

Supporting Information

Multifunctional Behavior by a Bis-(phosphinimino)methanide Ligand: η^2 - vs. η^3 -coordination vs. Bronsted Basicity

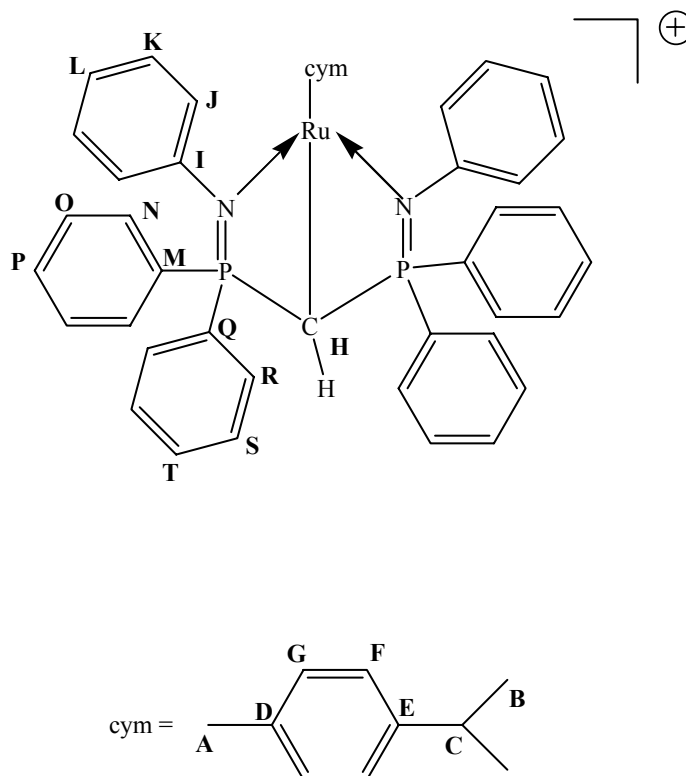
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Experimental

All synthetic work described here was carried out in an inert atmosphere glove box filled with argon, using dried and degassed solvents. $\text{H}_2\text{C}(\text{PPh}_2\text{NPh})_2$ and $(\text{RuCl}_2\text{cym})_2$ were synthesized according to the literature procedures.^{1,2}

^1H and ^{13}C NMR spectra were collected on Varian Inova 400MHz and 500MHz (^1H) spectrometers with ^1H assignments being obtained from 1-D, DQCOSY, and NOESY spectra, and ^{13}C assignments from 1-D and heteronuclear HMQC and HMBC spectra.

Preparation of $\text{CymRuCH}(\text{PPh}_2\text{NPh})_2^+\text{Cl}^-$



Method a)

Methylolithium (0.41 mmol, 0.26 mL) was added dropwise to a stirred solution of $\text{CH}_2(\text{PPh}_2\text{NPh})_2$ (0.2 g, 0.35 mmol) in THF at room temperature. After 20 min, the lithium salt (0.35 mmol) was slowly added to the dimer $(\text{RuCl}_2\text{cym})_2$ (0.1 g, 0.17 mmol) in THF at room temperature and the reaction mixture was stirred overnight. Solvent was removed under vacuum and the residue was extracted with toluene. A red powder was isolated from the toluene soluble fraction after cooling the solution at $-25\text{ }^\circ\text{C}$ for 1 day (0.22 g, 78 %).

Single crystals were obtained from a supersaturated benzene solution allowed to stand at room temperature for 1 day.

Mp: $218\text{ }^\circ\text{C}$ (decomp)

^1H NMR [499.8 MHz, CD_2Cl_2] (δ , ppm): 0.74 (d, $\text{C}(\text{H}_\text{B})_3$, $^3\text{J}_{\text{H/H}} = 7\text{ Hz}$, 6H); 1.53 (s, $\text{C}(\text{H}_\text{A})_3$, 3H); 1.96 (sept, CH_C , $^3\text{J}_{\text{H/H}} = 7\text{ Hz}$, 1H); 2.79 (s, $\text{PCH}_\text{H}\text{P}$, 1H); 5.25 (d, H_G , $^3\text{J}_{\text{H/H}} = 6\text{ Hz}$, 2H); 5.32 (d, H_F , $^3\text{J}_{\text{H/H}} = 6\text{ Hz}$, 2H); 6.82 (ddd, H_S , $^3\text{J}_{\text{H/H}} = 7.8\text{ Hz}$, $^3\text{J}_{\text{H/H}} = 8.0\text{ Hz}$, $^4\text{J}_{\text{P/H}} = 2.9\text{ Hz}$, 4H); 6.94 (tt, H_L , $^3\text{J}_{\text{H/H}} = 7.3\text{ Hz}$, $^4\text{J}_{\text{H/H}} = 1.4\text{ Hz}$, 2H); 7.01 (ddd, H_R , $^3\text{J}_{\text{H/H}} = 8.0\text{ Hz}$, $^4\text{J}_{\text{H/H}} = 1.3\text{ Hz}$, $^3\text{J}_{\text{P/H}} = 12.8\text{ Hz}$, 4H); 7.10 (m, H_T , $^3\text{J}_{\text{H/H}} = 7.8\text{ Hz}$, $^4\text{J}_{\text{H/H}} = 1.3\text{ Hz}$, $^5\text{J}_{\text{P/H}} = 1.5\text{ Hz}$, 2H); 7.21 (dd, H_K , $^3\text{J}_{\text{H/H}} = 7.3\text{ Hz}$, $^3\text{J}_{\text{H/H}} = 8.0\text{ Hz}$, 4H); 7.25 (dd, H_J , $^3\text{J}_{\text{H/H}} = 8.0\text{ Hz}$, $^4\text{J}_{\text{H/H}} = 1.4\text{ Hz}$, 4H); 7.71 (m, H_P , $^3\text{J}_{\text{H/H}} = 7.0\text{ Hz}$, $^4\text{J}_{\text{H/H}} = 1.0\text{ Hz}$, $^5\text{J}_{\text{P/H}} = 1.6\text{ Hz}$, 2H); 7.74 (ddd, H_O , $^3\text{J}_{\text{H/H}} = 7.0\text{ Hz}$, $^3\text{J}_{\text{H/H}} = 8.4\text{ Hz}$, $^4\text{J}_{\text{P/H}} = 2.6\text{ Hz}$, 4H); 8.25 (ddd, H_N , $^3\text{J}_{\text{H/H}} = 8.4\text{ Hz}$, $^4\text{J}_{\text{H/H}} = 1.0\text{ Hz}$, $^3\text{J}_{\text{P/H}} = 12.1\text{ Hz}$, 4H)

^{31}P NMR [162.0 MHz, CD_2Cl_2] (δ , ppm): 34.23 (s)

^{13}C NMR [125.7 MHz, CD_2Cl_2] (δ , ppm): -21.35 (t, $\text{C}_\text{H}\text{H}$, $^1\text{J}_{\text{P/C}} = 86.1\text{ Hz}$); 18.17 (s, $\text{C}_\text{A}\text{H}_3$); 22.41 (s, $\text{C}_\text{B}\text{H}_3$); 30.30 (s, $\text{C}_\text{C}\text{H}$); 81.12 (s, $\text{C}_\text{F}\text{H}$); 83.82 (s, $\text{C}_\text{G}\text{H}$); 96.10 (s, C_D); 106.19 (s, C_E); 121.18 (s, $\text{C}_\text{L}\text{H}$); 124.38 (d, $\text{C}_\text{J}\text{H}$, $^3\text{J}_{\text{P/C}} = 13.0\text{ Hz}$); 128.58 (d, $\text{C}_\text{S}\text{H}$, $^3\text{J}_{\text{P/C}} = 12.2\text{ Hz}$); 129.22 (s, C_K); 129.83 (d, $\text{C}_\text{O}\text{H}$, $^3\text{J}_{\text{P/C}} = 12.2\text{ Hz}$); 130.94 (d, C_Q , $^1\text{J}_{\text{P/C}} = 71.3\text{ Hz}$); 131.60 (d, $\text{C}_\text{R}\text{H}$, $^3\text{J}_{\text{P/C}} = 11.5\text{ Hz}$); 131.71 (dd, C_M , $^1\text{J}_{\text{P/C}} = 84.7\text{ Hz}$, $^3\text{J}_{\text{P/C}} = 8.7\text{ Hz}$); 132.28 (s, $\text{C}_\text{T}\text{H}$); 132.41 (d, $\text{C}_\text{N}\text{H}$, $^3\text{J}_{\text{P/C}} = 10.7\text{ Hz}$); 133.48 (s, C_P); 148.82 (s, C_I)

FAB (m, intensity): 801 (M, 28), 667 (M-cym, 100), 589 (M-cym- H^+ -Ph, 26).

Method b)

In a J-Young-tube, a mixture of the $\text{CH}_2(\text{PPh}_2\text{NPh})_2$ ligand (22 mg, 0.04 mmol) and the dimer $(\text{RuCl}_2\text{cym})_2$ (12 mg, 0.02 mmol) was dissolved in benzene. The

protonated imine $\text{CH}_2(\text{PPh}_2\text{NPh})_2\text{H}^+$ was immediately formed in the same ratio as the salt $\text{CymRuCH}(\text{PPh}_2\text{NPh})_2^+ \text{RucymCl}_3^-$. Selected resonances for the protonated imine are given.

The anion RucymCl_3^- comes from capture of free Cl^- by $(\text{RuCl}_2\text{cym})_2$. This was proven because the resonances in the above salt were identical to those formed from addition of NEt_4Cl to $(\text{RuCl}_2\text{cym})_2$.

Selected resonances for the protonated imine are also given. They match those of an independent preparation where HCl (15 μL , 0.03 mmol, 2M in Et_2O) was added via a micro-syringe to a solution of the $\text{CH}_2(\text{PPh}_2\text{NPh})_2$ ligand (15 mg, 0.03 mmol) in benzene.

$\text{CH}_2(\text{PPh}_2\text{NPh})_2\text{H}^+$:

^1H NMR [300.1 MHz, C_6D_6] (δ , ppm): 2.23 (t, CH_2 , $^2J_{\text{P/C}} = 4.5$ Hz, 2H); 6.70-8.88 (m, C_6H_5 , 30H); 11.76 (s, NH, 1H)

^{31}P NMR [121.5 MHz, C_6D_6] (δ , ppm): 25.62 (s)

MALDI-TOF (m, intensity): 567 (M; 100); 474 (M-NH₂Ph; 31).

RuCymCl_3^- :

^1H NMR [499.8 MHz, CD_2Cl_2] (δ , ppm): 1.32 (d, $\text{CH}_3(i\text{Pr})$, $^3J_{\text{H/H}} = 7$ Hz, 6H); 2.23 (s, CH_3 , 3H); 3.09 (sept, $\text{CH}(i\text{Pr})$, $^3J_{\text{H/H}} = 7$ Hz, 1H); 5.20 (d, H_G , $^3J_{\text{H/H}} = 5$ Hz, 2H); 5.43 (d, H_F , $^3J_{\text{H/H}} = 5$ Hz, 2H)

^{13}C NMR [100.6 MHz, CD_2Cl_2] (δ , ppm): 18.90 (s, C_AH_3); 22.37 (s, C_BH_3); 31.07 (s, C_CH); 79.95 (s, C_GH); 81.73 (s, C_FH); 96.39 (s, C_D); 100.98 (s, C_E)

X-ray Structure Determination of $[\text{Ru CH}(\text{PPh}_2\text{NPh})_2(\text{cym})]\text{Cl} \cdot 2$ benzene. A red crystal (approximate dimensions $0.21 \times 0.18 \times 0.10$ mm³) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a SMART6000 (Bruker) at 130(2) K.

The data collection was carried out using Mo $\text{K}\alpha$ radiation (graphite monochromator) with a frame time of 45 seconds and a detector distance of 5.0 cm. A randomly oriented region of reciprocal space was surveyed to the extent of 1.3 hemispheres. Three major sections of frames were collected with 0.30° steps in ω at different ϕ settings and a detector position of -43° in 2θ . An additional set of 50 frames was collected in order to model decay. Data to a resolution of 0.796 Å were considered in

the reduction. Final cell constants were calculated from the xyz centroids of 9989 strong reflections from the actual data collection after integration. The intensity data were corrected for absorption.

The structure has two molecules of benzene per asymmetric unit. *p*-Cymene is disordered over two positions (63.9:36.1) flipping 180°. The distance of Ru to the center of the phenyl ring (C38, ...C43) is 1.687 Å. One benzene molecule is disordered over three major sites (45.8:29.3:24.9).

Computational Details

Theoretical calculations in this work have been performed using density functional theory³, with the PBE⁴ functional, implemented in an original program package “Priroda” authored by Dr. D.N.Laikov.^{5,6} Relativistic Stevens-Basch- Krauss (SBK) effective core potentials (ECP)⁷⁻⁹ optimized for DFT-calculations have been used. A Gaussian-type triple zeta basis set was used: Ru [5,1,1,1,1/5,1,1,1,1/5,1,1,1] C,N,P [3,1,1/3,1,1/1,1] H [3,1,1/1]. Full geometry optimizations have been performed without symmetry constraint. For all species under investigation, frequency analysis has been carried out, and zero-point vibration energy corrections made. Second derivatives were evaluated analytically. All minima have been checked for the absence of imaginary frequencies.

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