998(2), Rh1-C27 2.059(3), P1-C27 1.806(3), Rh1-P2 2.2471(8), Rh1-Cl1 2.5836(8), P2-Rh1-C27 96.51(9), N1-Rh1-C27 89.30(10).

X-Ray data collection, solution, and refinement for compound 2. A green, multi-faceted block of suitable size (0.27 x 0.2 x 0.03 mm) was selected from a representative sample of crystals of the same habit using an optical microscope and mounted onto a nylon loop. Low temperature (110 K) X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, K_α = 0.71073 Å). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software.[8] An absorption correction was applied using SADABS.[9] The space group was determined on the basis of systematic absences and intensity statistics and the structure was solved by direct methods and refined by full-matrix least squares on F^2. The structure was solved in the monoclinic $P2_1/c$ space group using XS[10] (incorporated in SHELXTL). No missed symmetry was reported by PLATON.[11] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in idealized positions and refined using riding model. The structure was refined (weighted least squares refinement on F^2) and the final least-squares refinement converged to $R_1 = 0.0224$ ($I > 2\sigma(I)$, 5554 data) and $wR_2 = 0.0566$ (F^2, 6346 data, 389 parameters). A molecule of fluorobenzene, a crystallization solvent, was found in the asymmetric unit.

X-Ray data collection, solution, and refinement for compound 3. A yellow, multi-faceted block of suitable size (0.25 x 0.22 x 0.10 mm) was selected from a representative sample of crystals of the same habit using an optical microscope and mounted onto a nylon loop. Low temperature (110 K) X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, K_α = 0.71073 Å). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software.[8] An absorption correction was applied using SADABS.[9] The space group was determined on the basis of systematic absences and intensity statistics and the structure was solved by direct methods and refined by full-matrix least squares on F^2. The structure was solved in the monoclinic $P2_1/c$ space group using XS[10] (incorporated in SHELXTL). No missed symmetry was reported by PLATON.[11] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in idealized positions and refined using riding model. Deuterium atoms of the solvent molecules were not placed due to solvent disorder. The structure was refined (weighted least squares refinement on F^2) and the final least-squares refinement converged to $R_1 = 0.0275$ ($I > 2\sigma(I)$, 7449 data) and $wR_2 = 0.0697$ (F^2, 8369 data, 380 parameters, 51 restraints). A molecule of benzene-d6, a crystallization solvent, was found in the asymmetric unit.

X-Ray data collection, solution, and refinement for compound S1. A purple, multi-faceted block of suitable size (0.43 x 0.19 x 0.10 mm) was selected from a representative sample of crystals of the same habit using an optical microscope and mounted onto a nylon loop. Low temperature (110 K) X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, $K_\alpha = 0.71073$ Å). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software.[8] An absorption correction was applied using SADABS.[9] The space group was determined on the basis of systematic absences and intensity statistics and the structure was solved by direct methods and refined by full-matrix least squares on F^2. The structure was solved in the monoclinic $P2_1/c$ space group using XS[10] (incorporated in SHELXTL). No missed symmetry was reported by PLATON.[11] All non-hydrogen atoms were refined with anisotropic thermal parameters. All except two hydrogen atoms were placed in idealized positions and refined using riding model. The two hydrogens of the $RhCH_2$ fragment were located and refined. The structure was refined (weighted least squares refinement on F^2) and the final least-squares refinement converged to R_1 = 0.0307 ($I > 2\sigma(I)$, 7205 data) and wR_2 = 0.0864 (F^2, 8590 data, 388 parameters, 0 restraints). A molecule of CH_2Cl_2, a crystallization solvent, was found in the asymmetric unit.

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