

An aromatic dimetallapolycyclic complex with two rhenapyrylium rings

Wei Bai,^{*a} Yue Sun,^a Yilun Wang,^{a,b} Yan Zhou,^c Yue Zhao,^a Xiao Bao^a and Yang Li^{*a,b}

^a State Key Laboratory of Fine Chemicals, Department of Chemistry, School of Chemical Engineering, Dalian University of Technology, Liaoning 116024, P.R. China

^b School of Chemical Engineering, Dalian University of Technology, Panjin, Liaoning 124221, P.R. China

^c School of Chemistry and Chemical Engineering, Guangxi University for Nationalities, Guangxi Key Laboratory of Chemistry and Engineering of Forest Products, Key Laboratory of Guangxi Colleges and Universities for Food Safety and Pharmaceutical Analytical Chemistry, Nanning, 530008, P.R. China

Supporting Information

Table of Contents

1. Experimental details	S2-S4
2. Computational details	S5-S8
3. X-ray crystallographic study of complexes 4 and 5	S9-S10
4. NMR spectra	S11-S17
5. The Calculated Cartesian Coordinates	S18-S23
6. Reference	S24

1. Experimental details

General information. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Solvents were purged with a nitrogen flow before use. $\text{ReCl}_3(\text{PMePh}_2)_3$,^[1] 2,5-diethynyl-1,4-benzenedicarboxaldehyde,^[2] 1-(4-acetyl-2,5-bis-trimethylsilanylethynylphenyl)ethanone^[3] and 1-ethynyl-2-naphthaldehyde^[4] were prepared according to literature methods. Other reagents were used as purchased. Microanalyses were performed by Element Vario EL. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ spectra were collected on a Bruker Avance II (400 MHz) or a Varian DLG spectrometer (400 MHz). ^1H and ^{13}C NMR shifts are relative to TMS, and ^{31}P chemical shifts relative to 85% H_3PO_4 . Cyclic voltammetry (CV) experiments were conducted using a CHI610D electrochemical workstation from CH Instruments, Inc., and it was performed in 0.1 M anhydrous $\text{Bu}_4\text{NBF}_4/\text{CH}_2\text{Cl}_2$ solution at a scan rate of 100 mV s^{-1} under nitrogen atmosphere, using the glass-carbon electrode, Ag/Ag^+ electrode (Ag in 0.1 M AgNO_3 solution of MeCN) and platinum wire electrode as the working electrode, reference electrode and counter electrode, respectively. In addition, the ferrocene-ferrocenium (Fc/Fc^+) couple was selected as the internal standard.

1-(4-acetyl-2,5-diethynylphenyl)ethanone. To a solution of 1-(4-acetyl-2,5-bis-trimethylsilanylethynylphenyl)ethanone (0.540 g, 1.52 mmol) in THF (8 mL) and MeOH (4 mL) at room temperature, K_2CO_3 (0.440 g, 3.19 mmol) was added and the mixture was stirred for 15 minutes under air. The reaction mixture was extracted with DCM and washed with saturated NH_4Cl aqueous solution. The organic extractant was dried over anhydrous MgSO_4 and filtered through a pad of silica gel. After removal the solvent, a yellow solid was obtained. Yield: 0.270 g, 84.7%. ^1H NMR (400.1 MHz, CDCl_3): $\delta = 7.87$ (s, 2H), 3.52 (s, 2H), 2.70 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3): $\delta = 198.8, 143.2, 134.9, 120.9, 85.8, 81.3, 30.0$. HRMS (EI, m/z): $[\text{M}]^+$ Calcd For: $\text{C}_{14}\text{H}_{10}\text{O}_2$: 210.0681; Found: 210.0689.

Synthesis of complex 2. A mixture of $\text{ReCl}_3(\text{PMePh}_2)_3$ (0.200 g, 0.224 mmol) and 2,5-diethynyl-1,4-benzenedicarboxaldehyde (0.490 g, 0.269 mmol) in THF (10 mL) was stirred at room temperature for 12 h, producing a brown solid. The solid was filtered and washed with THF (8 mL) and ether (8 mL). Then it was dried under vacuum. Yield: 0.157 g, 80.1%. $^{31}\text{P}\{^1\text{H}\}$ NMR (162.0 MHz, CDCl_3): $\delta = 37.2$ (d, $J = 6.5$ Hz, $\text{CH}(\text{PMePh}_2)$), -11.6 (d, $J = 6.5$ Hz, RePMePh_2). ^1H NMR (400.1 MHz, CDCl_3): $\delta = 10.36$ (s, 1H, $-\text{CHO}$), 9.01 (s, 1H, $\text{ReO}=\text{CH}$), 7.77–7.72 (m, 2H, Ph), 7.68–7.62 (m, 4H, Ph), 7.53–7.49 (m, 2H, Ph), 7.35–7.32 (m, 3H, Ph), 7.23–7.10 (m, 9H, Ph), 6.73–6.69 (m, 3H, Ph, $\text{CH}(\text{PMePh}_2)$), 3.53 (s, 1H, $\text{C}\equiv\text{CH}$), 2.50 (d, $^2J(\text{PH}) = 16.0$ Hz, 3H, PMePh_2), 2.18 (d, $^2J(\text{PH}) = 8.0$ Hz, 3H, PMePh_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3): $\delta = 239.0$ – 238.8 (m, $\text{Re}=\text{C}$), 191.0 (s, CHO), 187.3 (s, $\text{ReO}=\text{CH}$), 141.2–120.2 (multiple ^{13}C signals of Ph), 86.9 (s, $\text{C}\equiv\text{CH}$), 78.0 (s, $\text{C}\equiv\text{CH}$), 21.4 (d, $^1J(\text{PC}) = 55.3$ Hz, $\text{CH}(\text{PMePh}_2)$), 14.6 (d, $^1J(\text{PC}) = 32.2$ Hz, PMePh_2), 10.9 (d, $^1J(\text{PC}) = 43.3$ Hz, PMePh_2). Anal. Calcd. For $\text{C}_{38}\text{H}_{32}\text{Cl}_3\text{O}_2\text{P}_2\text{Re}\cdot\text{H}_2\text{O}$: C, 51.10; H, 3.84. Found: C, 51.26; H, 4.27.

Synthesis of complex 3. A mixture of $\text{ReCl}_3(\text{PMePh}_2)_3$ (0.200 g, 0.224 mmol) and 1-(4-acetyl-2,5-diethynylphenyl)ethanone (0.560 g, 0.269 mmol) in THF (10 mL) was stirred at room temperature for 5 h, producing a brownish green solid. The solid was filtered and washed with

THF (8 mL) and ether (8 mL). Then it was dried under vacuum. Yield: 0.140 g, 69.2 %. $^{31}\text{P}\{^1\text{H}\}$ NMR (162.0 MHz, CDCl_3): $\delta = 38.7$ (d, $J = 8.1$ Hz, $\text{CH}(\text{PMePh}_2)$), -10.7 (d, $J = 8.1$ Hz, RePMePh_2). ^1H NMR (400.1 MHz, CDCl_3): $\delta = 7.95$ – 7.91 (m, 1H, Ph), 7.72 – 7.67 (m, 1H, Ph), 7.65 – 7.56 (m, 4H, Ph), 7.50 (t, $J = 8.0$ Hz, 1H, Ph), 7.38 – 7.28 (m, 6H, Ph), 7.24 – 7.16 (m, 5H, Ph), 7.15 – 7.09 (m, 2H, Ph), 6.70 (t, $J = 8.0$ Hz, 2H, Ph), 6.39 (d, $^2J(\text{PH}) = 16.0$ Hz, 1H, $\text{CH}(\text{PMePh}_2)$), 5.12 (s, 3H, CH_3), 3.52 (s, 1H, $\text{C}\equiv\text{CH}$), 2.52 (s, 3H, CH_3), 2.47 (d, $^2J(\text{PH}) = 12.0$ Hz, 3H, PMePh_2), 2.21 (d, $^2J(\text{PH}) = 12.0$ Hz, 3H, PMePh_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3): $\delta = 234.6$ – 234.4 (m, $\text{Re}=\text{C}$), 201.2 (s, $\text{C}=\text{O}$), 196.3 (s, $\text{C}=\text{O}$), 147.2 – 115.2 (multiple ^{13}C signals of Ph), 85.1 (s, $\text{C}\equiv\text{CH}$), 82.2 (s, $\text{C}\equiv\text{CH}$), 29.8 (s, CH_3), 24.4 (s, CH_3), 18.0 (d, $^1J(\text{PC}) = 54.2$ Hz, $\text{CH}(\text{PMePh}_2)$), 15.3 (d, $^1J(\text{PC}) = 30.2$ Hz, PMePh_2), 11.0 (d, $^1J(\text{PC}) = 43.3$ Hz, PMePh_2). Anal. Calcd. For $\text{C}_{40}\text{H}_{36}\text{Cl}_3\text{O}_2\text{P}_2\text{Re}\cdot 1.5\text{H}_2\text{O}$: C, 51.65; H, 4.23. Found: C, 51.31; H, 4.28.

Synthesis of complex 4. A mixture of complex 3 (0.140 g, 0.155 mmol) and $\text{ReCl}_3(\text{PMePh}_2)_3$ (0.152 g, 0.170 mmol) in THF/DCM (6 mL/6 mL) was stirred at 40°C for 3 h, producing a dark reddish solid. The solid was filtered and washed with THF (8 mL) and ether (6 mL). Then it was dried under vacuum. Yield: 0.180 g, 72.7 %. $^{31}\text{P}\{^1\text{H}\}$ NMR (162.0 MHz, CDCl_3): $\delta = 34.5$ (d, $J = 6.5$ Hz, $\text{CH}(\text{PMePh}_2)$), -9.8 (d, $J = 6.5$ Hz, RePMePh_2). ^1H NMR (400.1 MHz, CDCl_3): $\delta = 7.68$ – 7.63 (m, 6H, Ph), 7.60 – 7.51 (m, 9H, Ph), 7.46 – 7.38 (m, 9H, Ph), 7.33 – 7.31 (m, 3H, Ph), 7.20 – 7.06 (m, 11H, Ph), 6.44 (t, $J = 8.0$ Hz, 4H, Ph), 5.85 (d, $^2J(\text{PH}) = 12.0$ Hz, 2H, $\text{CH}(\text{PMePh}_2)$), 4.40 (s, 6H, CH_3), 2.10 (t, $^2J(\text{PH}) = 12.0$ Hz, 12H, PMePh_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3): $\delta = 235.7$ – 235.6 (m, $\text{Re}=\text{C}$), 198.3 (s, $\text{C}=\text{O}$), 133.8 – 123.6 (multiple ^{13}C signals of Ph), 23.8 (s, CH_3), 18.7 (d, $^1J(\text{PC}) = 54.3$ Hz, $\text{CH}(\text{PMePh}_2)$), 15.4 (d, $^1J(\text{PC}) = 31.2$ Hz, PMePh_2), 10.4 (d, $^1J(\text{PC}) = 42.3$ Hz, PMePh_2). Anal. Calcd. For $\text{C}_{66}\text{H}_{62}\text{Cl}_6\text{O}_2\text{P}_4\text{Re}_2$: C, 49.66; H, 3.92. Found: C, 49.34; H, 4.13.

Synthesis of complex 5. A mixture of $\text{ReCl}_3(\text{PMePh}_2)_3$ (0.200 g, 0.224 mmol) and 1-ethynyl-2-naphthaldehyde (0.048 g, 0.267 mmol) in THF (10 mL) was heated at 60°C for 1 h, producing a red solid. The solid was filtered and washed with THF (5 mL) and ether (2 mL \times 2). Then it was dried under vacuum. Yield: 0.145 g, 82.8 %. $^{31}\text{P}\{^1\text{H}\}$ NMR (162.0 MHz, methanol- d_4): $\delta = 37.7$ (d, $J = 4.9$ Hz, $\text{CH}(\text{PMePh}_2)$), -14.1 (d, $J = 4.9$ Hz, RePMePh_2). ^1H NMR (400.1 MHz, methanol- d_4): $\delta = 9.53$ (d, $J = 4.0$ Hz, 1H, $\text{C}(\text{O})\text{H}$), 8.43 (d, $J = 8.0$ Hz, 1H, Ph), 8.25 (d, $J = 8.0$ Hz, 1H, Ph), 8.17 (d, $J = 8.0$ Hz, 1H, Ph), 7.89 (t, $J = 8.0$ Hz, 1H, Ph), 7.82 (d, $J = 8.0$ Hz, 1H, Ph), 7.78 – 7.73 (m, 2H, Ph), 7.71 – 7.68 (m, 1H, Ph), 7.56 – 7.47 (m, 6H, Ph), 7.40 – 7.37 (m, 2H, Ph), 7.28 – 7.21 (m, 4H, Ph), 7.08 – 6.97 (m, 5H, Ph), 6.76 – 6.72 (m, 2H, Ph, $\text{CH}(\text{PMePh}_2)$), 2.64 (d, $^2J(\text{PH}) = 12.0$ Hz, 3H, PMePh_2), 1.75 (d, $^2J(\text{PH}) = 12.0$ Hz, 3H, PMePh_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, methanol- d_4): $\delta = 239.3$ – 239.1 (m, $\text{Re}=\text{C}$), 192.2 (s, $\text{C}=\text{O}$), 139.5 – 121.2 (multiple ^{13}C signals of Ph), 20.8 (d, $^1J(\text{PC}) = 54.3$ Hz, $\text{CH}(\text{PMePh}_2)$), 12.3 (d, $^1J(\text{PC}) = 29.2$ Hz, PMePh_2), 11.0 (d, $^1J(\text{PC}) = 45.3$ Hz, PMePh_2). Anal. Calcd. For $\text{C}_{39}\text{H}_{34}\text{Cl}_3\text{OP}_2\text{Re}$: C, 53.35; H, 4.04. Found: C, 53.64; H, 3.92.

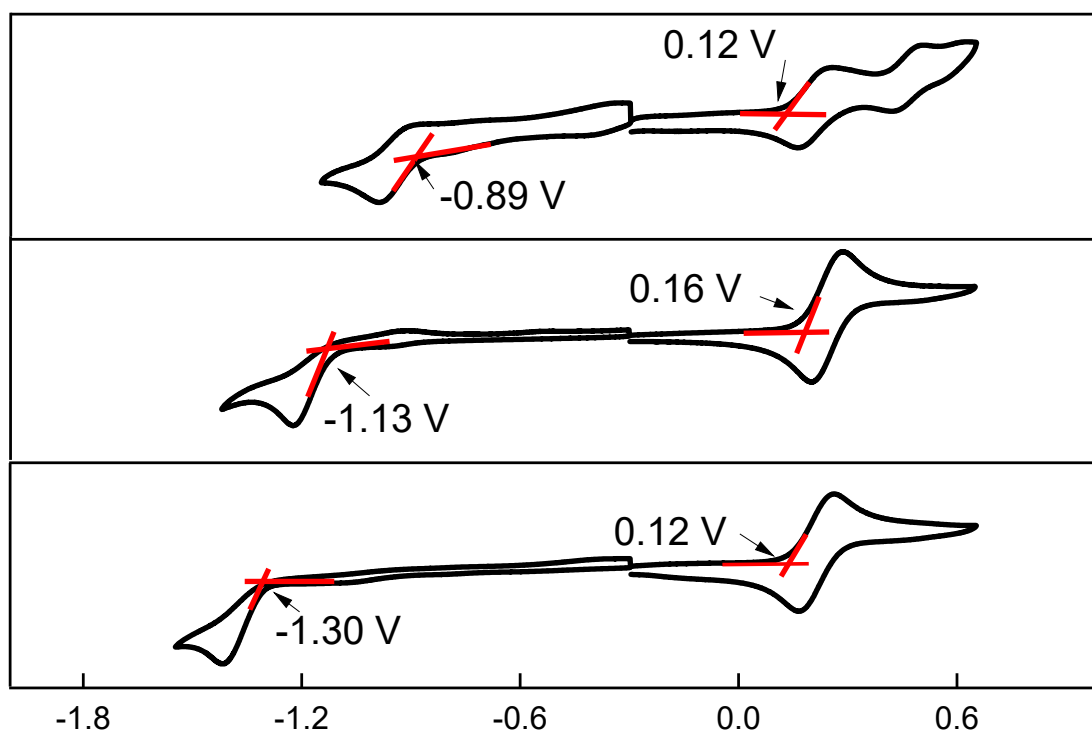


Figure S1. CV curves in 0.1 M $\text{Bu}_4\text{NBF}_4/\text{CH}_2\text{Cl}_2$ solution at a scan rate of 100 mV s^{-1}

Table S1. Measured and calculated potentials.

	E_{ox} (V)	E_{re} (V)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{g}^{CV} (eV)
Complex 4	0.12	-0.89	-4.87	-3.86	1.01
Complex 5	0.16	-1.13	-4.91	-3.62	1.29
Complex 6	0.12	-1.30	-4.87	-3.45	1.42

$$E_{\text{HOMO}} = -(E_{\text{ox}} - E_{1/2(\text{Fc})} + 4.8), E_{\text{LUMO}} = -(E_{\text{re}} - E_{1/2(\text{Fc})} + 4.8), E_{1/2(\text{Fc})} = 0.05,$$

$$E_{\text{g}}^{\text{CV}} = E_{\text{HOMO}} - E_{\text{LUMO}}$$

2. Computational details

All the optimizations were performed with the Gaussian 09 software package.^[5] The structures evaluated were optimized at the B3LYP level of density functional theory (DFT).^[6] DFT/GENECP level had been done by implementing def2-TZVP basis set for Re atom^[7] and 6-311G(2d,p) basis set for the rest of atoms.^[8] Nucleus-independent chemical shift (NICS)^[9] values were calculated at the B3LYP-GIAO//6-311G(2d,p)/def2-TZVP level, whereas we performed the TD-DFT calculations at the CAM-B3LYP/6-31G(d)+lanl2dz level on the ground-state optimized geometries of the complexes in CH₂Cl₂ medium. The anisotropy of the current density was calculated with the AICD 2.0 program computing the NMR properties using the CSGT method with the Gaussian09 Rev D.01 program with the geometries previously obtained for **4** and **5**.^[10] The molecular orbital composition and natural transition orbital (NTO) analysis were analyzed using Multiwfn, a multifunctional wavefunction analyzer.^[11] The MO pictures were drawn using the software of VMD.^[12] VMD was developed by the Theoretical and Computational Biophysics Group in the Beckman Institute for Advanced Science and Technology at the University of Illinois at Urbana-Champaign (<http://www.ks.uiuc.edu/Research/vmd/>).

Table S2. Selected Ultraviolet–Visible Absorption Energy Transitions at the TD-DFT/B3LYP Level for **4** and **5** in dichloromethane.

excited state	λ_{cal} nm	E_{exc} eV	oscillator strength (f)	key transitions	character
Complex 4					
1	954	1.299	0.0346	H→L(63.7%), H-1→L+2(16.0%), H→L+1(8.1%), H-2→L(7.1%)	MLCT, ILCT
3	535	2.318	0.2282	H-2→L(74.2%), H→L+1(14.2%)	$\pi \rightarrow \pi^*$
4	465	2.666	0.3719	H→L+1(62.6%), H→L(19.7%), H-2→L(7.1%)	MLCT, ILCT
11	377	3.293	0.3584	H-2→L+1(66.8%)	$\pi \rightarrow \pi^*$
Complex 5					
1	999	1.241	0.0056	H→L(86.2%)	MLCT, ILCT
2	469	2.644	0.1453	H-1→L(79.7%), H→L+1(8.0%)	$\pi \rightarrow \pi^*$
5	362	3.430	0.0758	H→L+1(32.1%), H→L+13(15.4%), H→L+2(12.6%), H→L+4(11.4%)	MLCT, ILCT
6	345	3.579	0.0705	H→L+1(25.3%), H→L+5(14.8%), H→L+13(14.3%), H-2→L(8.1%), H-3→L(7.6%)	MLCT, ILCT

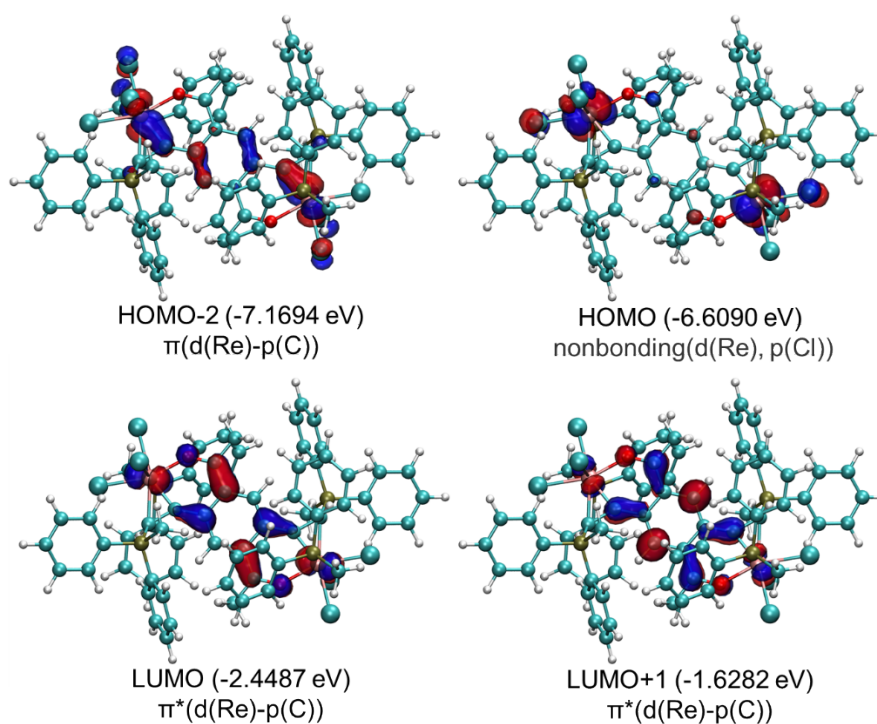


Figure S2. The molecular orbitals of complex **4** involved in the predicted transitions (isovalues = 0.04).

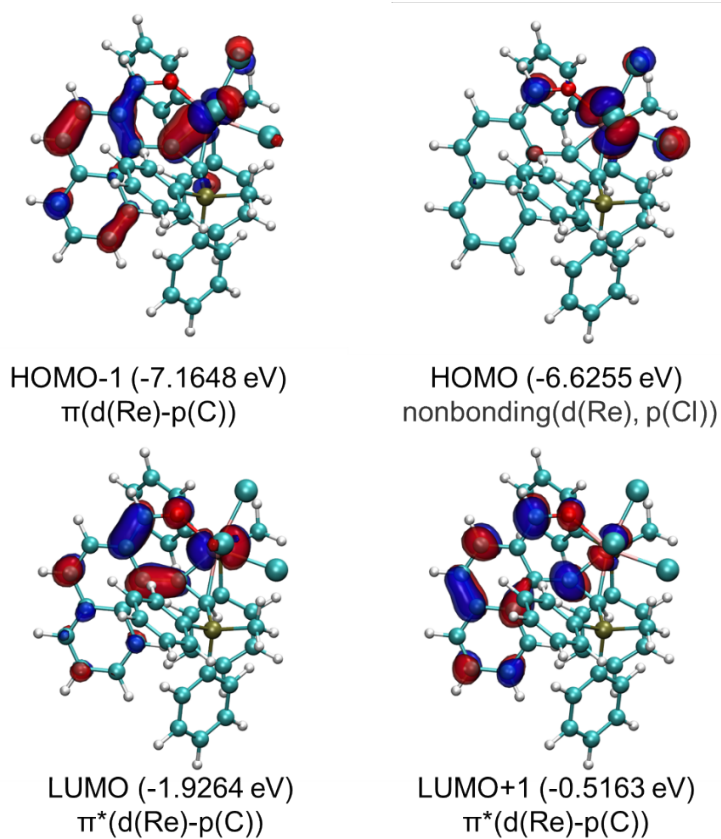
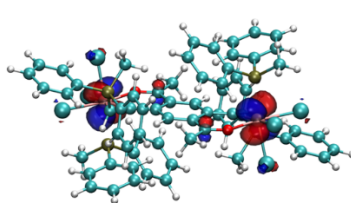
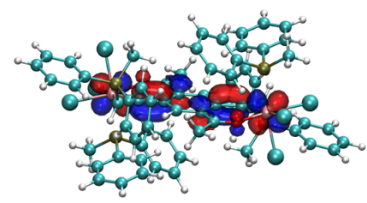
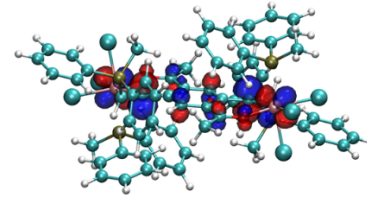
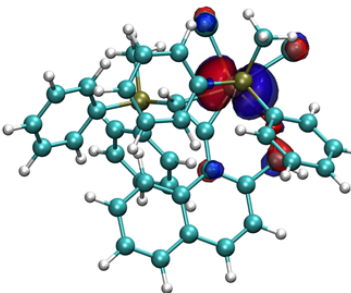
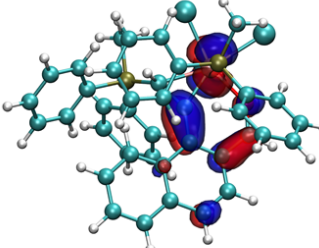


Figure S3. The molecular orbitals of complex **5** involved in the predicted transitions (isovalues = 0.04).

Table S3. NTOs illustrating the nature of optically active singlet excited states in the absorption bands at 954 nm for **4** and 999 nm for **5**.

		Hole	Electron
4	954 nm S1		 82.2%
			 18.5%
5	999 nm S1		 99.0%

The occupied (holes) and unoccupied (electrons) NTO pairs that contribute more than 10% to each excited state are only represented. All transitions are mixed MLCT/ILCT in character.

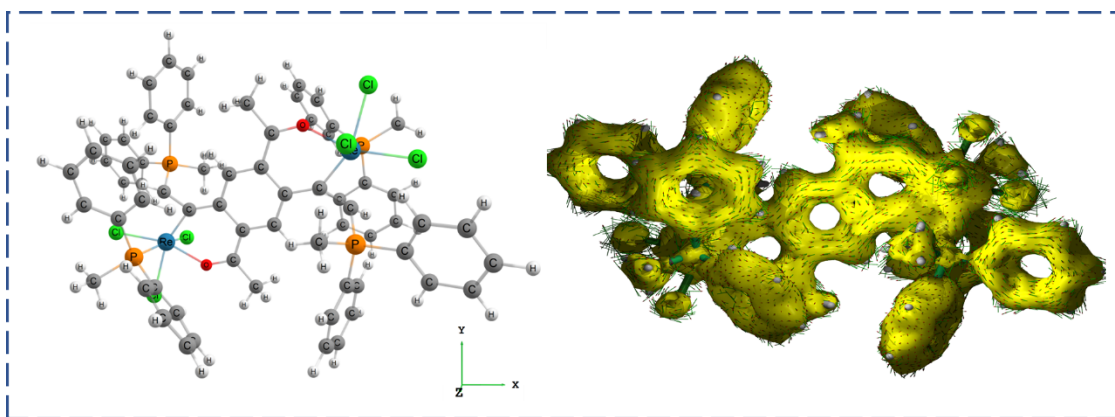


Figure S4. The AICD plots in **4** (isosurface value is 0.03). Magnetic field vector is orthogonal to the rhenapyrylium plane and directed along the Z axis. The clockwise currents are diatropic.

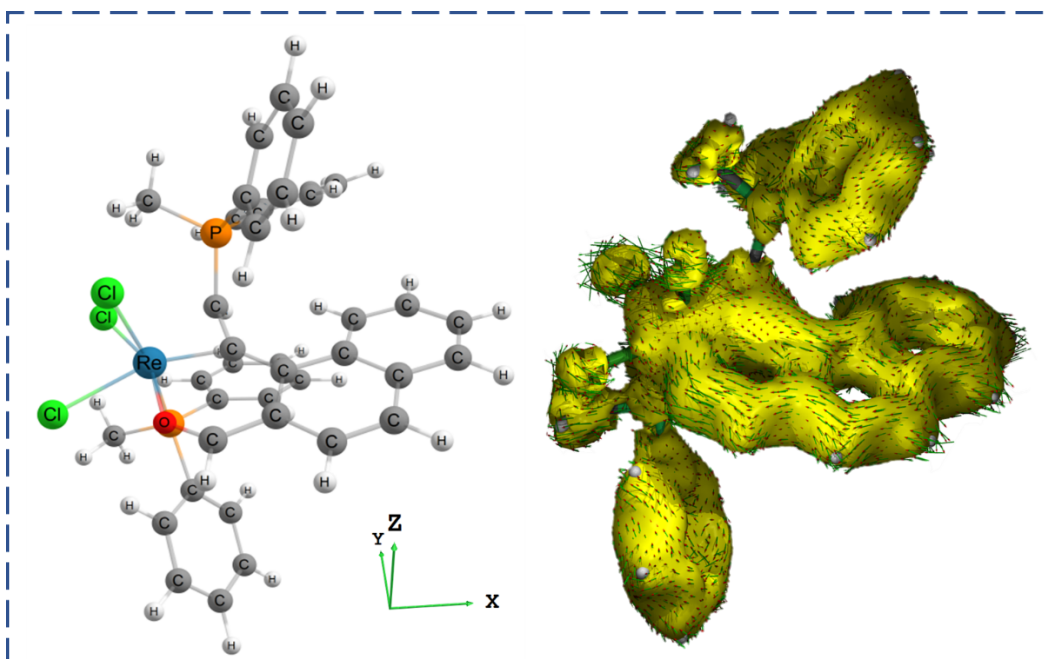


Figure S5. The AICD plots in **5** (isosurface value is 0.03). Magnetic field vector is orthogonal to the rhenapyrylium plane and directed along the Z axis. The clockwise currents are diatropic.

3. X-ray crystallographic study of complexes 4 and 5.

Single crystal data of **4** (CCDC no. 2145557) was collected on a Bruker Apex II CCD area-detector diffractometer using Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$), while that of **5** (CCDC no. 2150979) was collected on a Bruker Apex II CCD area-detector diffractometer using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Unit cell indexing was refined using SAINT, Absorption correction was applied by using multi-scan program SADABS. The structure was solved with OLEX2 software, and the SHELXT structure solution program using combined direct methods.^[13,14] The crystal structure was refined by least squares using SHELXL. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon atoms were placed at calculated positions and refined using a riding model approximation, with C–H = 0.95 (aromatic CH) and with Uiso(H) = 1.2 Ueq(C), C–H = 1.00 (-CH) and with Uiso(H) = 1.2 Ueq(C), C–H = 0.99 (-CH₂) and with Uiso(H) = 1.2 Ueq(C), C–H = 0.98 Å (-CH₃) and with Uiso(H) = 1.5 Ueq(C). The crystal data are listed in Table S4. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre.

Table S4. Crystallographic data and refinement details for **4** and **5**.

	4	5
CCDC Number	2145557	2150979
Empirical formula	C _{72.5} H ₇₄ Cl ₁₃ O ₂ P ₄ Re ₂	C ₄₀ H ₃₆ Cl ₅ OP ₂ Re
Color & habit	red, block	red, block
Crystal size (mm ³)	0.05 x 0.06 x 0.08	0.10 x 0.10 x 0.10
Temperature (K)	120K	120K
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
a/Å	13.5626(6)	10.3695(6)
b/Å	16.9269(8)	12.1973(8)
c/Å	17.6821(8)	16.6779(10)
α /°	87.311(4)	97.1060(10)
β /°	88.052(4)	96.7000(10)
γ /°	83.508(4)	102.4130(10)
V(Å ³), Z	4027.2(3), 2	2021.8(2), 2
D _{cal} (Mg/m ³)	1.420	1.574
Abs. coeff.(mm ⁻¹)	9.276	3.455
2 θ range for data collection (°)	7.418 to 133.192	6.484 to 54
Reflections collected	33288	53167

Indep. Reflection, R(int)	13766, 0.1394	8752, 0.0283
Completeness of data	96.8 %	99.0 %
Data/ restraints / parameters	13766/223/686	8752/0/471
Goodness-of-fit on F ²	1.058	1.048
R1 [I>2sigma(I)], wR2	0.1105, 0.2699	0.0243, 0.0623
R1 (all data), wR2	0.1568, 0.2942	0.0253, 0.0628
Largest diff. peak and hole	5.09, -1.61	1.96, -1.26
(e·Å ⁻³)		

4. NMR spectra

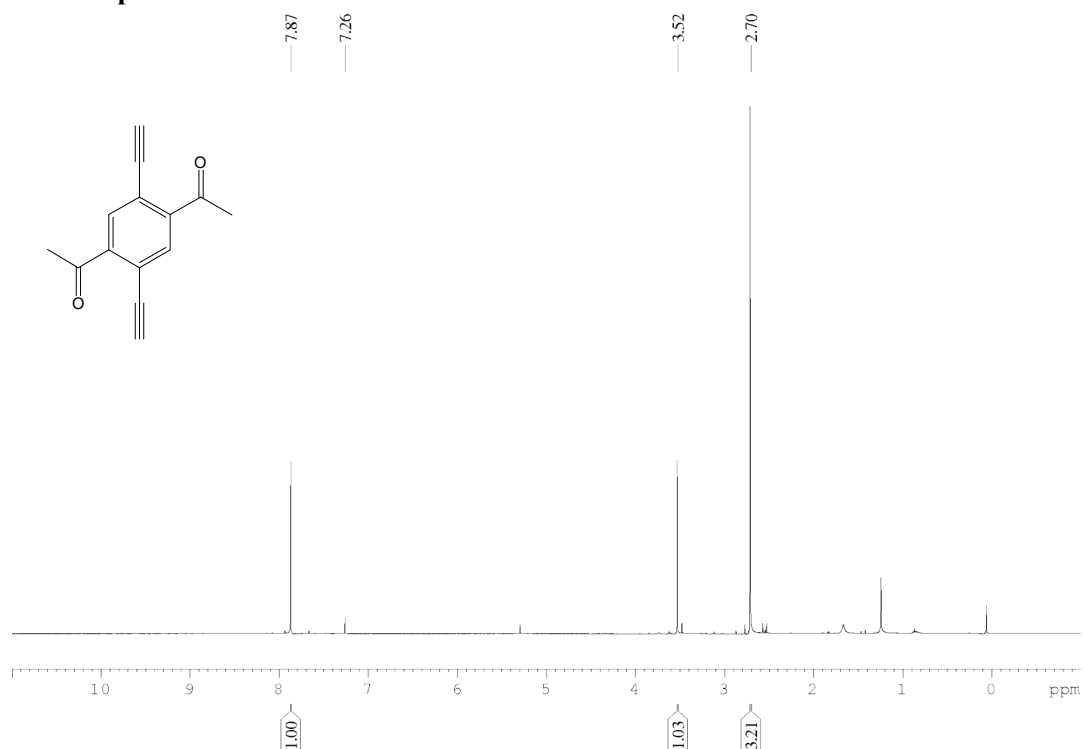


Figure S6. The ^1H NMR spectrum of 1-(4-acetyl-2,5-diethynylphenyl)ethanone in CDCl_3 at 400.1 MHz.

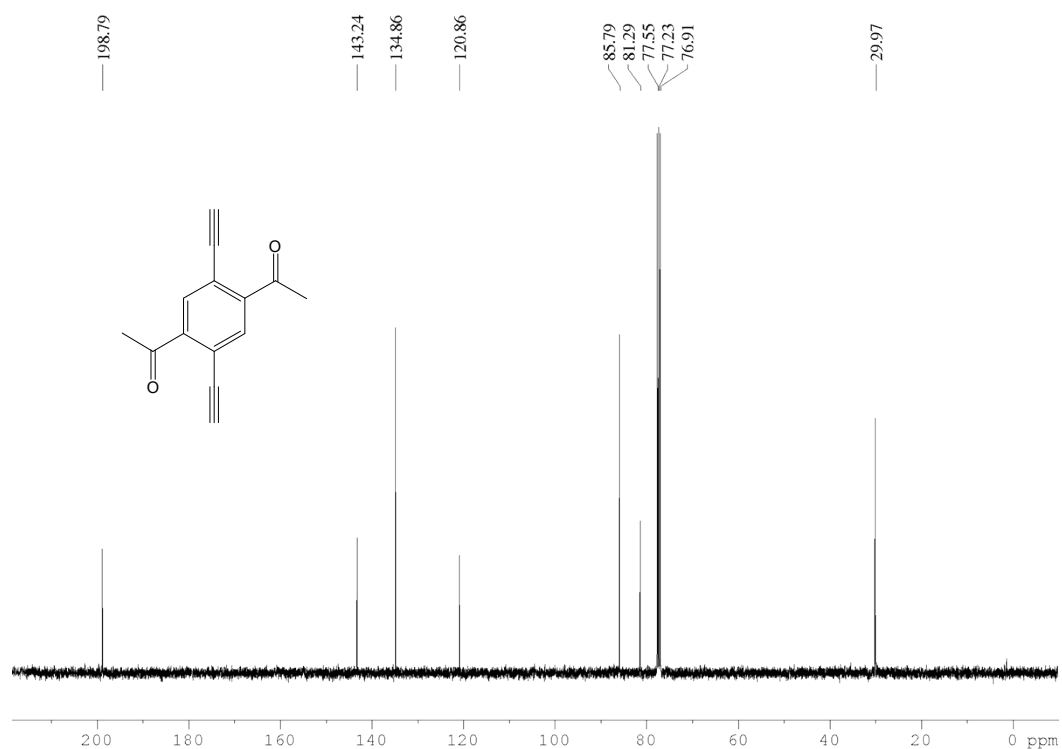


Figure S7. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 1-(4-acetyl-2,5-diethynylphenyl)ethanone in CDCl_3 at 100.6 MHz.

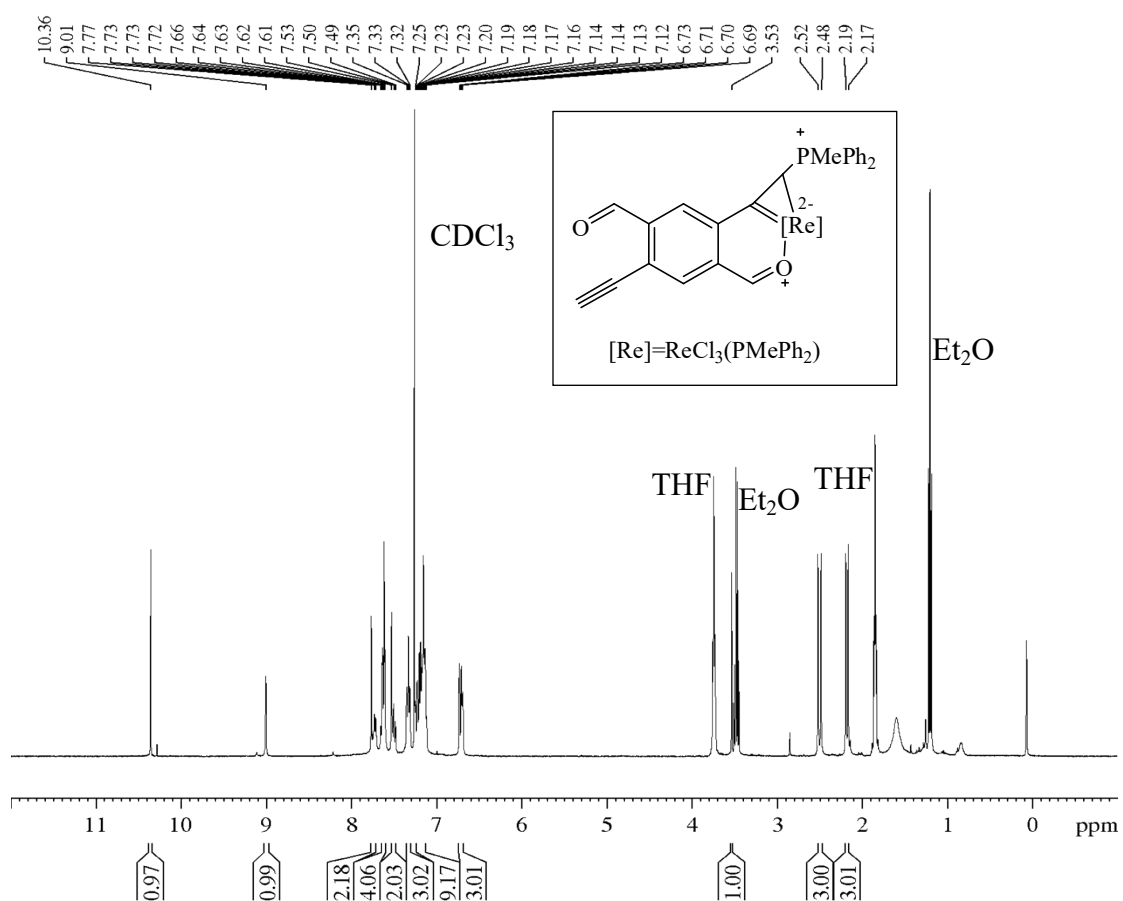


Figure S8. The 1H NMR spectrum of complex 2 in $CDCl_3$ at 400.1 MHz.

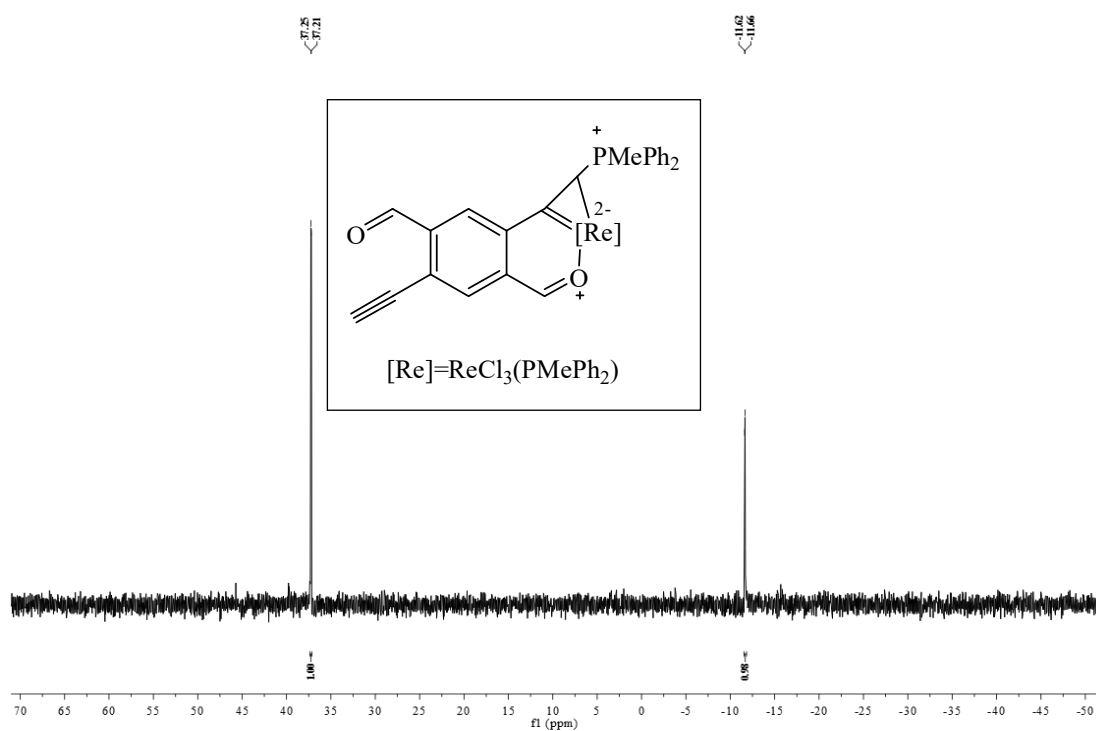


Figure S9. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **2** in CDCl_3 at 162.0 MHz.

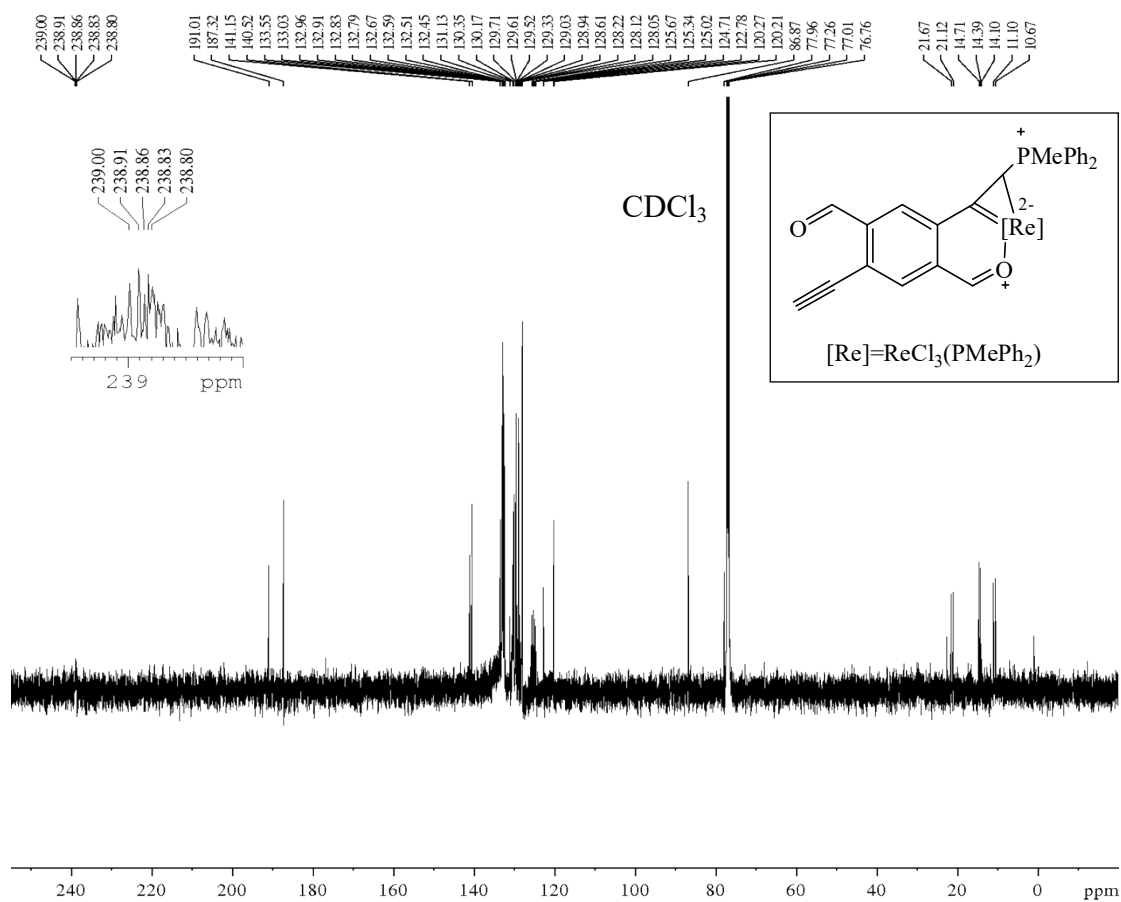


Figure S10. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex **2** in CDCl_3 at 100.6 MHz.

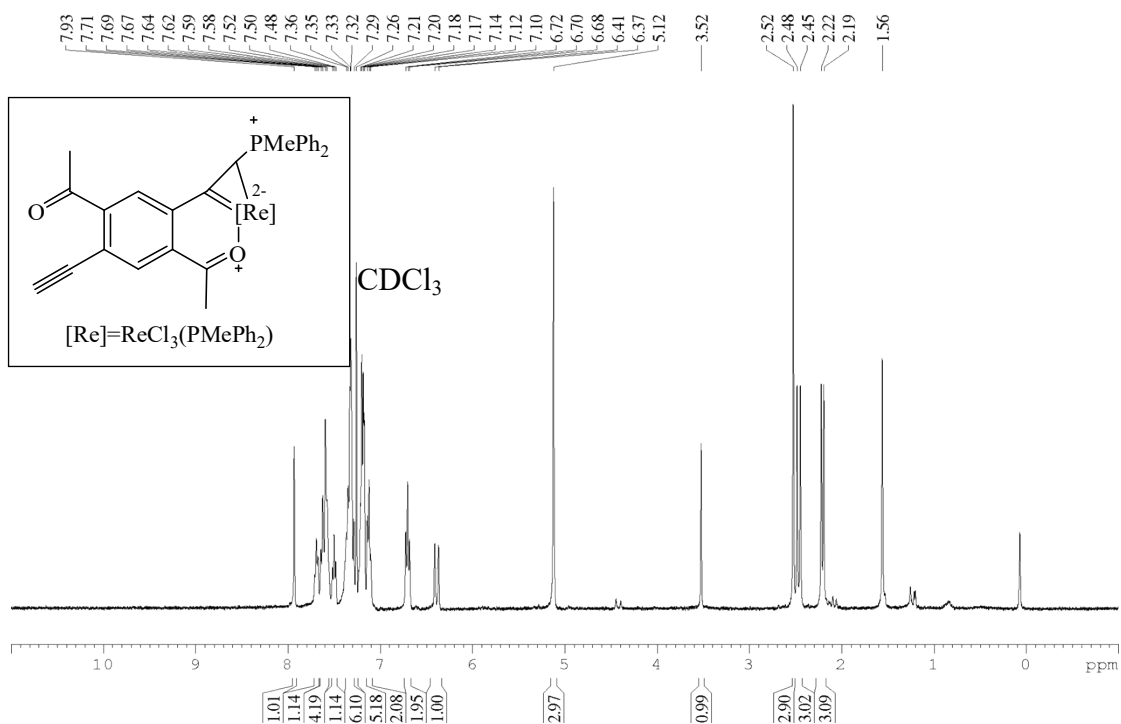


Figure S11. The ^1H NMR spectrum of complex **3** in CDCl_3 at 400.1 MHz.

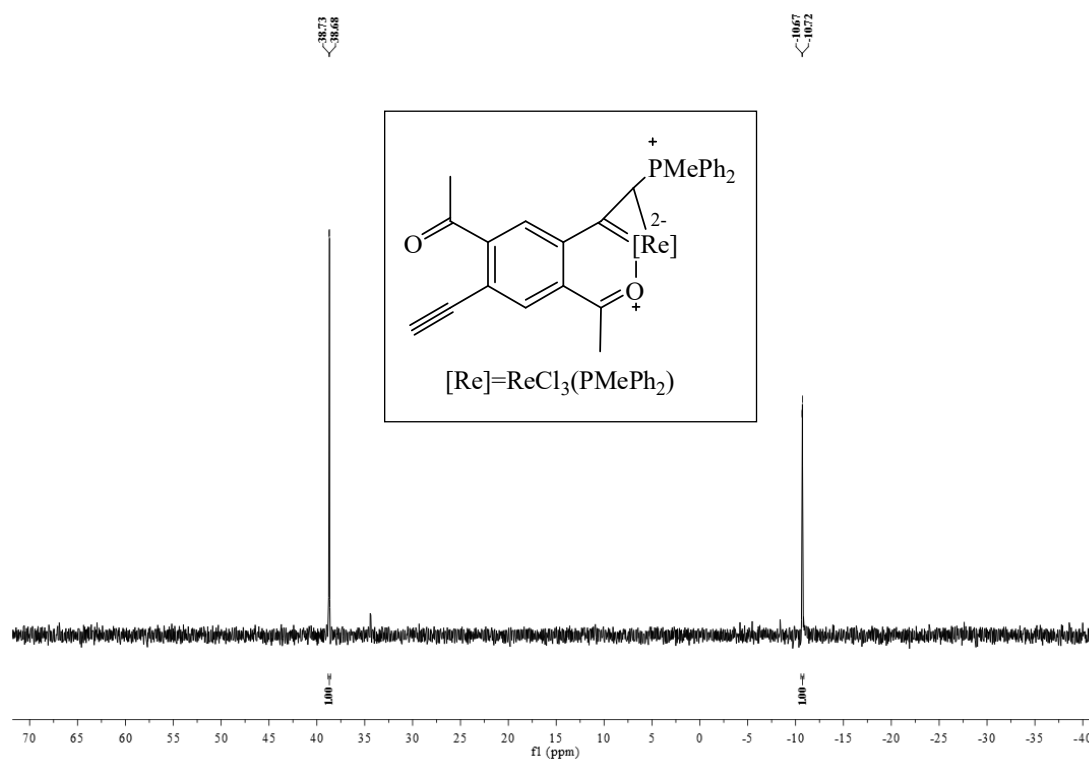


Figure S12. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **3** in CDCl_3 at 162.0 MHz.

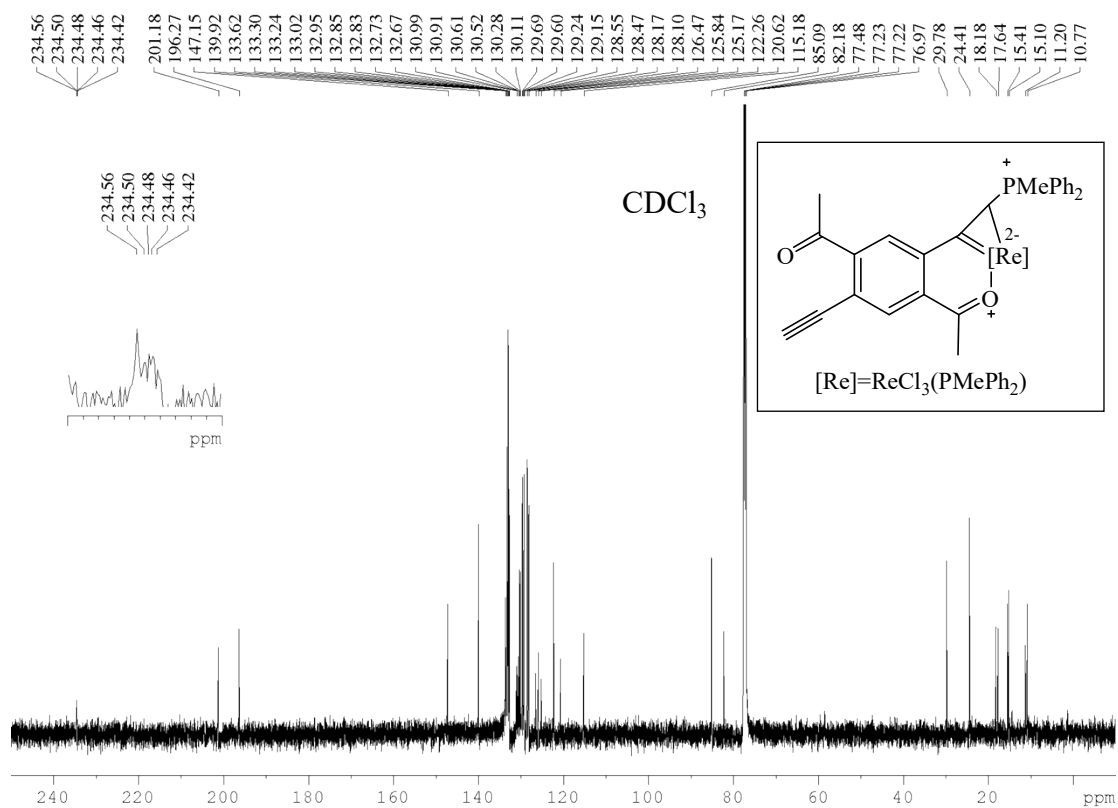


Figure S13. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex **3** in CDCl_3 at 100.6 MHz.

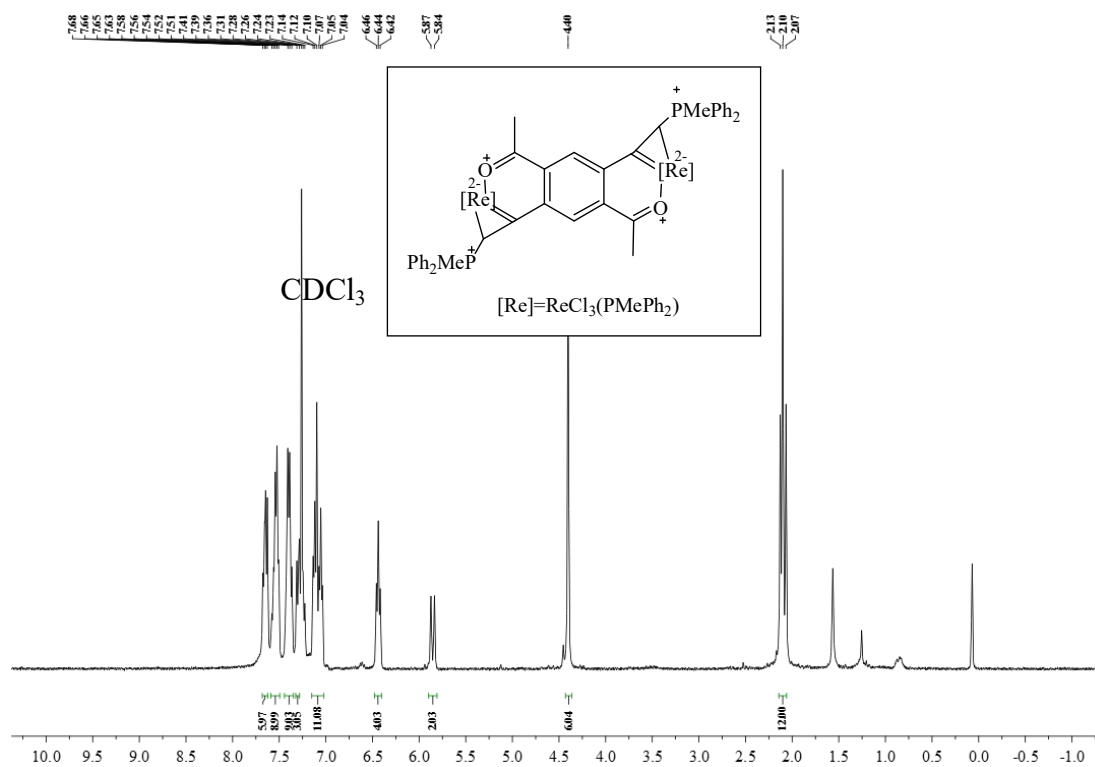


Figure S14. The ^1H NMR spectrum of complex 4 in CDCl_3 at 400.1 MHz.

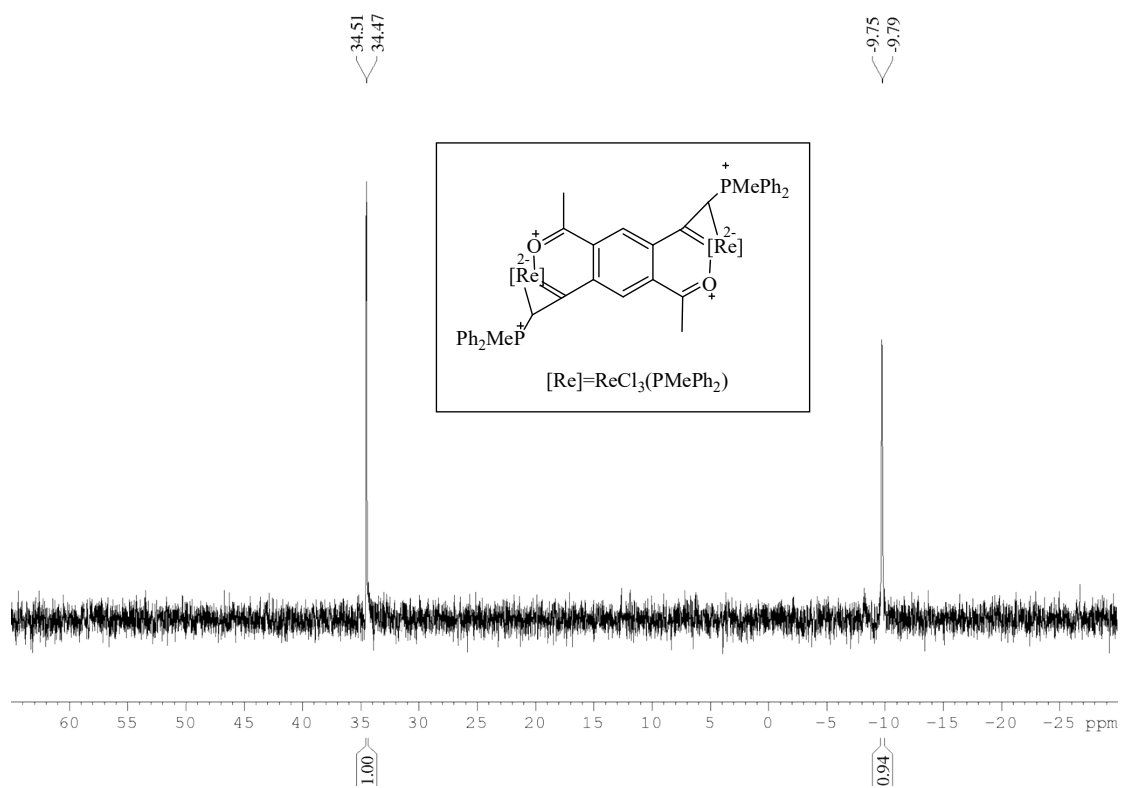


Figure S15. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex 4 in CDCl_3 at 162.0 MHz.

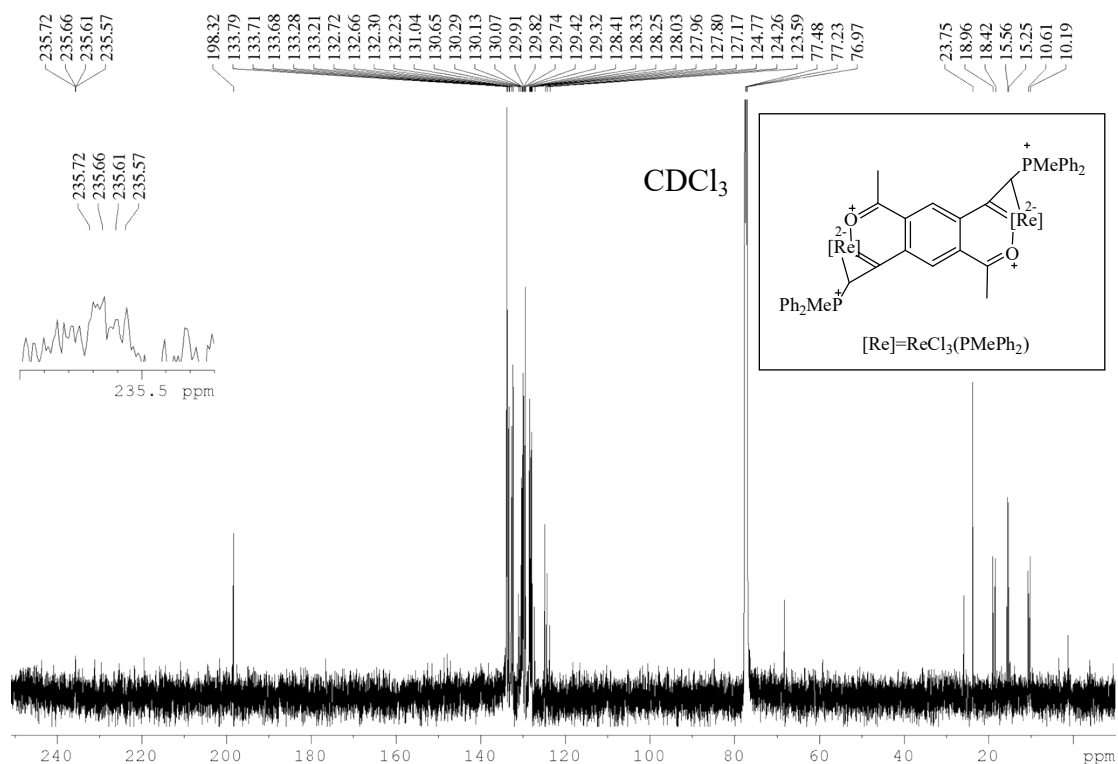


Figure S16. The $^{13}C\{^1H\}$ NMR spectrum of complex **4** in $CDCl_3$ at 100.6 MHz.

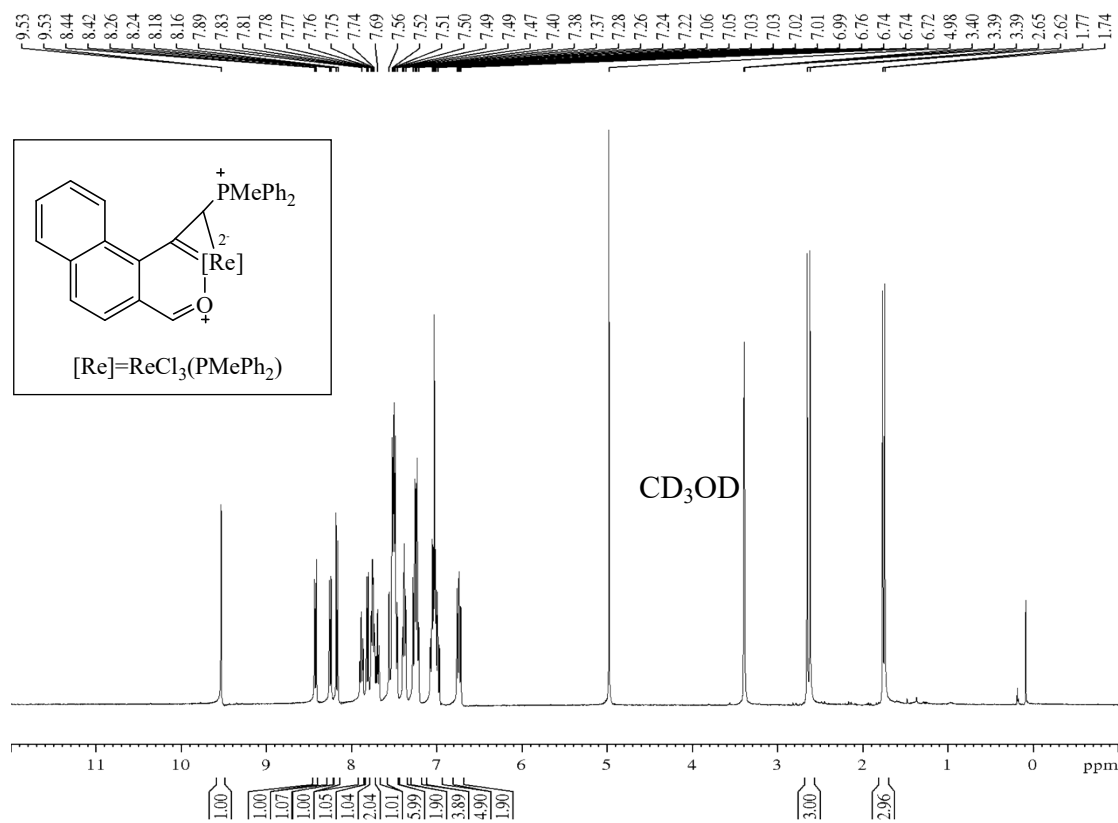


Figure S17. The 1H NMR spectrum of complex **5** in CD_3OD at 400.1 MHz.

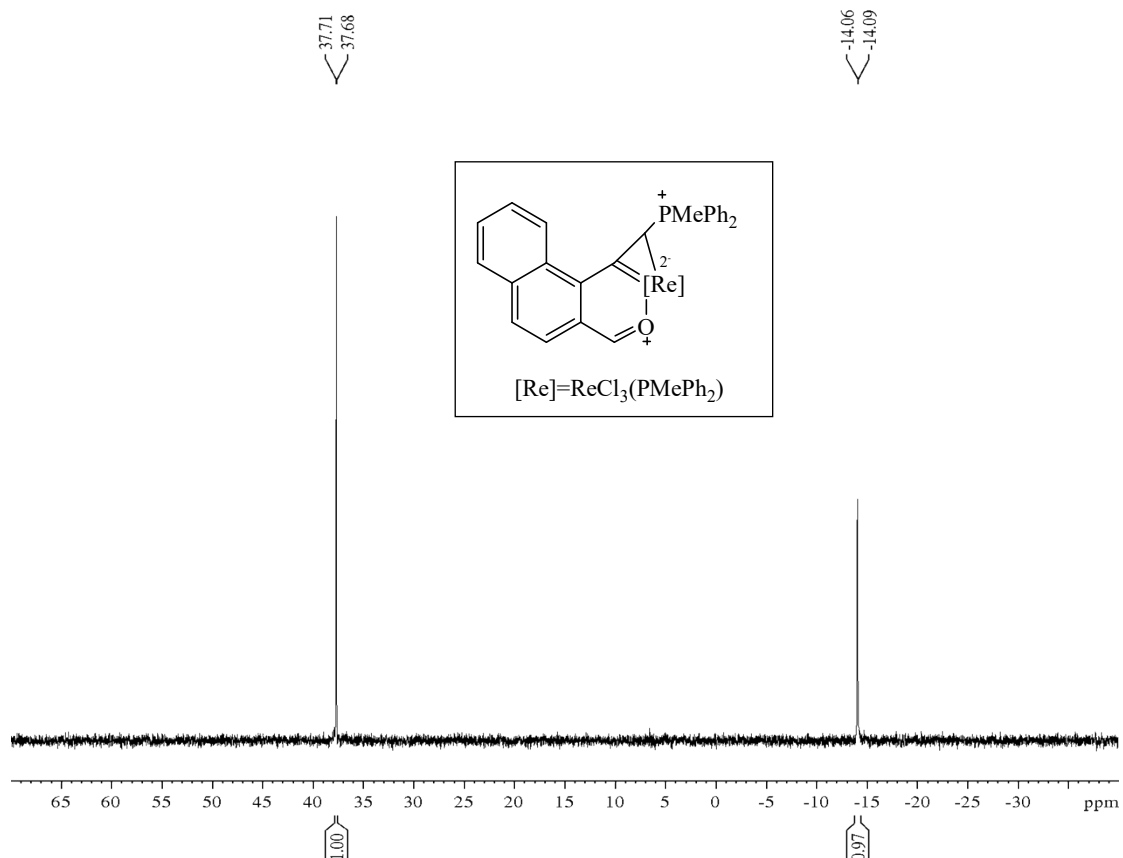


Figure S18. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **5** in CD_3OD at 162.0 MHz.

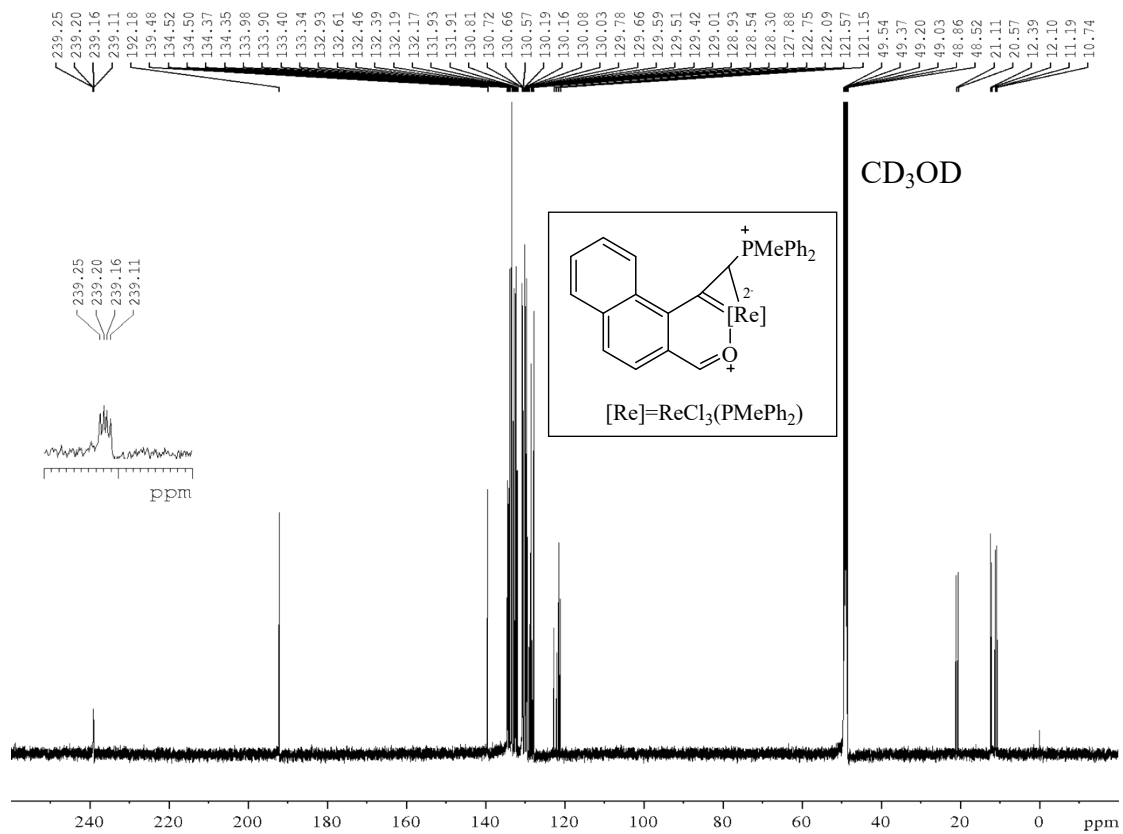
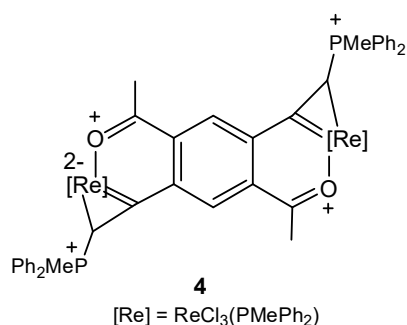


Figure S19. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex **5** in CD_3OD at 100.6 MHz.

5. The Calculated Cartesian Coordinates with Electronic Energies



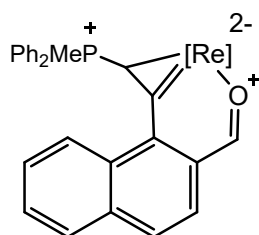
E= -6987.417402 A.U.

Re	-4.18746500	-1.24347100	0.94621900
Cl	-4.29460800	-0.23356100	3.18543400
Cl	-6.56472700	-0.75023700	0.59671100
Cl	-5.05655800	-3.32273600	2.00191500
P	-4.41849200	-2.56536700	-1.14471600
P	-4.15644400	2.34576000	0.40710600
O	-2.48225200	-2.17368600	1.61877600
C	-3.96989000	0.65522600	-0.17927100
H	-4.44291100	0.57376600	-1.15403900
C	-2.83865000	-0.15298500	0.14571400
C	-1.42142800	-0.07700600	0.06178800
C	-0.60604600	-1.00150800	0.79519400
C	-1.23532900	-2.02804700	1.58932900
C	-0.43528900	-3.00524800	2.40824900
H	-1.12639700	-3.64169600	2.95603600
H	0.21014600	-2.48645600	3.12079600
H	0.20508300	-3.62682800	1.77723200
C	-0.78437700	0.89713800	-0.71454800
H	-1.40479100	1.58328200	-1.27420800
C	-5.98691400	-3.50834500	-1.29124900
H	-5.98772900	-4.24983000	-0.49481400
H	-6.03930300	-3.99466200	-2.26574400
H	-6.83311200	-2.84421400	-1.13021900
C	-4.36819900	-1.54316000	-2.67682300
C	-5.55086700	-1.12162800	-3.29138900
H	-6.50928400	-1.42985900	-2.89658200
C	-5.51383100	-0.29515100	-4.41076200
H	-6.44194100	0.01397400	-4.87684700
C	-4.29594700	0.12296700	-4.93356700
H	-4.26754000	0.75141000	-5.81605400
C	-3.11189800	-0.27640800	-4.32018500
H	-2.15649700	0.04229200	-4.72025800
C	-3.14864900	-1.09430500	-3.19770200
H	-2.21824100	-1.39665400	-2.73408900

C	-3.17750400	-3.90430600	-1.45415600
C	-2.79283600	-4.27947400	-2.74552200
H	-3.16495700	-3.73875800	-3.60550200
C	-1.93249200	-5.35313500	-2.94514600
H	-1.64486600	-5.62826200	-3.95318000
C	-1.45398300	-6.07634100	-1.85878900
H	-0.79073600	-6.91916500	-2.01610300
C	-1.84519100	-5.72181700	-0.57281600
H	-1.49522400	-6.29203200	0.27992600
C	-2.69895600	-4.64314400	-0.36773800
H	-3.01857600	-4.38980800	0.63444200
C	-5.85426800	2.83652500	0.83274400
C	-6.56137900	3.74103700	0.03438800
H	-6.11315900	4.15632600	-0.85777200
C	-7.85108800	4.11897800	0.38572500
H	-8.39304800	4.81842700	-0.23928400
C	-8.43944500	3.60282000	1.53407200
H	-9.44563600	3.89861100	1.80687200
C	-7.73943300	2.70181000	2.32829700
H	-8.19855500	2.28284200	3.21495600
C	-6.45396600	2.31008600	1.98183200
H	-5.93279900	1.58191900	2.58997000
C	-3.08886800	2.67349800	1.83610100
H	-3.30364800	1.91507800	2.59078400
H	-3.30109100	3.66383900	2.23641800
H	-2.04425600	2.60469800	1.53425600
C	-3.63744600	3.49415700	-0.92059000
C	-3.04904000	4.72312400	-0.60626000
H	-2.86860300	4.99876900	0.42443900
C	-2.68818200	5.61000100	-1.61352300
H	-2.23118500	6.55741700	-1.35498200
C	-2.91462600	5.28349200	-2.94595200
H	-2.63328100	5.97567500	-3.73029000
C	-3.50081300	4.06466200	-3.26752900
H	-3.68022500	3.80202300	-4.30286000
C	-3.85985600	3.17304900	-2.26335400
H	-4.31226900	2.22901600	-2.53691100
P	4.15662800	-2.34569800	-0.40710600
O	2.48227100	2.17360800	-1.61891500
C	3.96992400	-0.65518700	0.17927700
H	4.44286100	-0.57370600	1.15408500
C	2.83866300	0.15295700	-0.14579800
C	1.42144200	0.07694500	-0.06191400
C	0.60606200	1.00143100	-0.79533800

C	1.23534900	2.02795500	-1.58949000
C	0.43531400	3.00511700	-2.40846000
H	1.12642400	3.64151900	-2.95629700
H	-0.21014700	2.48629700	-3.12096200
H	-0.20503000	3.62674800	-1.77746700
C	0.78439200	-0.89721100	0.71440800
H	1.40480500	-1.58335600	1.27406800
C	5.85451500	-2.83632700	-0.83264700
C	6.56164500	-3.74082000	-0.03428500
H	6.11340000	-4.15618400	0.85782600
C	7.85140800	-4.11863900	-0.38555400
H	8.39338200	-4.81807500	0.23945800
C	8.43980200	-3.60237800	-1.53383600
H	9.44603400	-3.89807600	-1.80658200
C	7.73977200	-2.70138600	-2.32806400
H	8.19892000	-2.28233600	-3.21467100
C	6.45424900	-2.30978300	-1.98166800
H	5.93306600	-1.58162700	-2.58980500
C	3.08916600	-2.67345400	-1.83618100
H	3.30397700	-1.91502400	-2.59084600
H	3.30143400	-3.66378800	-2.23649300
H	2.04453400	-2.60467800	-1.53440300
C	3.63760600	-3.49415600	0.92053000
C	3.04935100	-4.72317700	0.60613200
H	2.86904800	-4.99883300	-0.42458800
C	2.68847600	-5.61009600	1.61335200
H	2.23160100	-6.55755700	1.35475800
C	2.91474900	-5.28357200	2.94580600
H	2.63339100	-5.97578700	3.73011000
C	3.50077900	-4.06468500	3.26745200
H	3.68005300	-3.80203300	4.30280400
C	3.85983800	-3.17303000	2.26331900
H	4.31212400	-2.22895200	2.53692800
Re	4.18748500	1.24349400	-0.94622000
Cl	4.29489400	0.23355200	-3.18540000
Cl	6.56474600	0.75040200	-0.59648300
Cl	5.05656000	3.32277700	-2.00190300
P	4.41824600	2.56540000	1.14474500
C	5.98650300	3.50864600	1.29133400
H	5.98719400	4.25017400	0.49493900
H	6.03880200	3.99491900	2.26585500
H	6.83281700	2.84467100	1.13027300
C	4.36811400	1.54312800	2.67680900
C	5.55085900	1.12182800	3.29138800

H	6.50921800	1.43029700	2.89662700
C	5.51397400	0.29527800	4.41071300
H	6.44213900	-0.01366200	4.87680900
C	4.29616900	-0.12315600	4.93344800
H	4.26787500	-0.75166000	5.81589500
C	3.11204900	0.27597500	4.32004200
H	2.15670800	-0.04297900	4.72005600
C	3.14865000	1.09395100	3.19761100
H	2.21818800	1.39608900	2.73396900
C	3.17702200	3.90412200	1.45420600
C	2.79212800	4.27909600	2.74555700
H	3.16420600	3.73834000	3.60553000
C	1.93161400	5.35262300	2.94518500
H	1.64381500	5.62759600	3.95321200
C	1.45316500	6.07589400	1.85884800
H	0.78979300	6.91861900	2.01616500
C	1.84460200	5.72156900	0.57288700
H	1.49468800	6.29184300	-0.27983800
C	2.69853000	4.64302800	0.36780400
H	3.01832100	4.38985300	-0.63436100



5

[Re] = ReCl₃(PMePh₂)

E = -3724.209509 A.U.

Re	1.01766900	-0.86244800	-1.15484000
Cl	2.93845000	-1.78587100	-2.44318300
Cl	0.73122500	0.52318200	-3.18571900
Cl	-0.34270500	-2.65324500	-2.09088400
P	2.61853300	0.96281600	-0.56517700
P	-2.43816700	-0.02625900	-1.25721100
O	1.81448500	-2.21320400	0.12155800
C	-0.76164500	0.25340900	-0.58003800
H	-0.63110000	1.33446600	-0.60896700
C	-0.07138800	-0.51375900	0.40443300
C	-0.16874800	-0.92126700	1.75955100
C	0.64406800	-2.00457300	2.18148800
C	1.58969800	-2.58466300	1.30215400
H	2.21427700	-3.40192900	1.66871200
C	0.53415300	-2.53606100	3.49678800

H	1.16400700	-3.37572200	3.76841700
C	-0.33976100	-2.01028900	4.39165500
H	-0.42549700	-2.42407800	5.38978100
C	-1.14331200	-0.88345500	4.04700600
C	-2.00891800	-0.30441900	4.99889100
H	-2.06865500	-0.75316800	5.98419600
C	-2.75209000	0.81144300	4.69817800
H	-3.40760000	1.24865200	5.44185300
C	-2.64406400	1.39221800	3.42476100
H	-3.20917700	2.28561900	3.18741400
C	-1.81654900	0.84069500	2.47251000
H	-1.73138600	1.31848300	1.50957500
C	-1.05446400	-0.31772700	2.73807300
C	3.75066600	1.45833400	-1.92219000
H	4.36896600	0.59390400	-2.15392900
H	4.37117800	2.29518000	-1.60010500
H	3.17628600	1.70637900	-2.81191700
C	1.81247700	2.53489200	-0.05184900
C	1.73551100	3.62231800	-0.92619700
H	2.18960300	3.56695200	-1.90569600
C	1.06821300	4.78555100	-0.55549300
H	1.02313900	5.61846800	-1.24730700
C	0.46635100	4.88099900	0.69273300
H	-0.04881700	5.78921900	0.98242500
C	0.52721000	3.80152800	1.56824900
H	0.05745500	3.86092800	2.54275900
C	1.18831200	2.63765600	1.19675200
H	1.22301600	1.80668800	1.88988000
C	3.83068100	0.58248600	0.77710200
C	4.21154100	1.51165300	1.74870100
H	3.75152000	2.49001600	1.78044400
C	5.19232400	1.19491700	2.68272600
H	5.47425600	1.92658400	3.43095900
C	5.81298100	-0.04762400	2.65160800
H	6.57925300	-0.29195400	3.37806400
C	5.45074400	-0.97236100	1.67827200
H	5.93786400	-1.93958500	1.63781000
C	4.46515000	-0.66476900	0.74803600
H	4.19521100	-1.38801300	-0.01148100
C	-2.51070100	-0.22316200	-3.06342000
H	-3.55840200	-0.18529100	-3.36428700
H	-2.06234800	-1.18018900	-3.31969700
H	-1.93926800	0.56394900	-3.54845700
C	-3.32350600	1.54696600	-0.94481000

C	-2.97514600	2.66338200	-1.71413200
H	-2.21949700	2.58417900	-2.48602300
C	-3.58573200	3.89025100	-1.48868400
H	-3.30679000	4.74503000	-2.09255000
C	-4.55009500	4.01889500	-0.49532000
H	-5.03049500	4.97493500	-0.32488400
C	-4.89396300	2.91749600	0.27942600
H	-5.64243900	3.01093500	1.05721900
C	-4.28152600	1.68828000	0.06152300
H	-4.55358900	0.84244900	0.67791300
C	-3.45475300	-1.37015000	-0.56908300
C	-4.82201800	-1.39116700	-0.87487800
H	-5.26620400	-0.59825400	-1.46388200
C	-5.62582700	-2.42761400	-0.42276900
H	-6.68109000	-2.43394600	-0.66725800
C	-5.07472800	-3.45509600	0.33637200
H	-5.70212500	-4.26547200	0.68796700
C	-3.71813900	-3.44581400	0.63143800
H	-3.27901900	-4.25165500	1.20617500
C	-2.90637300	-2.41269900	0.17713200
H	-1.84737000	-2.44222000	0.37743700

References

- [1] W. A. Skupiński, J. C. Huffman, J. W. Bruno, K. G. Caulton, *J. Am. Chem. Soc.* **1984**, *106*, 8128-8136.
- [2] F. P. Jørgensen, J. F. Petersen, C. L. Andersen, A. B. Skov, M. Jevric, O. Hammerich, M. B. Nielsen, *Eur. J. Org. Chem.* **2017**, *2017*, 1253–1261.
- [3] C. R. Parker, E. Leary, R. Frisenda, Z. Wei, K. S. Jennum, E. Glibstrup, P. B. Abrahamsen, M. Santella, M. A. Christensen, E. A. D. Pia, T. Li, M. T. Gonzalez, X. Jiang, T. J. Morsing, G. Rubio-Bollinger, B. W. Laursen, K. Nørgaard, H. van der Zant, N. Agrait, M. B. Nielsen, *J. Am. Chem. Soc.* **2014**, *136*, 16497–16507.
- [4] T. Cadart, D. Nečas, R. P. Kaiser, L. Favereau, I. Císařová, R. Gyepes, J. Hodačová, K. Kalíková, L. Bednářová, J. Crassous, M. Kotorá, *Chem. Eur. J.* **2021**, *27*, 11279–11284.
- [5] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.
- [6] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652; b) B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* **1989**, *157*, 200-206; c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B.* **1988**, *37*, 785-789.
- [7] a) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305; b) F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057-1065.
- [8] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299-310.
- [9] a) P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. v. E. Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317-6318; b) Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Chem. Rev.* **2005**, *105*, 3842-3888; c) H. Fallah-Bagher-Shaidaei, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Org. Lett.* **2006**, *8*, 863-866.
- [10] a) R. Herges, D. Geuenich, *J. Phys. Chem. A* **2001**, *105*, 3214-3220; b) D. Geuenich, K. Hess, F. Kçhler, R. Herges, *Chem. Rev.* **2005**, *105*, 3758-3772.
- [11] a) T. Lu, F. Chen, *Acta Chim. Sinica* **2011**, *69*, 2393-2406; b) T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580-592.
- [12] W. Humphrey, A. Dalke, K. Schulten, *J. Mol. Graphics* **1996**, *14*, 33-38.
- [13] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122.
- [14] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. J. Puschmann, *Appl. Cryst.* **2009**, *42*, 339-341.