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One-pot Syntheses of Rhena-2-benzopyrylium Complexes with a Fused Metallacyclopropene Unit

Xiao Bao, ‡[a] Yang Li, ‡[b] Wei Bai,* [a] Yan Zhou,[c] Yilun Wang,[b] Yue Sun [a] and Jingyang Jiang [a]

[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 Petroleum and Chemical Engineering, Dalian University of Technology, Panjin, Liaoning 124221, P.R. China

[c] School of Chemistry and Chemical Engineering, Guangxi University for Nationalities, 188 Daxue East Road, Nanning, Guangxi 530006, P.R. China

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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. Other reagents were used as purchased. The complex $ReCl_3(PMePh_2)_3$,[1] 1-(2-ethynyl-phenyl)ethanone,[2] 2-ethynylbenzaldehyde,[3] and 2-ethynyl-5-trifluoromethylbenzaldehyde[4] were prepared according to literature methods. Microanalyses were collected on UNICUBE(CHN). ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} spectra were collected on a Bruker Avance II (400 MHz) or a Varian DLG spectrometer (400 MHz). ^{1}H and ^{13}C NMR shifts are relative to TMS, and ^{31}P chemical shifts relative to 85% H_3PO_4.

Synthesis of cyclopropametalla-2-benzopyrylium complex 2

A mixture of 1-(2-ethynylphenyl)ethanone (0.039 g, 0.271 mmol) and $ReCl_3(PMePh_2)_3$ (0.200 g, 0.224 mmol) in THF (10 mL) was heated at 60 ^{o}C for 1 h, producing a reddish solid. After cooling down to room temperature, the reddish solid was filtered and washed with THF (5 mL), and ether (5mL×2). Then it was dried under vacuum. Yield: 117 mg, 62.4 %. ^{31}P{^{1}H} NMR (162.0 MHz, methanol-d$_4$): δ = 36.3 (d, *J* = 3.2 Hz, CH(*P*MePh$_2$)), -9.1 (d, *J* = 3.2 Hz, Re*P*MePh$_2$). ^{1}H NMR (400.1MHz, methanol-d$_4$): δ = 8.14 (d, *J* = 8.0 Hz, 1H, Ph), 8.03 (t, *J* = 8.0 Hz, 1H, Ph), 7.79-7.74 (m, 3H, Ph), 7.67-7.64 (m, 2H, Ph), 7.56-7.32 (m, 10H, Ph), 7.19-7.10 (m, 5H, Ph), 6.64 (t, *J* = 8.0 Hz, 2H, Ph), 6.37 (d, ^2J(PH) = 12.0 Hz, 1H, C*H*(PMePh$_2$)), 4.63 (s, 3H, C(O)*Me*), 2.38 (d, ^2J(PH) = 12.0 Hz, 3H, P*Me*Ph$_2$), 1.89 (d, ^2J(PH) = 12.0 Hz, 3H, P*Me*Ph$_2$). ^{13}C{^{1}H} NMR (100.6 MHz, methanol-d$_4$): δ = 247.6 (dd, ^2J (PC) = 9.1 Hz, ^2J (PC) = 5.0 Hz, Re=*C*), 204.6 (s, *C*(O)Me), 139.2-122.5 (multiple ^{13}C signals of Ph), 24.1 (s, C(O)*Me*), 12.8 (d, ^1J(PC) = 56.3 Hz, *C*H(PMePh$_2$)), 12.6 (d, ^1J(PC) = 28.2 Hz, P*Me*Ph$_2$), 10.1 (d, ^1J(PC) = 44.3 Hz, P*Me*Ph$_2$). $C_{36}H_{34}Cl_3OP_2Re{\cdot}H_2O$: C, 50.56; H, 4.24. Found: C, 50.44; H, 4.24.

Synthesis of cyclopropametalla-2-benzopyrylium complex 3

A mixture of 2-ethynylbenzaldehyde (0.035 g, 0.269 mmol) and $ReCl_3(PMePh_2)_3$ (0.200 g, 0.224 mmol) in THF (10 mL) was heated at 60 ^{o}C for 1 h, producing a reddish solid. After cooling down to room temperature, the reddish solid was filtered and washed with THF (5 mL), and ether (5mL×2). Then it was dried under vacuum. Yield: 0.151 g, 81.9 %. ^{31}P{^{1}H} NMR (162.0 MHz, methanol-d$_4$): δ = 35.4 (d, *J* = 4.4 Hz, CH(*P*MePh$_2$)), -12.1 (br d, *J* = 3.2 Hz, Re*P*MePh$_2$). ^{1}H NMR (400.1MHz, methanol-d$_4$): δ = 9.43 (s, 1H, C(O)*H*), 8.01 (t, *J* = 6.0 Hz, 1H, Ph), 7.95 (d, *J* = 8.0 Hz, 1H, Ph), 7.78-7.75 (m, 3H, Ph), 7.69-7.65 (m, 2H, Ph), 7.53-7.51 (m, 2H, Ph), 7.44-7.32 (m, 8H, Ph), 7.18-7.12 (m, 5H, Ph), 6.69-6.66 (m, 2H, Ph), 6.60 (d, ^2J(PH) = 12.0 Hz, 1H, C*H*(PMePh$_2$)), 2.37 (d, ^2J(PH) = 11.6 Hz, 3H, P*Me*Ph$_2$), 1.78 (d, ^2J(PH) = 8.0 Hz, 3H, P*Me*Ph$_2$). ^{13}C{^{1}H} NMR (100.6 MHz, methanol-d$_4$): δ = 248.4 (dd, ^2J (PC) = 9.1 Hz, ^2J (PC) = 7.0 Hz, Re=C), 195.8 (s, *C*(O)H), 140.0-121.5 (multiple ^{13}C signals of Ph), 14.8 (d, ^1J (PC) = 55.3 Hz, *C*H(PMePh$_2$)), 12.0 (d, ^1J(PC) = 29.2 Hz, P*Me*Ph$_2$), 10.1 (d, ^1J(PC) = 43.3 Hz, P*Me*Ph$_2$). Anal. Calcd. For $C_{35}H_{32}Cl_3OP_2Re{\cdot}C_4H_8O$: C, 52.32; H, 4.50. Found: C, 52.78; H, 4.58.

Synthesis of cyclopropametalla-2-benzopyrylium complex 4

A mixture of 2-ethynyl-5-trifluoromethylbenzaldehyde (0.053 g, 0.267 mmol) and $ReCl_3(PMePh_2)_3$ (0.200 g, 0.224 mmol) in THF (10 mL) was heated at 60 °C for 2 h, producing a reddish solution. After cooling down to room temperature, the volume was reduced to ca. 2 mL and 10 mL of hexanes was added to precipitate a reddish solid. The solid was filtered and washed with ether (5mL×2). Then it was dried under vacuum. Yield: 0.135 g, 67.6 %. $^{31}P\{^1H\}$ NMR (162.0 MHz, methanol-d_4): δ = 38.2 (d, *J* = 3.2 Hz, CH(*P*MePh$_2$)), -12.0 (br s, Re*P*MePh$_2$). ^1H NMR (400.1MHz, methanol-d_4): δ = 9.30 (s, 1H, C(O)*H*), 8.25 (s, 1H, Ph), 7.86-7.80 (m, 3H, Ph), 7.72-7.68 (m, 2H, Ph), 7.53-7.48 (m, 3H, Ph), 7.44-7.37 (m, 5H, Ph), 7.34-7.31 (m, 3H, Ph), 7.22-7.18 (m, 2H, Ph), 7.13-7.10 (m, 2H, Ph), 6.99 (d, *J* = 12.0 Hz, 1H, C*H*(PMePh$_2$)), 6.76 (t, *J* = 6.0 Hz, 2H, Ph), 2.45 (d, ^2J(PH) = 12.0 Hz, 3H, P*Me*Ph$_2$), 1.76 (d, ^2J(PH) = 8.0 Hz, 3H, P*Me*Ph$_2$). $^{13}C\{^1H\}$ NMR (100.6 MHz, methanol-d_4): δ = 246.0 (dd, ^2J (PC) = 9.1 Hz, ^2J (PC) = 5.0 Hz, Re=C), 195.8 (s, *C*(O)H), 140.0-121.5 (multiple ^{13}C signals of Ph and CF_3), 15.8 (d, ^1J(PC) = 55.3 Hz, *C*H(PMePh$_2$)), 11.8 (d, ^1J(PC) = 29.2 Hz, P*Me*Ph$_2$), 10.2 (d, ^1J(PC) = 43.3 Hz, P*Me*Ph$_2$). Anal. Calcd. For $C_{36}H_{31}Cl_3F_3OP_2Re$: C, 48.52; H, 3.51. Found: C, 49.03; H, 4.02.

2.Computational details

All the optimizations were performed with the Gaussian 09 software package.[5] All of 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) values were calculated at the B3LYP-GIAO//6-311G(2d,p)/def2-TZVP level. The CMO-NICS calculations in simplified models were calculated with the NBO 7.0 program.[9] 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 **M1** and **M-H**.[10]

The molecular orbital composition and MO pictures 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/).

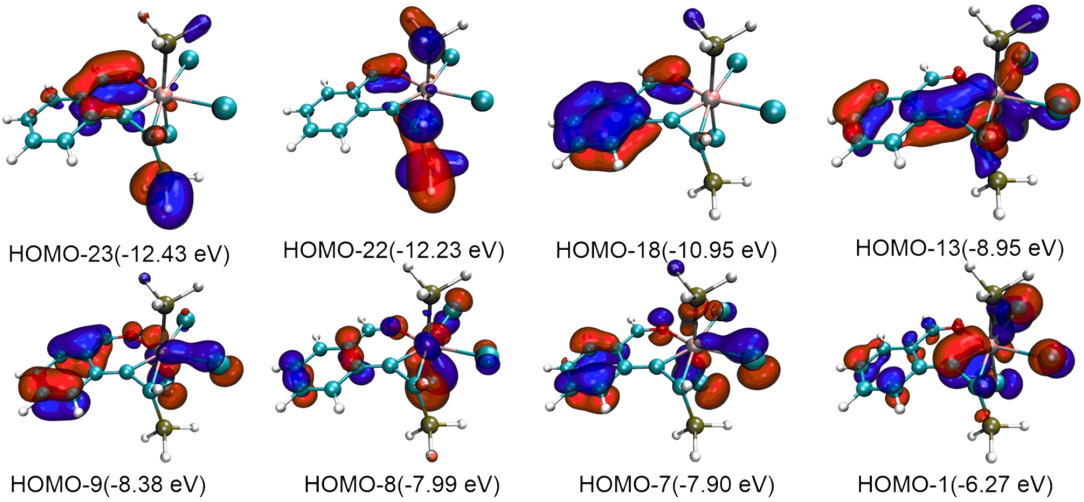


Figure S1. Key occupied π-MOs of **M1**. The isosurface of MOs is 0.04.

Table S1. Full Cartesian NMR shielding tensor (ppm) for NICS values of π-Canonical MO contributions in **M1** ($NICS(1)_{ZZ}$ and $NICS(-1)_{ZZ}$ are the $NICS(1)_{ZZ}$ values of the upper and lower directions of the rings, respectively. Orbital 85 is HOMO).

MO	NICS (0) for ring a	NICS (0) for ring b	NICS(1)zz for ring a	NICS(-1)zz for ring a	NICS(1)zz for ring b	NICS(-1)zz for ring b
62	1.64	6.90	2.79	3.22	7.68	8.35
63	1.28	1.42	1.55	1.51	2.47	2.47
67	1.07	3.36	2.83	3.18	6.42	6.28
72	2.48	1.98	-1.70	-1.34	0.21	-0.01
76	-0.77	0.39	0.15	-0.63	-0.30	-0.39
77	-0.76	-1.31	-2.10	-2.97	-1.14	-1.31
78	-2.36	-3.11	-1.27	-1.27	-5.96	-4.94
84	3.57	1.57	-3.18	-1.52	1.39	1.44
sum	6.15	11.20	-0.93	0.18	10.77	11.89

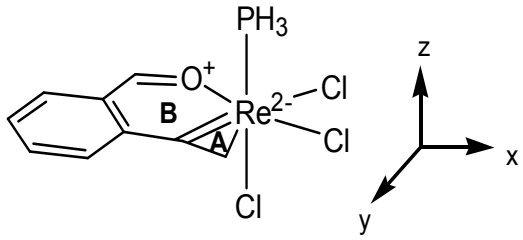
The signs of the NICS values are reversed from those of the shielding data in the output. Thus, the NICS value is the negative of the sum of the shielding contributions. Thus, NICS(0)-π value of ring A is -6.15 ppm; NICS(0)-π value of ring B is -11.2 ppm; $NICS(1)_{ZZ}$-π value of ring A is the mean value of $NICS(1)_{ZZ}$-π and $NICS(-1)_{ZZ}$-π: -(-0.93 + 0.18) / 2 = 0.375 ppm; $NICS(1)_{ZZ}$-π value of ring B is -11.33 ppm.

Table S2. Full Cartesian NMR shielding tensor (ppm) for NICS values of σ-Canonical MO contributions in **M1** ($NICS(1)_{ZZ}$ and $NICS(-1)_{ZZ}$ are the $NICS(1)_{ZZ}$ values of the upper and lower directions of the rings, respectively）.

MO	NICS (0) for ring a	NICS (0) for ring b	NICS(1)zz for ring a	NICS(-1)zz for ring a	NICS(1)zz for ring b	NICS(-1)zz for ring b
40	1.15	6.01	2.35	2.61	7.47	7.89

41	1.77	4.26	3.87	4.25	7.81	7.82
42	7.72	2.09	5.35	6.71	2.97	3.06
43	1.59	4.35	3.09	3.29	7.20	7.45
44	3.20	1.78	2.84	3.81	2.71	2.73
45	1.03	0.21	0.69	1.07	0.38	0.34
47	1.77	0.42	0.82	0.87	0.40	0.41
48	2.78	1.00	2.07	2.15	1.46	1.42
49	3.14	1.91	2.65	2.45	3.34	3.40
51	2.15	3.68	2.69	2.69	4.20	4.40
52	1.14	1.25	1.52	1.89	2.64	2.54
53	2.12	0.09	2.30	2.84	1.70	1.70
54	3.63	1.26	1.26	1.96	2.81	2.93
55	0.68	2.65	1.61	1.77	4.42	4.52
56	1.33	-2.68	-2.22	-2.01	-1.71	-1.62
57	1.54	-1.08	0.59	0.79	0.37	0.34
58	1.63	-1.46	1.16	1.09	-1.91	-2.05
59	4.30	0.46	2.49	0.64	1.26	0.89
60	-1.00	-4.37	-1.95	-3.42	-5.98	-6.00
61	-1.38	-3.96	-4.04	-4.90	-7.16	-7.51
66	-1.67	-3.83	-4.45	-4.65	-7.00	-7.01
68	0.39	-1.54	-0.73	-1.45	-3.32	-3.69
69	0.50	-3.95	-3.99	-4.28	-7.52	-7.62
70	-3.95	-6.02	3.54	1.30	-4.78	-5.01
71	-10.04	-6.00	-3.77	-4.58	-6.96	-7.53
73	-1.34	-0.44	-2.80	-0.23	-0.17	-0.49
74	-0.22	-0.42	-1.02	-1.06	-0.60	-0.38
75	0.40	-1.01	2.75	1.71	-0.68	-0.96
79	2.02	-6.10	0.66	-0.35	-6.45	-6.76
81	-0.93	-1.36	-0.51	0.18	-0.28	-0.52
82	-2.32	-0.98	0.46	1.37	-0.05	0.29
sum	23.13	-13.78	19.28	18.51	-3.43	-5.02

The signs of the NICS values are reversed from those of the shielding data in the output. Thus, the NICS value is the negative of the sum of the shielding contributions. Thus, NICS(0)-σ value of ring A is -23.13 ppm; NICS(0)-σ value of ring B is 13.78 ppm; $NICS(1)_{ZZ}$-σ value of ring A is the mean value of $NICS(1)_{ZZ}$-σ and $NICS(-1)_{ZZ}$-σ: -(19.28 + 18.51) / 2 = -18.895 ppm; $NICS(1)_{ZZ}$-σ value of ring B is 4.225 ppm.



M-H

M-H	ring A	ring B
NICS(0)	-36.7	-3.1
NICS(0)-π	-8.8	-13.3
NICS(0)-σ	-20.3	+17.1
$NICS(1)_{ZZ}$	-24.0	-20.5
$NICS(1)_{ZZ}$-π	-2.2	-16.4
$NICS(1)_{ZZ}$-σ	-15.9	+8.3

Figure S2. Computed NICS values for the model complex **M-H**.

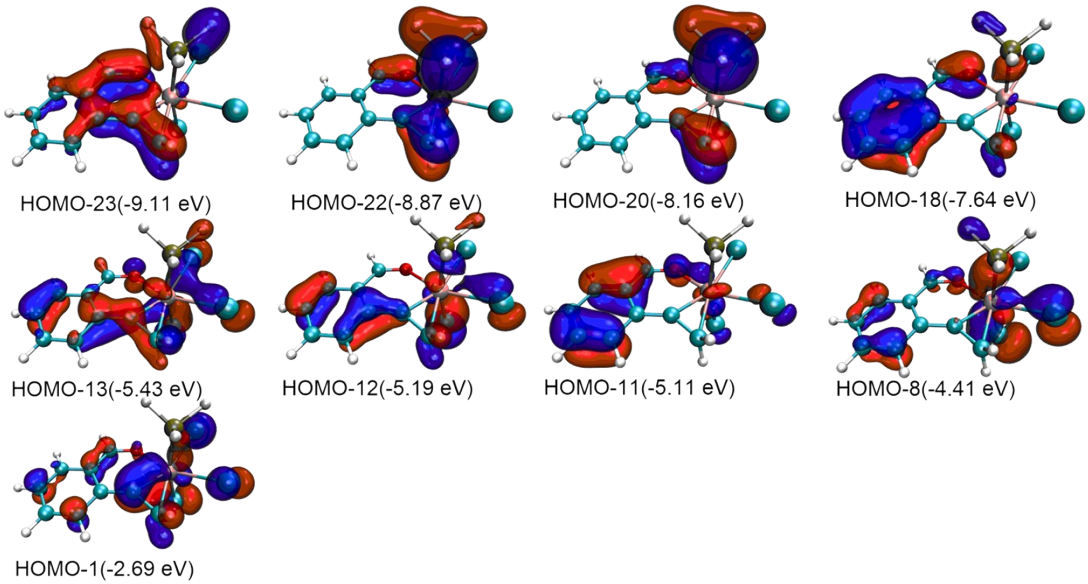


Figure S3. Key occupied π-MOs of **M-H**. The isosurface of MOs is 0.04.

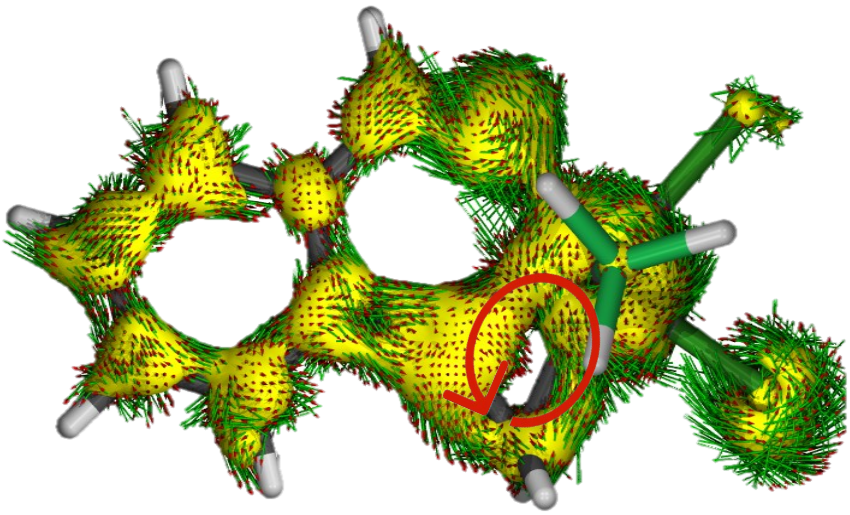


Figure S4. ACID isosurfaces of **M-H** separated into the σ-contribution (current density vectors are plotted onto the ACID isosurface of 0.050 and the magnetic field vector is orthogonal with respect to the ring plane and points downward (anti-clockwise currents are diatropic).

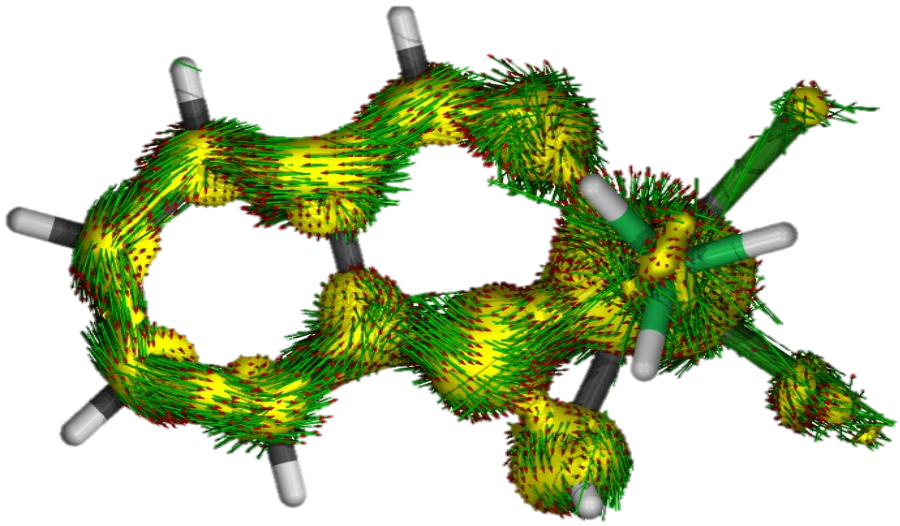
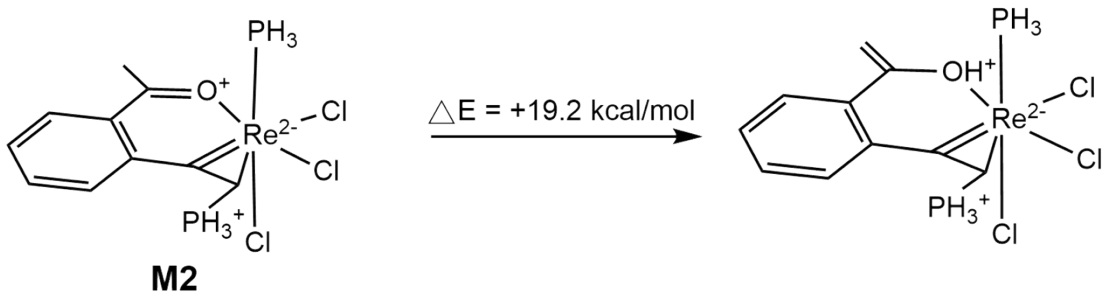


Figure S5. ACID isosurfaces of **M-H** separated into the π-contribution (current density vectors are plotted onto the ACID isosurface of 0.050 and the magnetic field vector is orthogonal with respect to the ring plane and points downward (anti-clockwise currents are diatropic).



Scheme S1. The isodesmic reaction and the calculated aromatic stabilization energy (ASE).

3. X-ray crystallographic study of complex 2 and 4.

Single crystals of **2** (CCDC No.2039487) and **4** (CCDC No.2039486) suitable for X-ray diffraction were grown from CH_2Cl_2 solutions layered with ether (for **2**), hexanes (for **4**). Intensity data were collected on a Bruker Smart APEXII diffractometer at 173 K. Diffraction data were processed using the CrysAlisPro software (version 1.171.35.19). Empirical absorption corrections were performed using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm in the CrysAlisPro software suite. Structure solution and refinement for all compounds were performed using the Olex2 software package (which embedded SHELXL).[24,25] All the structures were solved by direct methods, expanded by difference Fourier syntheses and refined by full matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically with a riding model for the hydrogen atoms except noted separately. Further crystallographic details are summarized in Table S5.

Table S3. Crystallographic data and refinement details for **2** and **4**

	2	**4**
CCDC Number	2039487	2039486
Empirical formula	C36H34Cl3OP2Re	C36.5H32Cl4F3O1.25P2Re
Color & habit	red, block	red, block
Crystal size (mm^3)	0.18 x 0.15 x 0.12	0.15 x 0.12 x 0.10
Temperature (K)	173K	173K
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
a(Å)	17.1481(6)	19.8031(11)
b(Å)	11.9633(7)	22.2110(12)
c(Å)	17.0822(6)	17.0555(9)
α(°)	90	90
β(°)	108.290(4)	96.387(2)
γ(°)	90	90
V(Å^3), Z	3327.3(3), 4	7455.2(7), 8
D_{cal} (Mg/m^3)	1.671	1.663
Abs. coeff.(mm^{-1})	4.018	3.676
2 θ range for data collection (°)	5.02 to 54	4.806 to 53.998
Reflections collected	22199	35394

Indep. Reflection, R(int)	3673, 0.0422	7929, 0.0891
Completeness of data	96.5 %	97.6 %
Data/ restraints / parameters	3673/0/391	7929/2/463
Goodness-of-fit on F^2	1.023	1.010
R1 [I>2sigma(I)], wR2	0.0303, 0.0664	0.0556, 0.1157
R1 (all data), wR2	0.0387, 0.0693	0.1042, 0.1278
Largest diff. peak and hole (e • $Å^{-3}$)	0.42, -0.51	2.48, -1.59

4. NMR spectra

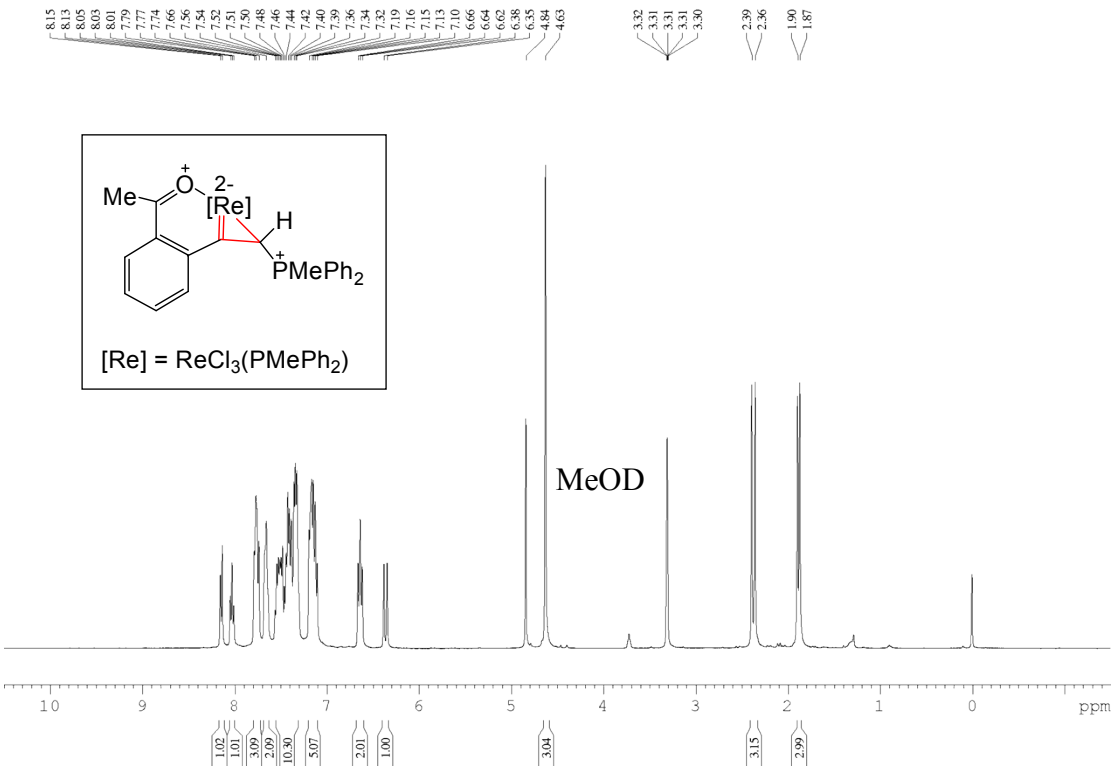


Figure S5. The ^{1}H NMR spectrum of complex **2** in methanol-d_4 at 400.1 MHz.

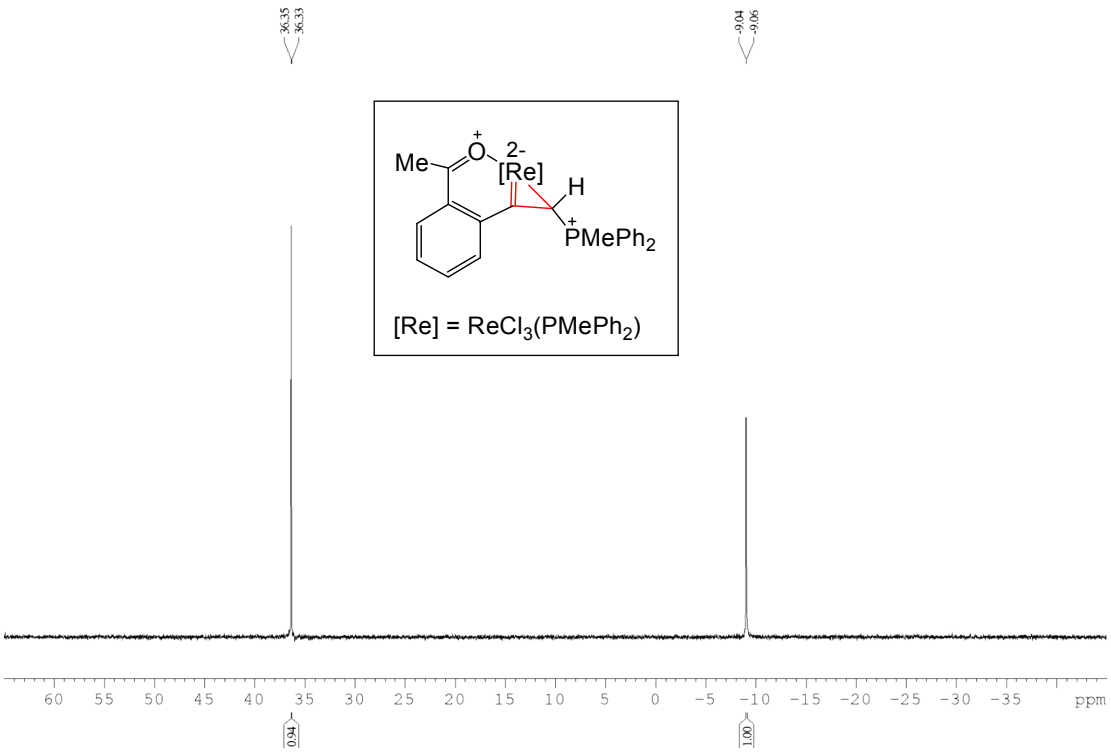


Figure S6. The $^{31}P\{^{1}H\}$ NMR spectrum of complex **2** in methanol-d_4 at 162.0 MHz.

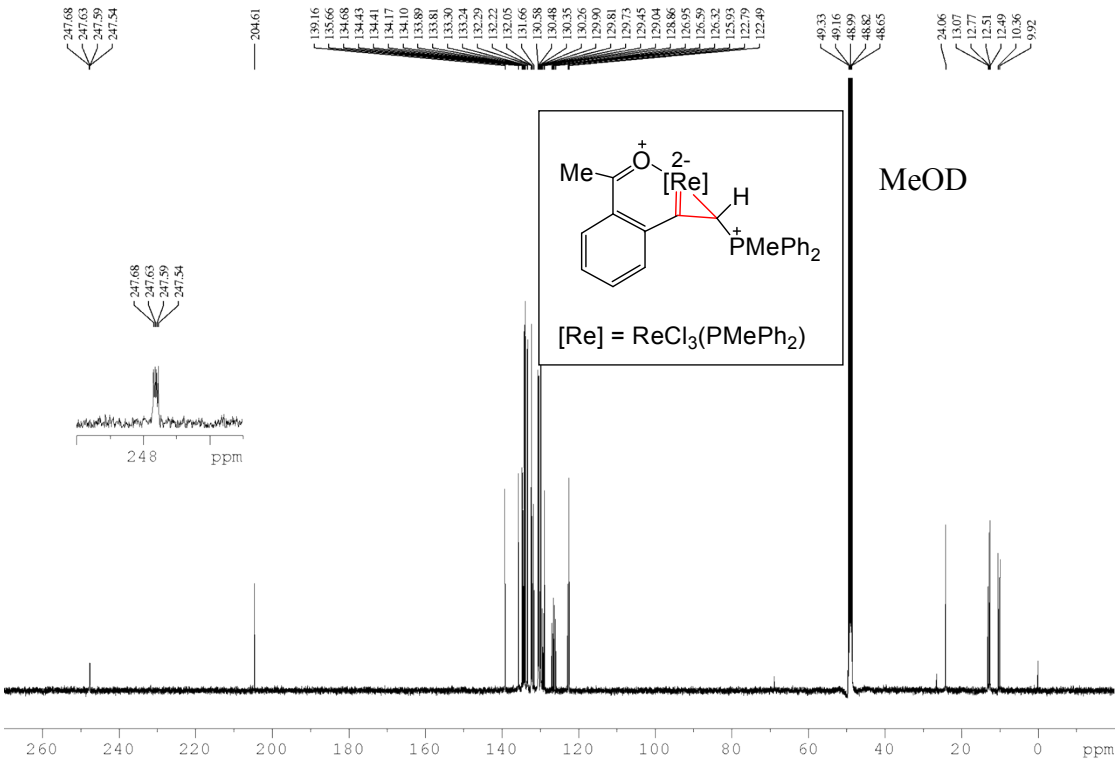


Figure S7. The $^{13}C\{^{1}H\}$ NMR spectrum of complex **2** in methanol-d_4 at 100.6 MHz.

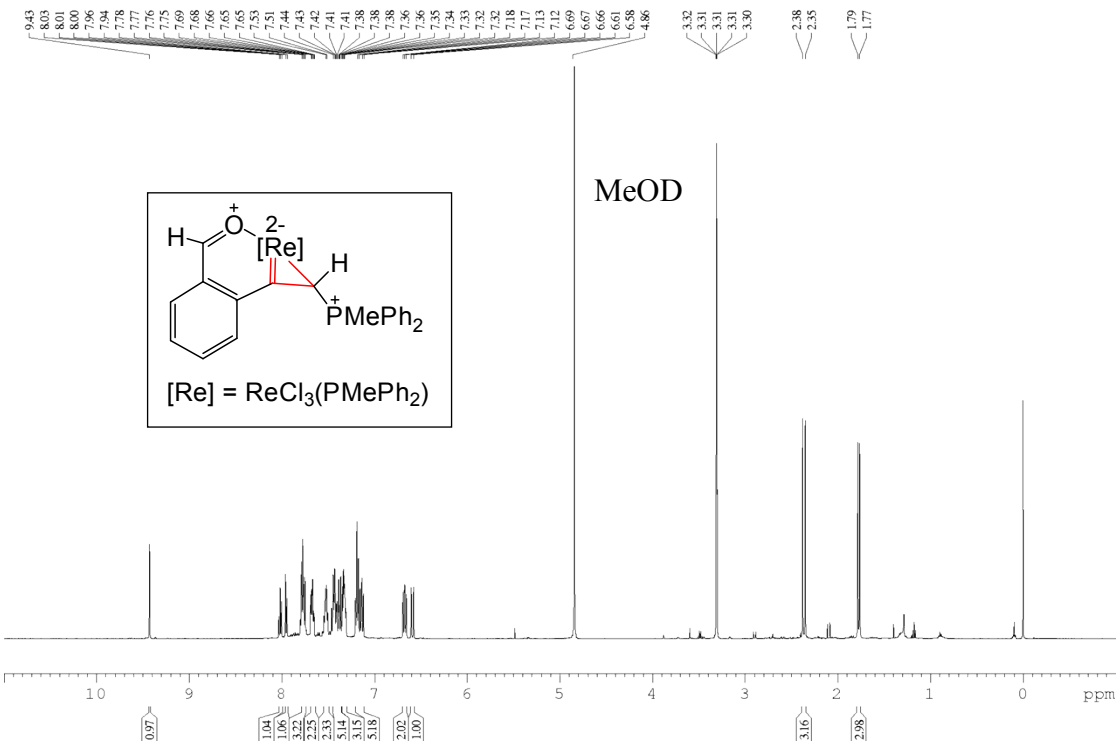


Figure S8. The ^{1}H NMR spectrum of complex **3** in methanol-d$_4$ at 400.1 MHz.

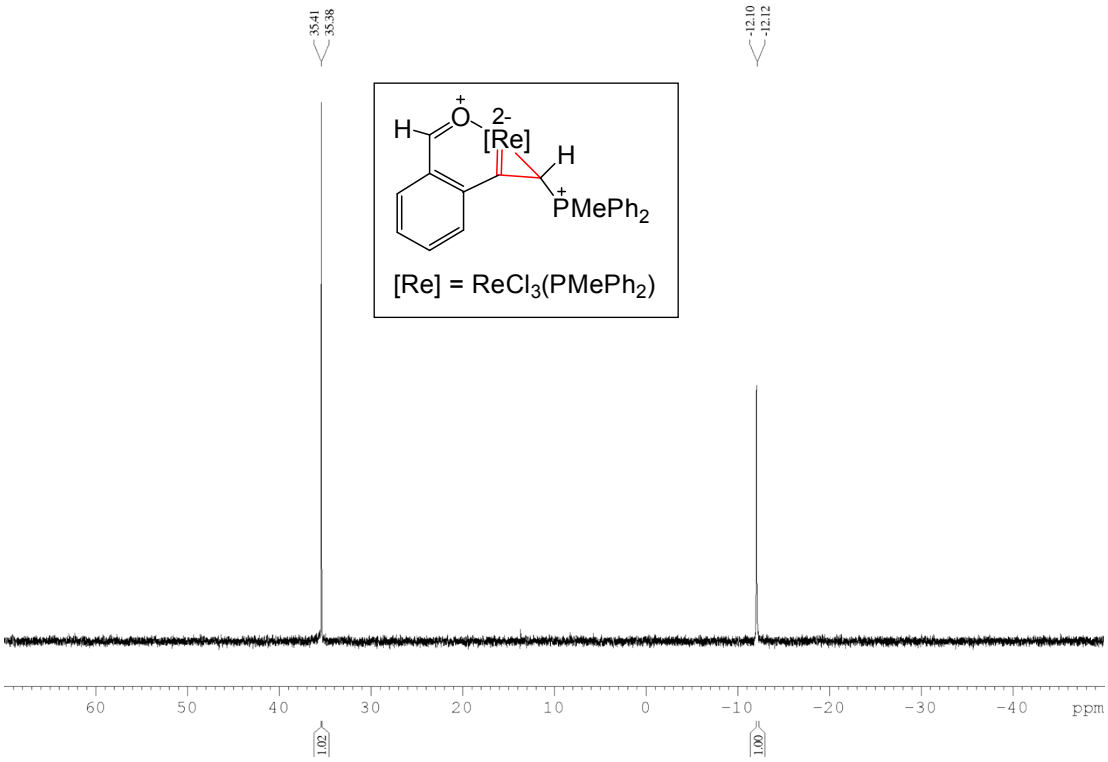


Figure S9. The ^{31}P{^{1}H} NMR spectrum of complex **3** in methanol-d$_4$ at 162.0 MHz.

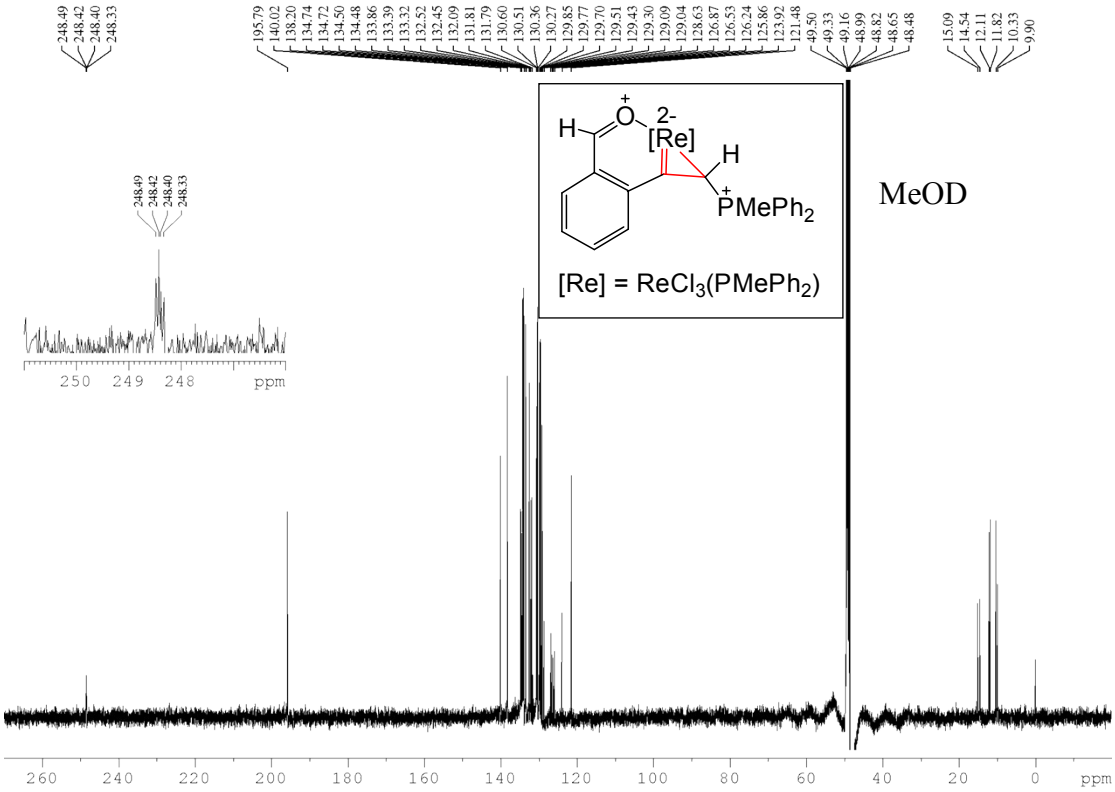


Figure S10. The $^{13}C\{^{1}H\}$ NMR spectrum of complex **3** in methanol-d_4 at 100.6 MHz.

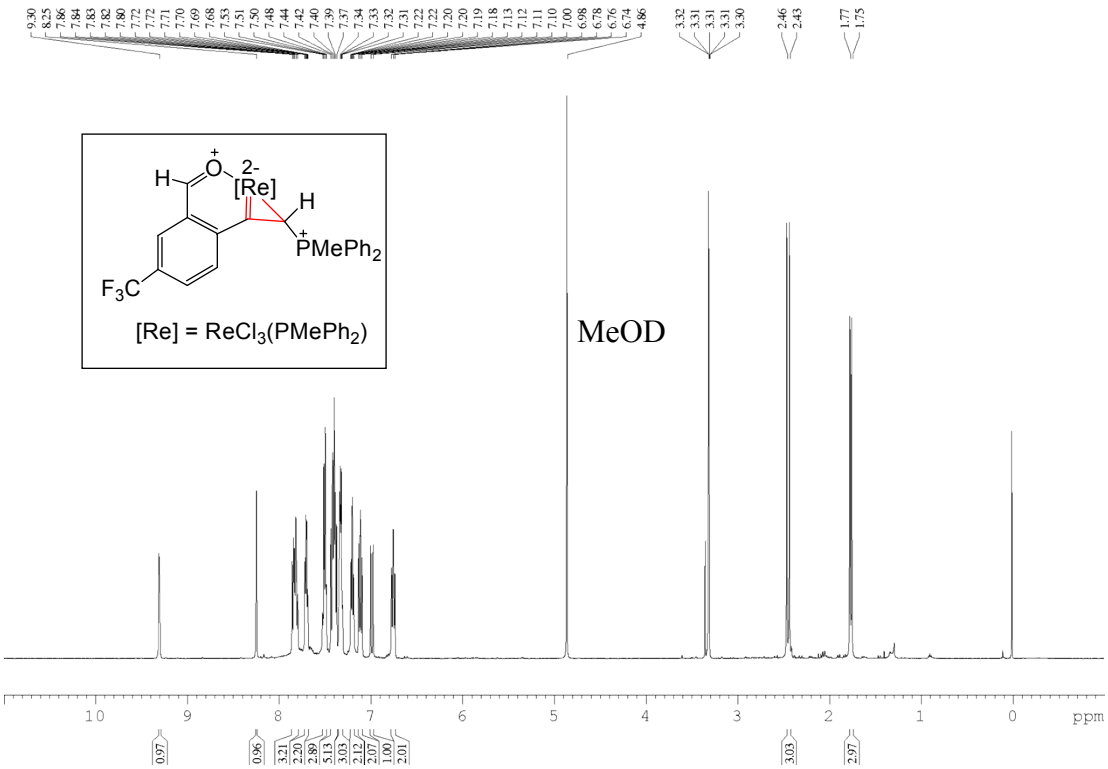


Figure S11. The ^{1}H NMR spectrum of complex **4** in methanol-d_4 at 400.1 MHz.

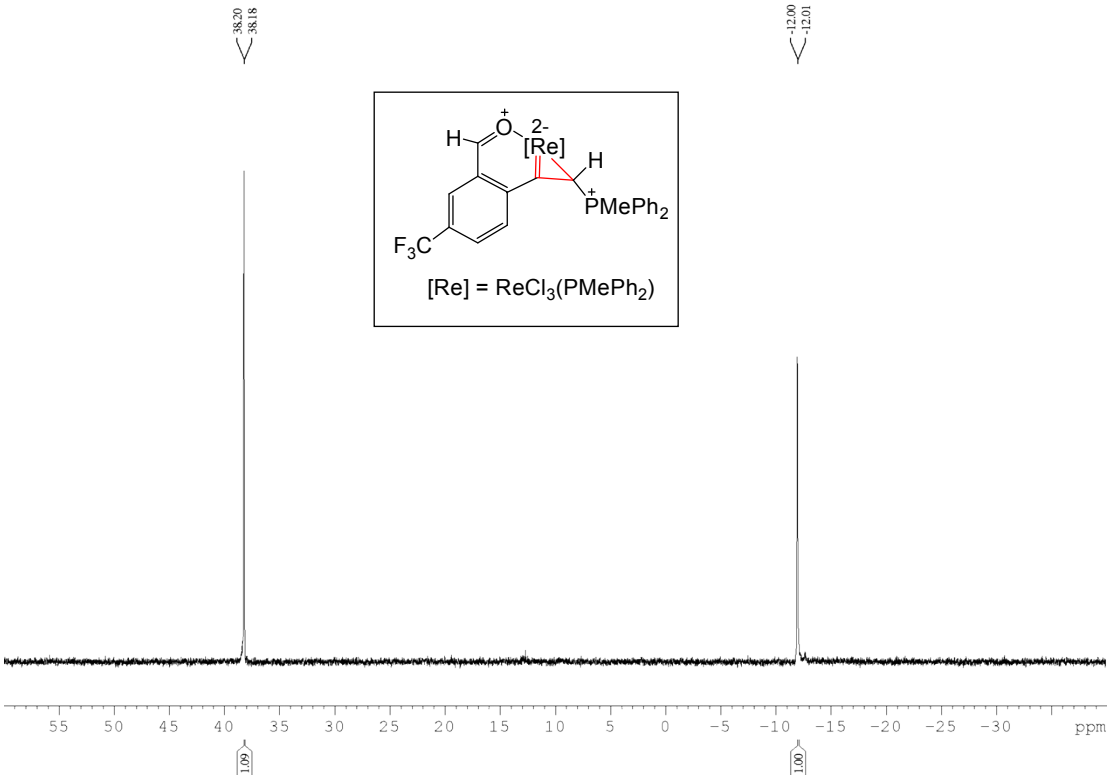


Figure S12. The $^{31}P\{^{1}H\}$ NMR spectrum of complex **4** in methanol-d_4 at 162.0 MHz.

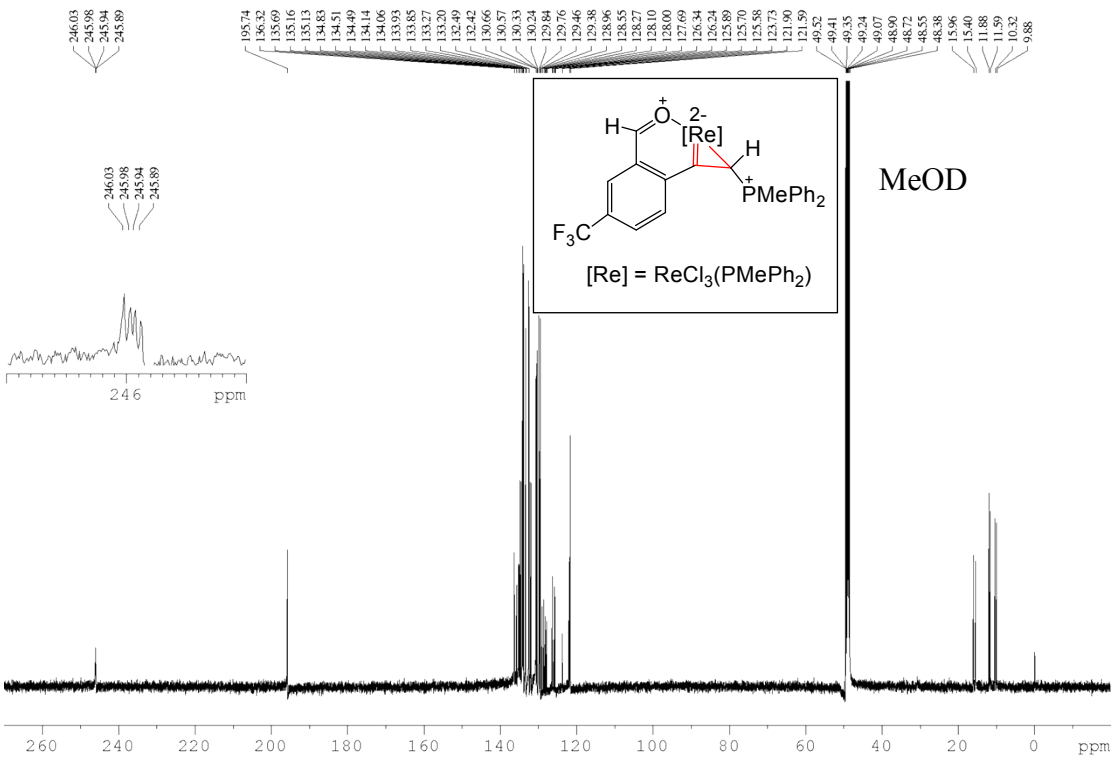
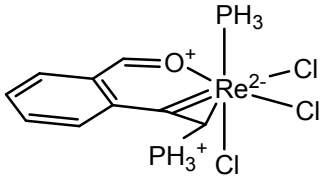


Figure S13. The $^{13}C\{^{1}H\}$ NMR spectrum of complex **4** in methanol-d_4 at 100.6 MHz.

5. The Calculated Cartesian Coordinates with Electronic Energies



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Cl	-0.67130555	-0.37078855	-2.77208357
Cl	-2.86252131	0.88982472	-0.39776248
P	-1.10998994	-0.34743001	2.06873379
P	-0.25467518	2.48937659	-2.01321053
O	0.63884152	-1.88555376	-0.22705524
C	0.00997592	1.72131801	-0.42222059
H	-0.28718295	2.40824793	0.36737790
C	0.91684561	0.64381920	-0.20918051
C	2.31821882	0.43125070	-0.16634643
C	2.80687801	-0.90412377	-0.15692866
C	1.88248299	-1.99522054	-0.18880553
C	3.25207130	1.48537497	-0.14925859
H	2.88911212	2.50627160	-0.14892237
C	4.60831453	1.22594713	-0.12079217
H	5.31335038	2.04850430	-0.10681400
C	5.08259328	-0.09412876	-0.10740641
H	6.14819823	-0.28493759	-0.08465151
C	4.18981571	-1.14581228	-0.12491019
H	4.54758568	-2.16934648	-0.11919978
H	-0.77492025	0.79236761	2.83313662
H	-2.44044751	-0.53216053	2.46754706

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H	-0.14559392	3.88334884	-1.84322281
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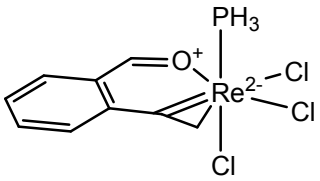
H	2.27626367	-3.01536346	-0.16568944



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P	-0.94625100	0.07161900	-2.30388200
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H	-0.09138100	-2.64593600	-0.78401900
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C	2.70942300	0.87169600	0.01416100
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H	5.51215000	-1.81473700	-0.18948800
C	5.06176500	0.29756700	-0.07880600
H	6.10356300	0.59804700	-0.08762500
C	4.07017500	1.24758400	-0.00347500
H	4.32336600	2.30165000	0.05231900
H	-0.68815800	-1.08226200	-3.08188400

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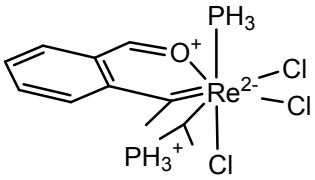

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C	2.44095300	-0.01262900	-0.62476500
C	2.64161500	1.29418500	-0.09230900
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H	0.97125300	0.55826100	2.88321900
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H	-0.96517000	-0.37486500	3.34639400
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H	-2.48207700	3.42814900	-1.44488500
H	-3.88597600	2.02109300	-0.56504000
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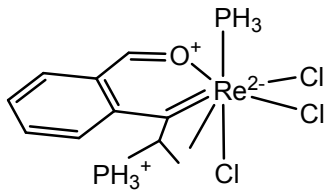

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O	-0.38672700	-2.02536100	0.76937500
P	2.26026300	-0.05850200	-1.87086300
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H	-4.09834100	-2.60735300	0.94264900
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H	3.56034500	0.31967100	-1.52654600
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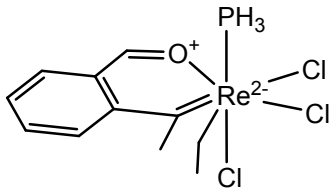

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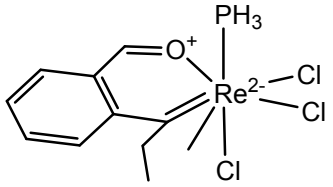

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C	-2.28036300	0.26598300	-0.18469800
C	-2.53653100	-0.93791500	0.55818200
C	-1.52829500	-1.57036600	1.32505800
C	-3.43539100	0.83344500	-0.80098600
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C	-4.68295400	0.25936500	-0.73471300
H	-5.51047100	0.72629500	-1.25888400
C	-4.90334200	-0.91529600	0.00673800
H	-5.89260200	-1.35268800	0.06991700
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H	-3.97406300	-2.37891600	1.25280600
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H	1.32569700	-2.49827500	-2.14374500
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H	0.08145100	-0.46280500	-2.82334700
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H	1.82416000	-0.12477000	-2.61060100
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H	-0.84133600	3.11817200	1.36568800
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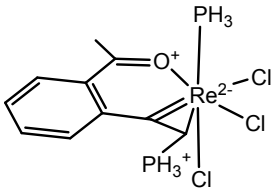

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Cl	-2.98231900	0.90846600	0.43511700
P	-1.11057100	-1.04769100	2.26650000
P	-0.46234600	3.08178900	-0.53000300
O	0.62783100	-1.57905800	-0.48485000
C	-0.12750100	1.80689600	0.67274700
H	-0.42234100	2.15094700	1.66180800
C	0.80840500	0.75171400	0.46484600
C	2.21702000	0.58617000	0.40057100
C	2.76345700	-0.62914800	-0.09930200
C	1.87354300	-1.68689900	-0.53929400
C	2.40238300	-2.98860200	-1.08064700
H	3.03403300	-3.49773800	-0.34798700
H	3.00467400	-2.82086100	-1.97716700
H	1.55888800	-3.62604800	-1.33434900
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H	2.67648500	2.53008000	1.19237700
C	4.46432900	1.44144200	0.73180100
H	5.12533800	2.23826700	1.05114400
C	4.99976000	0.24349500	0.24532400
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C	4.15946300	-0.77362400	-0.16435200
H	4.58640100	-1.69234400	-0.54358000
H	-2.42162300	-1.41486400	2.59947000
H	-1.75263600	3.06479300	-1.06221900
H	-0.38635700	4.32840100	0.12155200
H	0.44220500	3.22798800	-1.58140800
H	-0.41736900	-2.21541300	2.64951400
H	-0.79211000	-0.23413000	3.37706200

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