

SUPPORTING INFORMATION

fac-Tricarbonyl Rhenium(I) Azadipyrromethene Complexes

David V. Partyka,[†] Nihal Deligonul,[‡] Marlena P. Washington,[‡] and Thomas G. Gray^{*‡}

Department of Chemistry, Case Western Reserve University, Cleveland Ohio, 44106 and

Creative Chemistry L.L.C., Cleveland Ohio, 44106

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Experimental

All solvents and were used as received. Tris(aquo)rhenium(I) tricarbonyl chloride ($[\text{Re}(\text{H}_2\text{O})_3(\text{CO})_3]\text{Cl}$) was synthesized according to the literature procedure.¹ The protonated form of [(3,5-diphenyl-1*H*-pyrrol-2-yl)(3,5-diphenylpyrrol-2-ylidene)amine] was synthesized according to the literature procedure.² All other chemicals and solvents were purchased and used as received. Microanalyses (C, H, and N) were performed by Quantitative Technologies Inc. All NMR spectra (^1H , ^{13}C and $^{31}\text{P}\{^1\text{H}\}$) were recorded in CDCl_3 on a Varian AS-400 spectrometer operating at 399.7, 100.5 and 161.8 MHz respectively. For compounds **1-3**, abbreviations for tetrahydrofuran, pyridine, tetrahydrothiophene, and triphenylphosphine are written as THF, pyr, THT, and PPh_3 respectively.

[(3,5-Diphenyl-1*H*-pyrrol-2-yl)(3,5-diphenylpyrrol-2-ylidene)amine] $\text{Re}(\text{CO})_3(\text{THF})$ • THF (1**).** In a round bottom flask, $[\text{Re}(\text{CO})_3(\text{H}_2\text{O})_3]\text{Cl}$ (60 mg, 0.017 mmol) and 1 equiv tetraphenylazadipyrromethene (74.5 mg, 0.17 mmol) were suspended in 1 mL of 1-butanol. A solution of potassium *tert*-butoxide (19 mg, 0.17 mmol) in 4 mL of 1-butanol was added to the mixture and the resultant mixture was refluxed under argon for 24 h. The 1-butanol was removed by rotary evaporation, and dry THF (10 mL) was added to dissolve the residue. The solution was heated in a 65 °C oil bath for 12 h, and the THF removed by rotary evaporation. The residue was re-dissolved in a minimum of dry THF, filtered through Celite, and pentane vapor was diffused into the saturated THF solution, causing separation of bronze crystalline chunks. The crystalline chunks were carefully collected to the exclusion of the blue residue, redissolved in a minimum of dry THF, filtered through Celite and recrystallized again (by vapor diffusion of pentane). The bronze, crystalline chunks that separated were again collected to the exclusion of the accompanying blue residue (much less residue than in first iteration) and dried. Yield: 66 mg (46%). ^1H NMR: δ 7.88-7.94 (m, 4H), 7.79-7.84 (m, 4H), 7.49-7.57 (m, 6H), 7.34-7.40 (m, 6H), 7.04 (s, 2H, pyrrolic *CH*), 3.75 (m, 4H, lattice THF), 3.20 (m, 4H, coordinated THF), 1.86 (m, 4H, lattice THF), 1.62 (m, 4H, coordinated THF) ppm. UV-Vis (CHCl_3): λ (ϵ) 253 (38100), 288 (38300), 298 (sh, 35700), 367 (4900), 594 (49500) nm. IR (KBr, cm^{-1}): 2015, 1904, 1891, 1887 (ν_{CO} , vs) cm^{-1} . Anal. Calcd. for $\text{C}_{39}\text{H}_{30}\text{N}_3\text{O}_4\text{Re} \cdot \text{C}_4\text{H}_8\text{O}$: C, 59.85; H, 4.44; N, 4.86. Found: C, 60.32; H, 4.39; N, 4.78.

{[(3,5-Diphenyl-1*H*-pyrrol-2-yl)(3,5-diphenylpyrrol-2-ylidene)amine] Re(CO)₃(pyr)} (2).

Compound **1** (35 mg, 0.041 mmol) was dissolved in a minimum of pyridine and filtered through a small amount of Celite. Pentane vapor was diffused into the saturated solution of **1**, yielding **2** (over ~2-3 days) in quantitative yield as sparkling, dark green crystals. Yield: 32 mg (99%). ¹H NMR: δ 7.91 (d, 4H, *J* = 6.4 Hz), 7.50-7.70 (m, 14H), 7.21-7.31 (m, 5H), 7.09 (s, 2H, pyrrolic *CH*), 7.06-7.11 (m, 2H) ppm. UV-Vis (CHCl₃): λ (ε) 253 (38100), 288 (38300), 298 (sh, 35700), 367 (4900), 594 (49500) nm. IR (KBr, cm⁻¹): 2015, 1924, 1919, 1898 (ν_{CO}, vs) cm⁻¹. Anal. Calcd. for C₄₀H₂₇N₄O₃Re: C, 60.21; H, 3.41; N, 7.02. Found: C, 60.49; H, 3.20; N, 7.29.

{[(3,5-Diphenyl-1*H*-pyrrol-2-yl)(3,5-diphenylpyrrol-2-ylidene)amine] Re(CO)₃(THT)} (3).

Compound **1** (35 mg, mol) was dissolved in a minimum of tetrahydrothiophene and filtered through a small amount of Celite. Pentane vapor was diffused into the saturated solution of **1**, yielding **3** (over ~2-3 days) in quantitative yield as lime green crystals. Yield: 33 mg (100%). ¹H NMR: δ 7.90-7.94 (m, 4H), 7.76-7.80 (m, 4H), 7.48-7.56 (m, 6H), 7.34-7.40 (m, 6H), 7.04 (s, 2H, pyrrolic *CH*), 2.60-2.65 (m, 4H, (CH₂)₄S), 1.74-1.80 (m, 4H, (CH₂)₄S) ppm. UV-Vis (CHCl₃): λ (ε) 251 (24500), 299 (sh, 24500), 374 (3800), 589 (43300) nm. IR (KBr, cm⁻¹): 2014, 1924, 1919, 1896 (ν_{CO}, vs) cm⁻¹. Anal. Calcd. for C₃₉H₃₀N₃O₃ReS: C, 58.05; H, 3.75; N, 5.21. Found: C, 58.30; H, 3.51; N, 5.20.

{[(3,5-Diphenyl-1*H*-pyrrol-2-yl)(3,5-diphenylpyrrol-2-ylidene)amine]Re(CO)₃(*N*-benzylimidazole)} (4). In 2 mL dichloromethane **1** (29 mg, 0.034 mmol) was dissolved. To this solution, *N*-benzylimidazole (5.4 mg, 0.034 mmol) in 1 mL of dichloromethane was added. The solution was stirred for 2 h and the solvent removed by rotary evaporation. Recrystallization (pentane/THF) yielded bronze, crystalline chunks that were collected. Yield: 22 mg (74%). ¹H NMR: δ 7.85-7.90 (m, 4H), 7.68-7.73 (m, 4H), 7.47-7.58 (m, 6H), 7.24-7.35 (m, 6H), 7.19 (t, 1H, *J* = 7.2 Hz), 7.03 (s, 2H, pyrrolic *CH*), 6.90 (t, 2H, *J* = 7.6 Hz), 6.79 (d, 2H, *J* = 6.8 Hz), 6.66-6.68 (m, 1H), 6.52 (t, 1H, *J* = 1.6 Hz), 6.30 (t, 1H, *J* = 1.6 Hz), 4.85 (s, 2H, benzyl-CH₂) ppm. UV-Vis (CHCl₃): λ (ε) 255 (46100), 285 (46500), 300 (sh, 39900), 373 (3200), 590 (52000) nm. IR (KBr, cm⁻¹): 2007, 1891, 1876 (ν_{CO}, vs) cm⁻¹. Anal. Calcd. for C₄₅H₃₂N₅O₃Re: C, 61.63; H, 3.68; N, 7.99. Found: C, 61.90; H, 3.96; N, 7.74.

{[(3,5-Diphenyl-1*H*-pyrrol-2-yl)(3,5-diphenylpyrrol-2-ylidene)amine]Re(CO)₃(*tert*-butylisocyanide)} (**5**). In a glovebox, **1** (29.5 mg, 0.034 mmol) was dissolved in 4 mL of dichloromethane, and 2 drops (using a 9 inch disposable glass Pasteur pipet) of *tert*-butylisocyanide were added (isocyanide was in molar excess). The solution was stirred for 1 h, and the solvent removed by rotary evaporation. The residue was pumped on a vacuum line for several hours to remove trace, unreacted isocyanide. In air, the residue was dissolved in a minimum of dry THF, filtered through Celite, and pentane vapor was diffused to cause separation of metallic-brown crystalline blocks, which were collected, washed with pentane and dried. Yield: 24.5 mg (89%). ¹H NMR: δ 7.89-7.94 (m, 4H), 7.76-7.80 (m, 4H), 7.45-7.56 (m, 6H), 7.32-7.40 (m, 6H), 7.05 (s, 2H, pyrrolic CH), 1.18 (s, 9H, C(CH₃)₃) ppm. ¹³C NMR: δ 195.61 (s, C_{CO-axial}), 190.23 (s, C_{CO-equatorial}), 167.62 (s, C_{CNtBu}), 145.09 (s), 144.71 (s), 137.18 (s), 134.27 (s), 129.62 (s), 129.35 (s), 129.22 (s), 128.21 (s), 128.10 (s), 128.01 (s), 127.57 (s), 120.06 (s), 57.50 (s, C(CH₃)₃), 29.98 (s, C(CH₃)₃) ppm. UV-Vis (CHCl₃): λ (ε) 255 (45600), 286 (46500), 299 (sh, 35800), 371 (3600), 588 (38500) nm. IR (KBr, cm⁻¹): 2188 (ν_{C≡NtBu}, s), 2013, 1906 (ν_{CO}, vs) cm⁻¹. Anal. Calcd. for C₄₀H₃₁N₄O₃Re: C, 59.91; H, 3.90; N, 6.99. Found: C, 60.07; H, 3.95; N, 7.01.

Luminescence Measurements. Steady state emission spectra were recorded on an automated Photon Technology International (PTI) QM 4 fluorimeter equipped with a 150-W Xe arc lamp and a Hamamatsu R928 photomultiplier tube. Excitation light was excluded with appropriate glass filters. Sample solutions were added to a quartz EPR tube, freeze pump thaw degassed (4 cycles, 1 × 10⁻⁵ Torr) and flame sealed. Low temperature emission spectra were recorded in rigid solvent glass at 77 K by immersion of the sealed EPR tubes into a liquid nitrogen filled dewer.

Electrochemistry. Tetrabutylammonium hexafluorophosphate (Fluka) was recrystallized using ethyl acetate and ether. It was dried thoroughly under vacuum and stored in a nitrogen drybox. Tetrahydrofuran (Fisher Scientific) was distilled over sodium/benzophenone and stored in a nitrogen drybox. Ferrocene (Aldrich) was purified via sublimation and stored under nitrogen. All glassware was cleaned and oven-dried overnight before use. Cyclic voltammetry experiments were performed in a nitrogen-filled Vacuum Atmospheres drybox

outfitted with a CH Instrument Workstation at room temperature. A glassy carbon working electrode was polished with 0.05- μm alumina and thoroughly cleaned and dried before use. A silver wire was utilized as a quasi-reference electrode, and a platinum wire was the counter electrode. All scans were performed at a scan rate of 0.1V/s.

Concentration of Supporting Electrolyte: 0.1M Bu_4NPF_6

Concentration of all azadipyrromethenes and their complexes: 0.001M

Concentration of Ferrocene: 0.001M

Crystallography. Single crystal X-ray data were collected on a Bruker AXS SMART APEX CCD diffractometer using monochromatic Mo $K\alpha$ radiation with omega scan technique. The unit cells were determined using SMART³ and SAINT+.⁴ Data collection for all crystals was conducted at 100 K (-173.5°C). All structures were solved by direct methods and refined by full matrix least squares against F^2 with all reflections using SHELXTL.⁵ Refinement of extinction coefficients was found to be insignificant. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in standard calculated positions and all hydrogen atoms were refined with an isotropic displacement parameter 1.2 times that of the adjacent carbon.

Computations. Spin-restricted density-functional theory computations were performed within the Gaussian 03 program suite.⁶ Calculations employed the modified Perdew-Wang exchange functional of Adamo and Barone⁷ and the original Perdew-Wang correlation functional.⁸ Nonmetal atoms were described with the TZVP basis set of Godbelt, Andzelm, and co-workers.⁹ Rhenium orbitals were described with the Stuttgart effective core potential and the associated basis set,¹⁰ which was contracted as follows: Re, (8s,7p,6d) \rightarrow [6s,5p,3d]. Relativity with the Stuttgart ECP and its associated basis set is introduced with a potential term (*i.e.*, a one-electron operator) that replaces the two-electron exchange and Coulomb operators resulting from interaction between core electrons and between core and valence electrons. In this way relativistic effects, especially scalar effects, are included implicitly rather than as four-component, one-electron functions in the Dirac equation. Geometries were optimized without imposed symmetry, and harmonic frequency calculations find all structures to be potential energy minima. All calculated properties reported here include implicit chloroform solvation ($\epsilon = 4.9$, 298.15 K), which was incorporated in single-point calculations of the gas-phase

geometries with Tomasi's polarizable continuum model (PCM).^{11,12} The stability of each converged density was confirmed by calculation of the eigenvalues of the A matrix.^{13,14} Percentage compositions of molecular orbitals, overlap populations, and bond orders between fragments were calculated using the AOMix program of Gorelsky.^{15,16}

Table S1. Optimized Cartesian coordinates (Å) of **2**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	75	0	-1.661412	0.017897	0.211386
2	6	0	-2.830390	-1.299306	1.018727
3	8	0	-3.546250	-2.046423	1.576721
4	6	0	-2.733530	0.032634	-1.382799
5	8	0	-3.394735	0.040273	-2.357747
6	6	0	-2.800905	1.363243	1.014746
7	8	0	-3.500255	2.131616	1.564831
8	6	0	1.191830	-1.203934	-0.518217
9	7	0	-0.354883	-0.004598	2.074763
10	6	0	0.026945	1.150870	2.673903
11	6	0	0.036241	-1.173407	2.640742
12	6	0	0.790355	1.178109	3.843031
13	1	0	-0.294098	2.069833	2.182213
14	6	0	0.799775	-1.227315	3.809095
15	1	0	-0.277582	-2.080548	2.122939
16	6	0	1.184184	-0.031628	4.427213
17	1	0	1.067833	2.138598	4.279444
18	1	0	1.084426	-2.197428	4.218841
19	1	0	1.779057	-0.042163	5.342792
20	7	0	1.780508	-0.017709	-0.435991
21	7	0	-0.190286	-1.484267	-0.504816
22	7	0	-0.151899	1.493509	-0.481994
23	6	0	1.222615	1.185479	-0.419979
24	6	0	1.948354	-2.445449	-0.624250
25	6	0	0.991688	-3.454416	-0.665488
26	6	0	-0.297151	-2.842634	-0.618047
27	6	0	-0.226009	2.854244	-0.582525
28	6	0	1.075227	3.440172	-0.541212
29	6	0	2.008206	2.413971	-0.437008
30	1	0	1.160471	-4.516515	-0.828652
31	1	0	1.270722	4.507776	-0.612683
32	6	0	-1.455549	3.641473	-0.764391
33	6	0	-1.626930	4.844263	-0.041344
34	6	0	-2.436156	3.276744	-1.712454
35	6	0	-2.763836	5.636169	-0.233345
36	1	0	-0.871057	5.140806	0.690421
37	6	0	-3.568049	4.075748	-1.907910
38	1	0	-2.291844	2.380996	-2.315492
39	6	0	-3.740800	5.252432	-1.164387
40	1	0	-2.889544	6.553183	0.347141
41	1	0	-4.314285	3.779012	-2.648482
42	1	0	-4.628370	5.871434	-1.314314
43	6	0	-1.547959	-3.606636	-0.751317
44	6	0	-1.711011	-4.804319	-0.017882
45	6	0	-2.557077	-3.230564	-1.664379
46	6	0	-2.866791	-5.578722	-0.163312
47	1	0	-0.930812	-5.110871	0.683679
48	6	0	-3.707919	-4.012181	-1.813779
49	1	0	-2.421242	-2.340882	-2.278048
50	6	0	-3.871829	-5.182648	-1.058568

51	1	0	-2.984853	-6.491825	0.424906
52	1	0	-4.476147	-3.707022	-2.527973
53	1	0	-4.774188	-5.787798	-1.172369
54	6	0	3.402907	-2.615315	-0.702365
55	6	0	4.250273	-1.639167	-1.278069
56	6	0	3.991675	-3.809441	-0.219263
57	6	0	5.631009	-1.853281	-1.360600
58	1	0	3.813790	-0.716762	-1.659556
59	6	0	5.370599	-4.020188	-0.306909
60	1	0	3.355766	-4.565634	0.247831
61	6	0	6.198679	-3.041733	-0.878972
62	1	0	6.264989	-1.085634	-1.810902
63	1	0	5.802108	-4.947794	0.077517
64	1	0	7.276703	-3.206001	-0.948594
65	6	0	3.467978	2.552732	-0.405758
66	6	0	4.300665	1.615956	0.251812
67	6	0	4.079483	3.674032	-1.018086
68	6	0	5.687984	1.798714	0.291241
69	1	0	3.848034	0.744912	0.724900
70	6	0	5.464611	3.854763	-0.972174
71	1	0	3.457457	4.392806	-1.556643
72	6	0	6.277237	2.917180	-0.315898
73	1	0	6.311041	1.061830	0.804032
74	1	0	5.913209	4.724377	-1.458763
75	1	0	7.360389	3.056894	-0.281268

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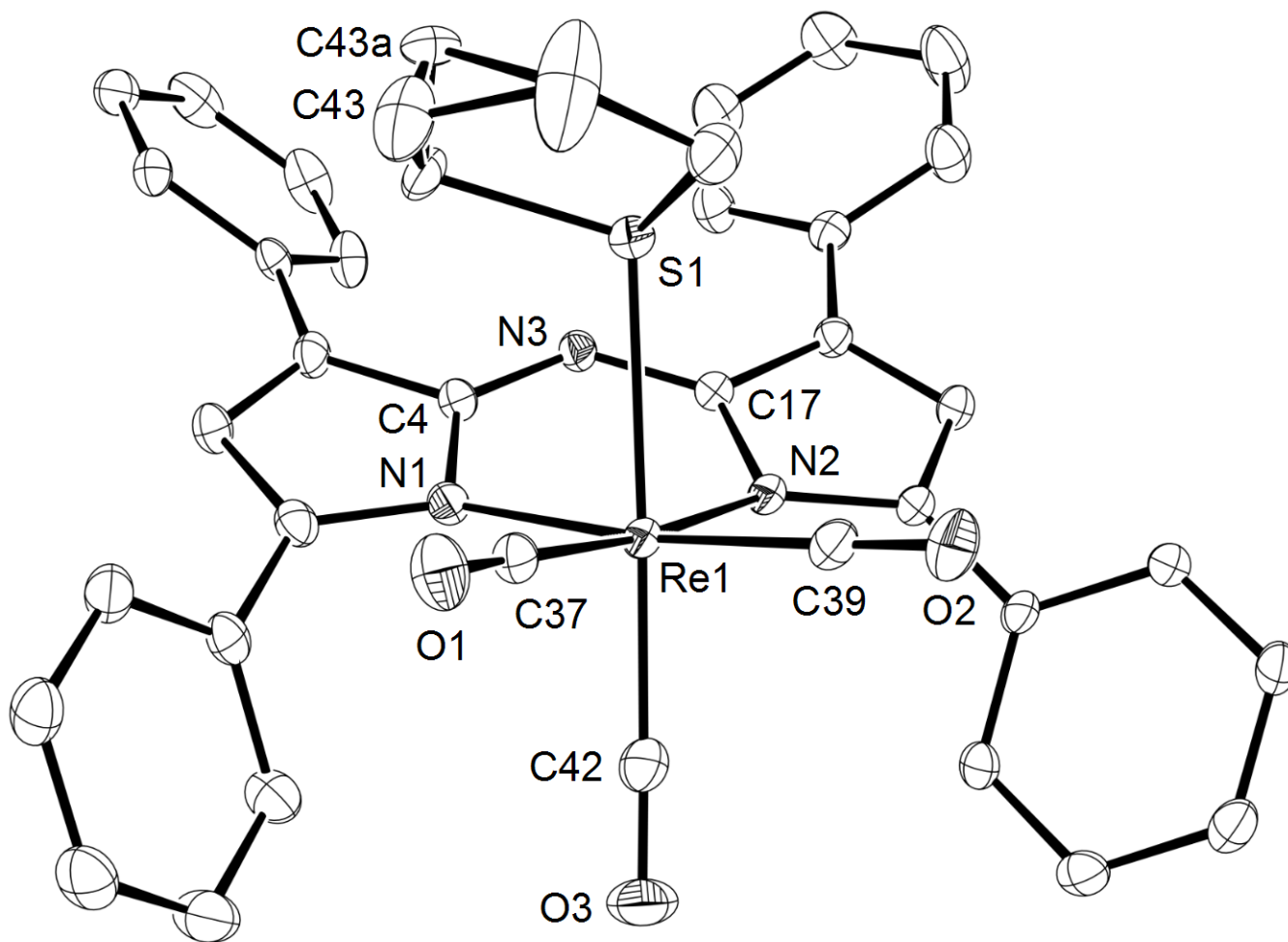


Figure S1. Crystal structure of **3** (100 K, 50% probability). H atoms are omitted for clarity. Unlabeled atoms are carbon.

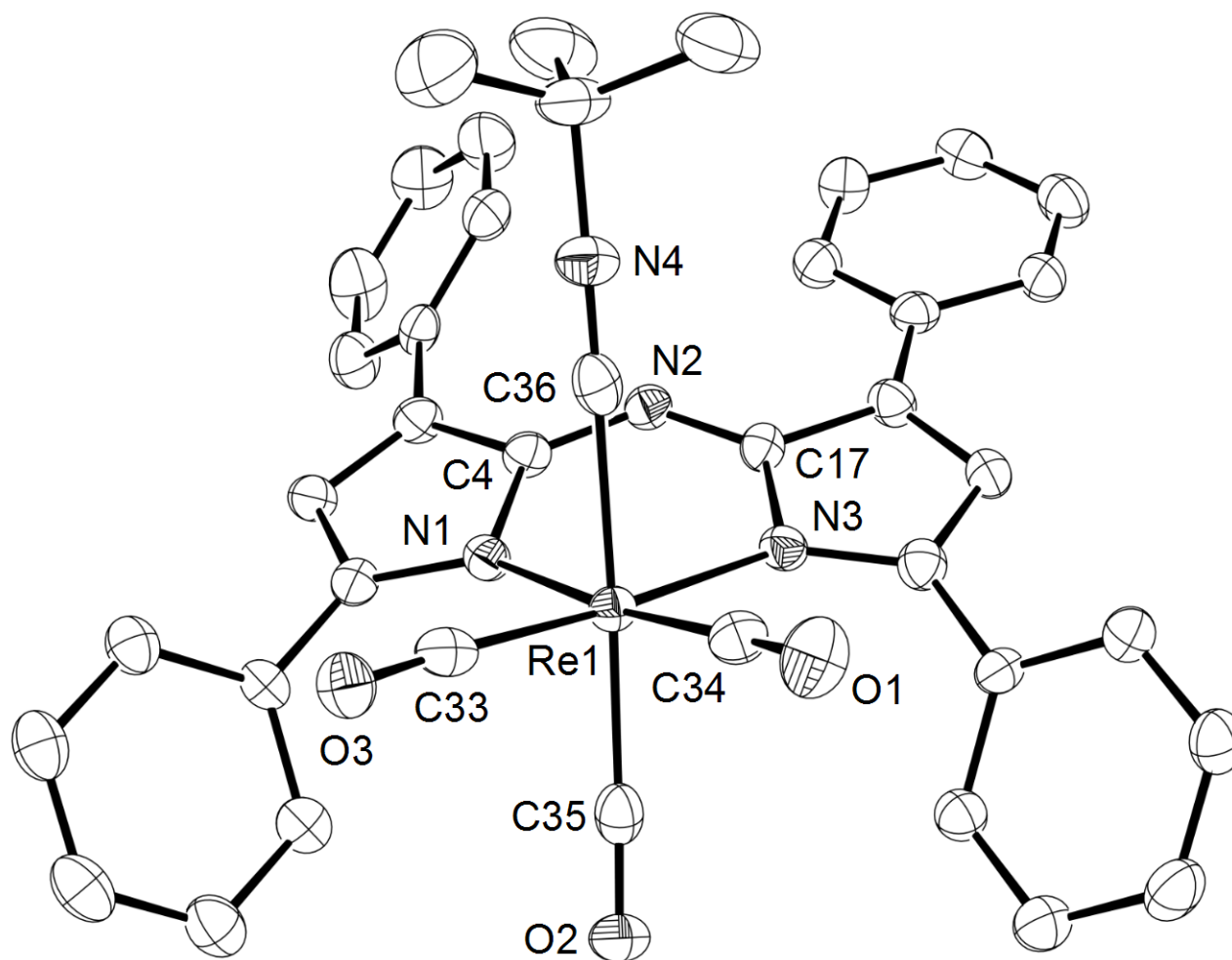


Figure S2. Crystal structure of **5** (100 K, 50% probability). H atoms are omitted for clarity. Unlabeled atoms are carbon.

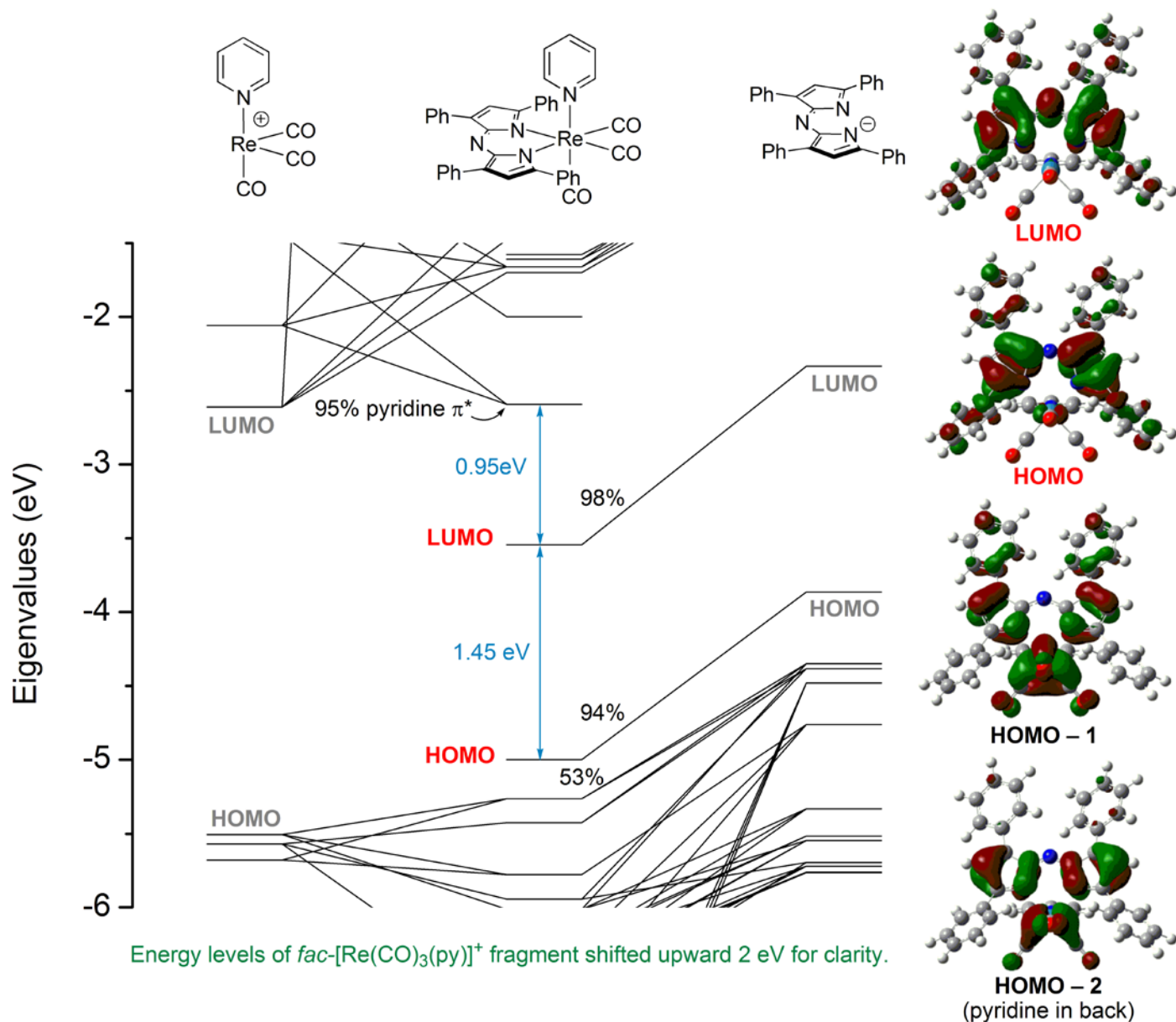


Figure S3. Partial Kohn-Sham orbital correlation diagram of pyridine complex **2** (mpmpw91/Stuttgart ECP and basis on Re); implicit chloroform solvation is included through a continuum dielectric model (PCM). Right: plots of selected orbitals (contour level 0.03 a.u.). Percentage contributions of fragments are indicated.

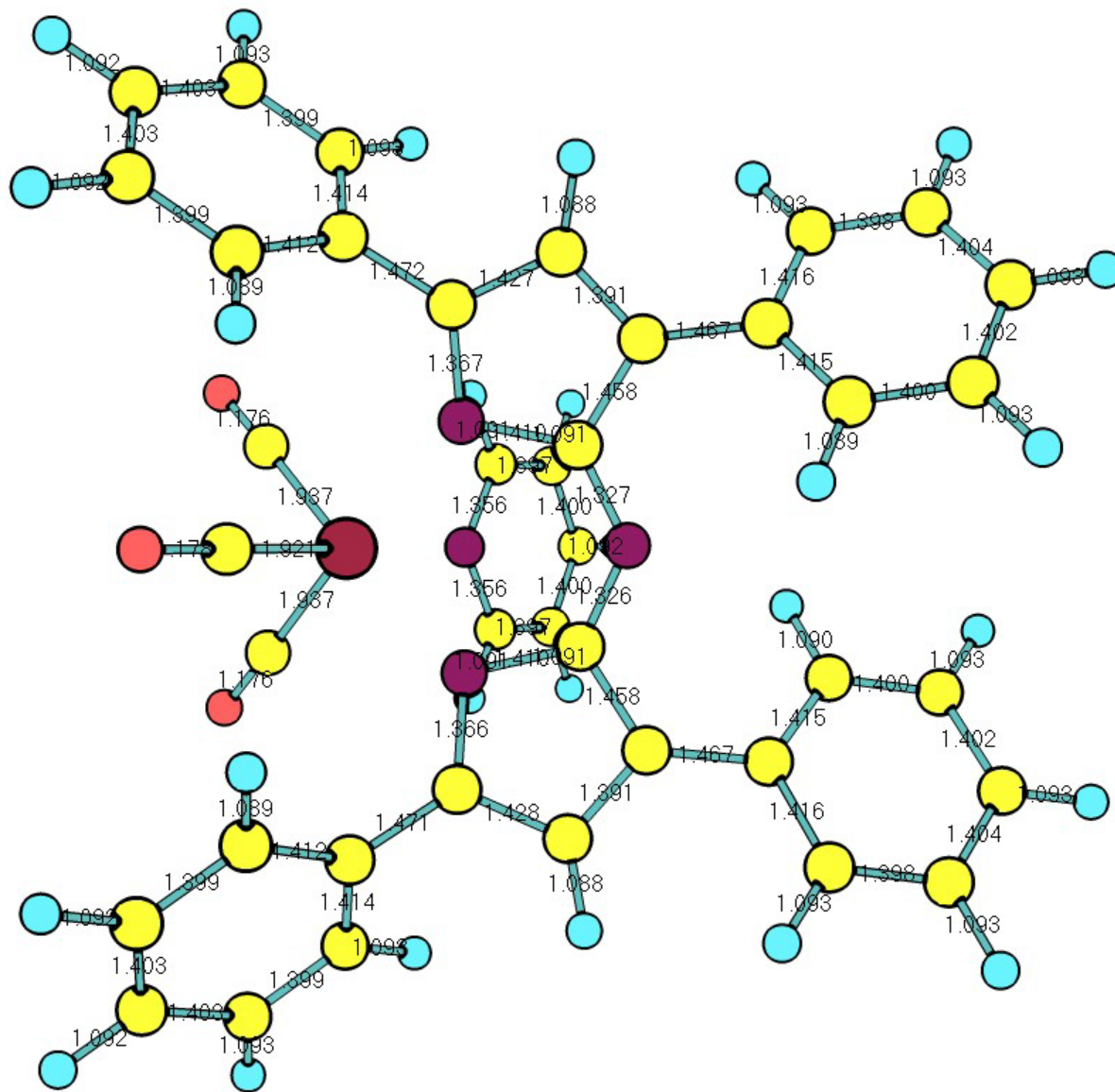


Figure S4. Optimized bond lengths (Å) of **2**.