Organometallic Rhenium(III) Chalcogenide Clusters: Coordination of N-Heterocyclic Carbenes

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Supporting Information

General. $[Re_6Se_8(PEt_3)_5I]I$, *cis*- $(Bu_4N)_2[Re_6S_8(PEt_3)_2CI_4]$, $[Re_6Se_8(PEt_3)_5(OTs)](OTs)$ and $Ag(IMes)_2PF_6$ were prepared according to previously published procedures.¹⁻⁴ SIMes was deprotonated according to a previously published procedure⁵ and was handled in an inert atmosphere glovebox. NMR experiments were performed using a Bruker 400 MHz Ultrashield Plus instrument and a Bruker 500 MHz Ultrashield instrument. All phosphorus-31 and carbon-13 NMR data were proton decoupled.

[Re₆Se₈(PEt₃)₅(SIMes)](OTs)₂ (1(OTs)₂). In the glovebox, 150.8 mg (0.056 mmol) [Re₆Se₈(PEt₃)₅(OTs)](OTs) was dissolved in 20 mL THF in a 50 mL round bottom flask. To the solution, a 23.5 mg (0.076 mmol) sample of SIMes was added. The reaction mixture was stirred for 1 h under an atmosphere of nitrogen outside of the glovebox. The solution was reduced to dryness using a rotary evaporator. The product was dissolved in minimal CH₂Cl₂ and precipitated in Et₂O to afford a solid (149.6 mg, 87% yield). Found: C, 25.8; H, 3.7; N, 1.0. Calc. for C₆₅H₁₁₅N₂O₆P₅S₂Se₈Re₆: C, 25.6; H, 3.8; N, 0.9%. λ_{max}(CH₃CN)/nm 224 (ε/M⁻¹cm⁻¹ 110 000), 225 (30 000), 282 (16 000). δ_{H} (400 MHz; acetone-*d*₆; protiated solvent) 1.08 (45 H, m, -CH₂CH₃), 2.16 (30 H, m, -CH₂CH₃), 2.27 (6 H, s, OSO₂C₆H₄CH₃ anion), 2.31 (6 H, s, *para*-CH₃ on mesityl groups), 4.10 (4 H, s, -CH₂- on imidazoline ring), 7.03 (4 H, d, OSO₂C₆H₄CH₃ anion), 7.09 (4 H, s, meta-*H* on mesityl groups), 7.66 (4 H, d, OSO₂C₆H₄CH₃ anion). δ_{P} (162 MHz; acetone-*d*₆; protiated solvent) -29.08, -29.97. *m/z* 1323.2 ([Re₆Se₈(PEt₃)₅(SIMes)]²⁺).

[Re₆Se₈(PEt₃)₄(SIMes)₂](OTs)₂ (2(OTs)₂). In the glovebox, 149.8 mg (0.056 mmol)

[Re₆Se₈(PEt₃)₅(OTs)](OTs) was dissolved in 50 mL THF in a 100 mL round bottom flask. To the solution, 103.7 mg SIMes (0.338 mmol) was added. The reaction mixture was heated at reflux for 6 h under an atmosphere of nitrogen, then reduced to dryness by rotary evaporation. Crystals were grown via vapor diffusion crystallization in acetone/Et₂O, affording orange crystalline solid (148.9 mg, 84% yield). Acetone was used to separate the desired disubstituted product by solubility from the small amount of monosubstituted present. The crystals were placed upon a plug of Celite in a pipet and 4 mL acetone was run through the pipet. A band of monosubstituted complex eluted from the crystalline material and 5 mL CH₂Cl₂ was used to dissolved the remaining solid. The disubstituted band was reduced to dryness via rotary evaporation and precipitated in minimal CH₂Cl₂/Et₂O. δ_{H} (400 MHz; CDCl₃; protiated solvent) 0.91 (36 H, m, -CH₂CH₃), 1.80 (24 H, m, -CH₂CH₃), 2.22 (12 H, s, *para-CH*₃ on mesityl groups), 2.25 (6 H, s, OSO₂C₆H₄CH₃ anion), 2.28 (24 H, s, *ortho-CH*₃ on mesityl groups), 3.94 (8 H, s, *-CH*₂- on imidazoline ring), 6.82 (8 H, s, *meta-H* on mesityl groups), 7.02 (4 H, d, OSO₂C₆H₄CH₃ anion), 7.76 (4 H, d, OSO₂C₆H₄CH₃ anion). δ_P (162 MHz; CDCl₃; protiated solvent) -33.20. *m/z* 1417.2 ([Re₆Se₈(PEt₃)₄(SIMes)₂]²⁺).

 $[\operatorname{Re}_6 S_8(\operatorname{PEt}_3)_2(\operatorname{IMes})_2 \operatorname{Cl}_2]$ (3). A solution containing *cis*- $(\operatorname{Bu}_4 \operatorname{N})_2[\operatorname{Re}_6 S_8(\operatorname{PEt}_3)_2 \operatorname{Cl}_4]$ (398.0 mg, 0.18 mmol) and $[\operatorname{Ag}(\operatorname{IMes})_2]\operatorname{PF}_6$ (305.7 mg, 0.36 mmol) dissolved in 84 mL of chlorobenzene was heated at reflux under $\operatorname{N}_{2(g)}$ for 19 h, and then dried *in vacuo*. Repreciptation of the resulting residue using CH₂Cl₂ and Et₂O led to the isolation of an orange solid. This material was originally purified via column chromatography using silica gel as the solid support. The first band, which was eluted using a 19:1 CH₂Cl₂/acetone

mixture, was determined to be an impurity. The desired product was then eluted using a 9:1 $CH_2Cl_2/acetone$ mixture. The product that was obtained after reprecipitation (CH_2Cl_2/Et_2O) was clean except for the presence of Bu_4NPF_6 ; this impurity was removed by washing the solid with MeOH (2 mL). The resulting pure product was obtained (123.5 mg, 30% yield). Found: C, 27.7; H, 3.3; N, 2.4. Calc. for $C_{54}H_{78}N_4P_2Cl_2Se_8Re_6\bullet CH_2Cl_2$: C, 27.8; H, 3.4; N, 2.4%. $\delta_{H}(500 \text{ MHz}; CD_2Cl_2$; protiated solvent) 0.92 (18 H, m, P(CH_2CH_3)₃), 1.73 (12 H, m, P(CH_2CH_3)₃), 2.09 (24 H, s, *o*- CH_3), 2.31 (12 H, s, *p*- CH_3), 6.90 (8 H, s, Ar-H), 6.97 (4 H, s, NCH). $\delta_{C}(126 \text{ MHz}; CD_2Cl_2; CD_2Cl_2)$ 8.43 (d, $^2J_{CP}$ 4.24 Hz, PCH₂ CH_3) 19.42 (s, *o*- CH_3), 21.53 (d, $^1J_{CP}$ 28.17 Hz, P CH_2CH_3), 125.72, 129.45, 136.72, 138.76 (s, $C_6H_2(CH_3)_3$), 139.58 (s, NCH), 161.43 (s, C-Re). $\delta_{P}(202.5 \text{ MHz}; CD_2Cl_2; CD_2Cl_2) -23.10$. m/z 2289.86 ([Re₆S₈(PEt₃)₂(IMes)₂Cl_2]⁺).

Excited-State Lifetime and Quenching Experiments

A previously reported procedure was used for the acquisition of the time-resolved luminescence of the complexes.² Samples were prepared in acetonitrile and the concentrations of the complexes in these samples were between 150 and 700 μ M. The parameters and settings of the laser apparatus were the same as a previously reported procedure with the exception of the excitation wavelength, which was set to vary between 400-410 nm, and the average number of laser pulses that was used for data analysis, which was set to 30 pulses.⁶ Time-resolved luminescence was measured at three different concentrations of O₂ in order to study the effect of O₂ quenching. This was done by measuring the timeresolved luminescence of an air-saturated sample, an N₂-saturated sample, and an O₂-saturated sample. The N₂-saturated sample was prepared by sparging the sample cuvette with N₂ for 10 min, and the $O_{2^{-1}}$ saturated sample was prepared in a similar fashion, but with O₂ instead. Ten independently measured rate constants for each condition (e.g., air-saturated, O₂-saturated, and N₂-saturated) were determined from the slope of the linear region in plots of the natural log of intensity vs. time and were used to calculate an average rate constant for each condition. Linear Stern-Volmer plots were obtained from plotting the average rate constant for each condition vs. [O₂], which was calculated by dividing the partial pressure of O₂ (for air-saturated, p = 0.20 atm, O₂-saturated, p = 1.00 bar, N₂-saturated, p = 0.00bar) by the appropriate Henry's Law constant.^{7,8} The slope of the Stern-Volmer plot gave k_{a} and the inverse of the y-intercept gave τ_0 (1/ $\tau = k_0[O_2] + 1/\tau_0$). All determinations were made at 292 ± 1 K.

Quantum Yield Measurements

Absorption spectra were measured with a Cary 5E UV-Vis-NIR spectrophotometer and emission spectra were measured with a PerkinElmer LS 55 luminescence spectrometer. Quantum yield values for the complexes were determined by means of the comparative/relative method of quantum yield determination.⁹ This method allows for the determination of quantum yield values with the knowledge of the quantum yield of a reference species, the slope of the reference and sample species obtained from plotting integrated fluorescence intensity vs. absorbance for samples having absorbance values between 0.02 and 0.08 AU at the excitation wavelength, and the refractive index of the solvents that the reference and sample species were dissolved in for analysis. For each complex, seven absorption and emission measurements were made from solutions that gave absorbance values between 0.02 and 0.08 AU increments) at an excitation wavelength of 410 nm. The samples were sparged for ten minutes with pre-purified Ar before their absorption and emission spectra were acquired. Plotting

integrated fluorescence intensity vs. absorbance yielded linear slopes. The quantum yield values for three complexes with previously reported quantum yield values by absolute quantum yield determination ($[Re_6Se_8(PEt_3)_5(p-aminobenzonitrile)](BF_4)_2$, $[Re_6Se_8(PEt_3)_5(p-methoxybenzonitrile)](BF_4)_2$, $[Re_6Se_8(PEt_3)_5(p-acetylbenzonitrile)](BF_4)_2$) were calculated in order to check for consistency in the quantum yield measurements and calculations.⁶ The reference used in these calculations was (Bu_4N)₄[$Re_6S_8Cl_6$] and its reported quantum yield, which is an absolute measurement, is 0.028.² The calculated values for the complexes were within 10% of their reported values, and a correction factor was calculated by taking the average of the ratios of the previously reported values to the experimentally calculated values; the correction factor was calculated to be 1.095. This correction factor was then used to calculate the quantum yield values of the complexes reported in this paper by multiplying the experimentally determined quantum yield by the correction factor (1.095).

Figures

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Figure S2. ³¹P {¹H} NMR (202.5 MHz) of $[Re_6Se_8(PEt_3)_5(SIMes)](SbF_6)_2$ in acetone- d_6 .



Figure S3. ¹³C {¹H} NMR (125 MHz) of $[Re_6Se_8(PEt_3)_5(SIMes)](SbF_6)_2$ in acetone- d_6 . The peak at ~30 ppm is due to the solvent. The PEt₃ moiety *trans* to SIMes is unique compared to the phosphines *cis* to SIMes which results in two methylene resonances and two methyl resonances. In addition, the methylene and methyl resonances are split due to coupling with phosphorus (¹ J_{PC} = 32 Hz and ² J_{PC} = 5 Hz, respectively).



Figure S4. ³¹P {¹H} NMR (162 MHz) of [Re₆Se₈(PEt₃)₄(SIMes)₂](OTs)₂ in CDCl₃.



Figure S5. ³¹P {¹H} NMR (202.5 MHz) of [Re₆S₈(PEt₃)₂(IMes)₂Cl₂] in CD₂Cl₂.



Figure S6. Electronic absorption and emission spectra of $[Re_6Se_8(PEt_3)_5(SIMes)](SbF_6)_2$ in MeCN under argon (λ_{ex} = 410 nm).



Figure S7.Electronic absorption and emission spectra of $[Re_6S_8(PEt_3)_2(IMes)_2Cl_2]$ in chlorobenzene
under argon (λ_{ex} = 410 nm).



Figure S8. ORTEP Diagram of [Re₆S₈(PEt₃)₂(IMes)₂Cl₂]. H atoms omitted for clarity and ellipsoids at 35% probability.



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