Oxidation induced coupling reactions of bi(metallacycloprop-1-ene) complexes

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Supporting Information

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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 distilled under nitrogen from sodium benzophenone (hexane, ether, tetrahydrofuran THF), sodium (toluene), or CaH_2 (dichloromethane, DCM). The starting materials $ReX_3(PPh_3)_2(N{\equiv}CMe)$ (X = Cl and Br),[1] $ReCl_3(\eta^2\text{-}C(Ar){=}CH(PPh_3))_2$ (Ar = Ph, **1a**; *p*-$C_6H_4\text{-}C_6H_5$, **1c**, and *o*-$C_6H_4CF_3$, **1e**)[2] were prepared following the procedure described in the literature. All other reagents were used as purchased from Aldrich Chemical Co.. Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ) or MEDAC Ltd (Egham, UK). ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were collected on a Bruker-400 spectrometer (400 MHz) and JEOL 600 MHz spectrometer. ^1H and ^{13}C NMR shifts are relative to TMS, and ^{31}P chemical shifts are relative to 85% H_3PO_4.

Preparation of $ReBr_3\{\eta^2\text{-}C(Ph){=}CH(PPh_3)\}_2$ (1b). A mixture of $ReBr_3(PPh_3)_2(N{\equiv}CMe)$ (500 mg, 0.504 mmol) and phenylacetylene (0.221 mL, 2.01 mmol) in dibromomethane (5 mL) in a sealed Schlenk tube was heated at 70 °C for 4 h. The reddish solution was transferred to a Schlenk flask and the solvent was removed under vacuum to give an oily residue. The residue was redissolved in dichloromethane (10 mL). Addition of hexane (100 mL) produced an orange suspension with red oily residue stuck on the flask wall. The orange suspension was separated from the oily residue and was redissolved in DCM and re-precipitated with hexane. The resulting orange suspension (solid) was collected by filtration, and dried under vacuum. Yield: 60 mg, 10.3%. $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 22.69 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.80 – 7.62 (m, 12H, P*Ph*), 7.61 – 7.47 (m, 6H, P*Ph*), 7.44 – 7.35 (m, 12H, P*Ph*), 6.91 – 6.75 (m, 6H, Re=C*Ph*), 6.72 – 6.63 (m, 4H, Re=C*Ph*), 5.04 (d, *J* = 10.1 Hz, 2H, C*H*(PPh_3)). Anal. Calcd. for $C_{52}H_{42}Br_3P_2Re$: C, 54.09; H, 3.67. Found: C, 53.88; H, 3.62.

Preparation of $ReCl_3\{\eta^2\text{-}C(4\text{-}(9H\text{-carbazol-9-yl})phenyl){=}CH(PPh_3)\}_2$ (1d). A mixture of $ReCl_3(PPh_3)_2(N{\equiv}CMe)$ (500 mg, 0.582 mmol) and 9-(4-ethynylphenyl)carbazole (0.33 g, 1.23 mmol) in dichloromethane (20 mL) was heated at 70 °C for 3 h in a sealed Schlenk tube. The solvent was removed by vacuum evaporation. The residue was treated with hexane (50 mL). The solid was collected by filtration, washed with a minimal amount of acetone until the filtrate not showing dark red colour. The remaining red-orange solid was dried under vacuum. Yield: 588 mg, 76.1%. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 24.36 (s). ^1H NMR (400 MHz, $CDCl_3$): δ

8.16 – 7.92 (m, 3H), 7.91 – 7.68 (m, 12H), 7.65 – 7.34 (m, 19H), 7.15 – 6.83 (m, 20H), 5.29 (d, *J* = 10.4 Hz, 2H, C*H* (PPh_3)). Anal. Calcd. for $C_{76}H_{56}Cl_3N_2P_2Re \cdot CH_2Cl_2$: C, 64.37; H, 4.07; N, 1.95. Found: C, 64.23; H, 3.70. 2.02.

Preparation of $ReCl_4\{\eta^4$-$(Ph_3P)CH=C(Ph)$-$C(Ph)=CH(PPh_3)\}$ (2a). $ReCl_3\{\eta^2$-$C(Ph)=CH(PPh_3)\}_2$ (**1a**) (78 mg, 0.076 mmol) was dissolved in air-saturated dichloromethane (DCM, 10 mL) in a vial. The vial containing the solution was placed in a chamber containing hexane (see Figure S1 for the set-up). The setup was stood on a bench for two weeks with regular refilling of dichloromethane to give green crystals and a brownish red solution. The resulting green crystals were collected by filtration, washed with dichloromethane (1 mL) and dried under vacuum to give crystalline solid of **2a** (co-crystallized with CH_2Cl_2 as revealed by an X-ray diffraction study and elemental analysis). Yield: 49 mg, 56.2% calculated based on the molar ratio of **2a**·CH_2Cl_2 to **1a**. Anal. Calcd. for $C_{52}H_{42}Cl_4P_2Re \cdot CH_2Cl_2$: C, 55.75; H, 3.88. Found: C, 56.01; H, 3.95.

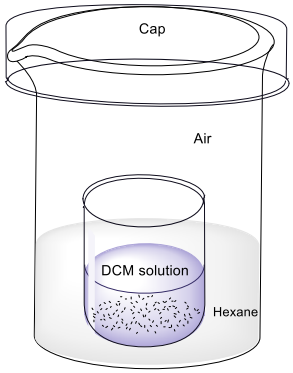


Figure S1. The set-up of the vapor diffusion method to prepare complexes **2** from **1**.

Preparation of $ReBr_4\{\eta^4$-$(Ph_3P)CH=C(Ph)$-$C(Ph)=CH(PPh_3)\}$ (2b). $ReBr_3\{\eta^2$-$C(Ph)=CH(PPh_3)\}_2$ (**1b**) (12 mg, 0.010 mmol) was dissolved in air-saturated dichloromethane (10 mL) in a vial. The vial containing the solution was placed in chamber containing hexane (see Figure S1 for the set-up). The setup was stood on a bench for two weeks with regularly refilling of dichloromethane to give brown crystals and a brownish red solution. The resulting brown crystals were collected by filtration, washed with dichloromethane (1 mL) and dried under vacuum to give crystalline solid of **2b** (co-crystallized with CH_2Cl_2 as revealed by an X-ray diffraction study and elemental analysis). Yield: 2.5 mg, 18.4% calculated based on the molar ratio of **2b**·$1.5CH_2Cl_2$ to **1b**. Anal. Calcd. for $C_{52}H_{42}Br_4P_2Re \cdot 1.5CH_2Cl_2$: C, 47.18; H, 3.33. Found: C, 47.38; H, 3.27.

Preparation of $ReCl_4\{\eta^4$-(Ph$_3$P)CH=C(Ar)-C(Ar)=CH(PPh$_3$)$\}$ (2c, Ar = *p*-C$_6$H$_4$-Ph). Method 1. $ReCl_3\{\eta^2$-C(4-biphenyl)=CH(PPh$_3$)$\}_2$ (**1c**) (75 mg, 0.064 mmol) was dissolved in air-saturated dichloromethane (10 mL) in a vial. The vial containing the solution was placed in a chamber containing hexane (see Figure S1 for the set-up). The setup was stood on a bench for two weeks with regular refilling of dichloromethane to give green crystals of **2c** and a brownish red solution. The resulting green crystals were collected by filtration, washed with dichloromethane (1 mL) and dried under vacuum. Yield: 26 mg, 33.7%. Anal. Calcd. for $C_{64}H_{50}Cl_4P_2Re$: C, 63.58; H, 4.17. Found: C, 62.96; H, 4.05.

Method 2. $ReCl_3\{\eta^2$-C(4-biphenyl)=CH(PPh$_3$)$\}_2$ (**1c**) (67 mg, 0.057 mmol) was dissolved in THF (10 mL). The solution was stirred under a O_2 atmosphere (with a O_2 ballon) for a week to give a green suspension and a brownish red solution. The solvent was removed under vacuum, and the green residue was washed with MeOH (5 mL x 3), and dried under vacuum to give the diene complex **2c** (Yield: 31 mg, 45.0%).

Preparation of $ReCl_4\{\eta^4$-(Ph$_3$P)CH=C(Ar)-C(Ar)=CH(PPh$_3$)$\}$ (2d, Ar = 4-(9H-carbazol-9-yl)phenyl). $ReCl_3\{\eta^2$-C(4-(9H-carbazol-9-yl)phenyl)=CH(PPh$_3$)$\}_2$ (**1d**) (52 mg, 0.038 mmol) was dissolved in air-saturated dichloromethane (20 mL) in a vial. The vial containing the solution was placed in a chamber containing hexane (see Figure S1 for the set-up). The setup was stood on a bench for two weeks with regular refilling of dichloromethane to give green crystals of **2d** and a brownish red solution. The resulting green crystals were collected by filtration, washed with dichloromethane (1 mL) and dried vacuum to give crystals of **2d**. Yield: 16 mg, 28.3% calculated based on the molar ratio of **2d**·CH_2Cl_2 to **1d**. Anal. Calcd. for $C_{76}H_{56}Cl_4N_2P_2Re \cdot CH_2Cl_2$: C, 62.82; H, 3.97; N, 1.90. Found: C, 62.95; H, 3.88; N, 1.83.

Isolation of cis-[PhCH=CH(PPh$_3$)]BPh$_4$ (3aBPh$_4$). A solution of the complex $ReCl_3(\eta^2$-C(Ph)=CH(PPh$_3$))$_2$ (**1a)** (100 mg, 0.098 mmol) in dichloromethane (10 mL) was stirred under an oxygen atmosphere (with a O_2 balloon) for a week to give a green suspension. The solvent was removed under vacuum. The residue was washed with MeOH (5 mL x 3) and dried under vacuum to give the diene complex **2a** (Yield: 64 mg, 61.9%). The methanol washings were combined and treated with $NaBPh_4$ (100 mg, 0.292 mmol) dissolved in MeOH (3 mL) to give a brown precipitate. The precipitate was collected by filtration, washed with MeOH (2 mL x 2) and dried under vacuum. The crude product was recrystallized with DCM/Hexane to give a pale yellow crystalline solid of **3aBPh$_4$**. Yield: 24 mg, 17.9%. $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$):

δ 13.80 (s). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.62 (t, *J* = 7.7 Hz, 3H, P*Ph*$_3$), 7.49 (dd, *J* = 47.0, 12.2 Hz, 1H, Ph_3P–CH=C*H*Ph), 7.47 – 7.38 (m, 14H, 6H of PPh_3 and 8H of BPh_4), 7.31 – 7.24 (m, 6H, P*Ph*$_3$) 7.07 (t, *J* = 7.4 Hz, 1H, Ph), 6.94 (t, *J* = 7.3 Hz, 8H, BPh_4), 6.88 (t, *J* = 7.6 Hz, 2H, Ph), 6.82 (t, *J* = 7.2 Hz, 4H, BPh_4), 6.75 (d, *J* = 7.7 Hz, 2H, Ph), 5.58 (dd, *J* = 19.2, 13.5 Hz, 1H, Ph_3P–C*H*=CHPh). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 164.29 (1:1:1:1, q, *J* = 49.5 Hz, BPh_4), 158.98 (s, Ph_3P–CH=*C*HPh), 136.39, 135.16 (d, *J* = 2.9 Hz), 133.49 (d, *J* = 10.7 Hz), 130.71, 130.49 (d, *J* = 13.0 Hz), 128.99, 128.16, 125.66 (d, *J* = 3.0 Hz), 121.80, 118.39 (d, *J* = 89.9 Hz, ipso-P*Ph*), 105.23 (d, *J* = 84.6 Hz, Ph_3P–*C*H=). Anal. Calcd. for $C_{50}H_{42}BP \cdot 0.5CH_2Cl_2$: C, 83.42; H, 5.96. Found: C, 83.14; H, 5.87.

Isolation of diene [(Ph$_3$P)CH=C(Ph)-C(Ph)=CH(PPh$_3$)]$^{2+}$ (4a). A mixture of $ReCl_4${η^4-(Ph_3P)CH=C(Ph)-C(Ph)=CH(PPh_3)} (**2a**) (0.25 mg, 0.237 mmol) and $NaBPh_4$ (0.175 g, 0.511mmol) in dichloromethane (15 mL) was s sonicated to give a green solution. To the green solution was added 30w/w% H_2O_2 (134 mg, 5 equiv.), and the resulting mixture was stirred at RT for 1 h to give a faint-green solution. The solvent of the solution was removed under vacuum and the residue was washed with MeOH (5 mL x 3) to give a white solid. The NMR and MS data indicate that the white solid is the salts of [(Ph_3P)CH=C(Ph)-C(Ph)=CH(PPh_3)]$^{2+}$ (**4a**) with ReO_4^- (major) and BPh_4^- (minor) as the counter anions**.** The solid was washed with dichloromethane (0.5 ml x 2) to give pure [(Ph_3P)CH=C(Ph)-C(Ph)=CH(PPh_3)](ReO_4)$_2$, **4a[ReO$_4$]$_2$**. Yield: 144 mg, 49.5%. ^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2): δ 14.36 (s). ^{1}H NMR (600 MHz, CD_2Cl_2): δ 7.70 (t, *J* = 7.6 Hz, 6H, P*Ph*$_3$), 7.63 – 7.48 (m, 24H, P*Ph*$_3$), 7.26 (d, *J* = 7.6 Hz, 4H, *Ph*), 7.16 (t, *J* = 7.5 Hz, 2H, *Ph*), 7.05 (t, *J* = 7.5 Hz, 4H, *Ph*), 6.60 (d, *J* = 17.5 Hz, 2H, Ph_3P–C*H*=). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2): δ 168.61 (d, *J* = 21.9 Hz, =*C*Ph), 135.26, 134.84 – 133.97 (m), 133.30, 131.32 – 130.73 (m), 130.40, 130.23, 129.48, 118.73 (d, *J* = 91.3 Hz, ipso-P*Ph*), 116.99 (d, *J* = 89.8 Hz, Ph_3P–*C*H=). Anal. Calcd. for $C_{52}H_{42}P_2 \cdot 2ReO_4$: C, 50.81; H, 3.44. Found: C, 50.40; H, 3.44. Mass spectroscopy (m/z): negative mode: 250.9380 (ReO_4^-); positive mode: 364.1393 (**4a**/2).

2. X-ray crystallographic study of complexes 2a-d.

Crystals were grown in $CDCl_3$ or DCM/*n*-hexane. All the crystals were mounted on the glass fibers. The diffraction intensity data of **2a** (CCDC no. 2244843), **2b** (CCDC no. 2325118), **2c** (CCDC no. 2244844), and **2d** (CCDC no. 2244845) were collected on a Rigaku SuperNova, Dual, Atlas diffractometer, using monochromatized Cu-Kα radiation (λ =1.54184Å). Lattice determination, data collection and reduction were carried out using 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.[3] All the structures were solved with the SHELXT[4] structure solution program using Intrinsic Phasing and refined with the SHELXL[5] refinement package using Least Squares minimisation. All non-hydrogen atoms were refined anisotropically with a riding model for the hydrogen atoms. The crystal data are listed in Table S1. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre.

Table S1. *Crystal data and structure refinement for complexes* ***2a-d***

Complexes	**2a**·$2CH_2Cl_2$	**2b**·$2CHCl_3$	**2c**	**2d**·$7CH_2Cl_2$
CCDC	2244843	2325118	2244844	2244845
Empirical formula	$C_{52}H_{42}Cl_4P_2Re·2CH_2Cl_2$	$C_{52}H_{42}Br_4P_2Re·2CHCl_3$	$C_{64}H_{50}Cl_4P_2Re$	$C_{76}H_{56}Cl_4N_2P_2Re·7CH_2Cl_2$
Formula weight	1226.65	1473.37	1208.98	1981.65
Temperature/K	172.99(10)	173.00(10)	173	100.01(10)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	C2/c	C2/c	$P2_1/n$	$P2_1/c$
a/Å	12.0537(3)	12.08870(10)	15.5823(3)	19.6823(7)
b/Å	23.1354(5)	24.3009(2)	22.9599(3)	18.6829(7)
c/Å	20.0755(3)	19.85410(10)	18.0278(3)	24.3283(8)
α/°	90	90	90	90
β/°	102.929(2)	102.0850(10)	107.9434(17)	110.713(4)
γ/°	90	90	90	90
Volume/$Å^3$	5456.5(2)	5703.21(8)	6136.07(18)	8367.8(5)
Z	4	4	4	4
$\rho_{calc}g/cm^3$	1.493	1.716	1.309	1.573
μ/mm^{-1}	8.780	10.835	6.239	8.850

F(000)	2444.0	2860.0	2428.0	3972.0
Crystal size/mm^3	0.1 × 0.08 × 0.05	0.1 × 0.04 × 0.03	0.12 × 0.1 × 0.05	0.08 × 0.06 × 0.06
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.442 to 153.536	7.276 to 148.512	6.432 to 153.572	4.8 to 153.888
Index ranges	-13 ≤ h ≤ 15, -26 ≤ k ≤ 29, -17 ≤ l ≤ 25	-15 ≤ h ≤ 15, -28 ≤ k ≤ 29, -24 ≤ l ≤ 16	-18 ≤ h ≤ 19, -22 ≤ k ≤ 28, -20 ≤ l ≤ 22	-24 ≤ h ≤ 23, -23 ≤ k ≤ 15, -30 ≤ l ≤ 28
Reflections collected	9902	16796	39181	52122
Independent reflections	5536 [R_{int} = 0.0281, R_{sigma} = 0.0363]	5672 [R_{int} = 0.0350, R_{sigma} = 0.0347]	12655 [R_{int} = 0.0587, R_{sigma} = 0.0675]	17288 [R_{int} = 0.1086, R_{sigma} = 0.1273]
Data/restraints/ parameters	5536/71/330	5672/79/339	12655/0/640	17288/38/766
Goodness-of-fit on F^2	1.031	1.041	1.002	1.016
Final R indexes [I>=2σ (I)]	R_1 = 0.0325, wR_2 = 0.0815	R_1 = 0.0330, wR_2 = 0.0866	R_1 = 0.0443, wR_2 = 0.1084	R_1 = 0.0733, wR_2 = 0.1818
Final R indexes [all data]	R_1 = 0.0363, wR_2 = 0.0840	R_1 = 0.0361, wR_2 = 0.0896	R_1 = 0.0648, wR_2 = 0.1167	R_1 = 0.1103, wR_2 = 0.2027
Largest diff. peak/hole / e $Å^{-3}$	0.81/-0.90	1.40/-0.82	1.47/-1.28	2.19/-1.72

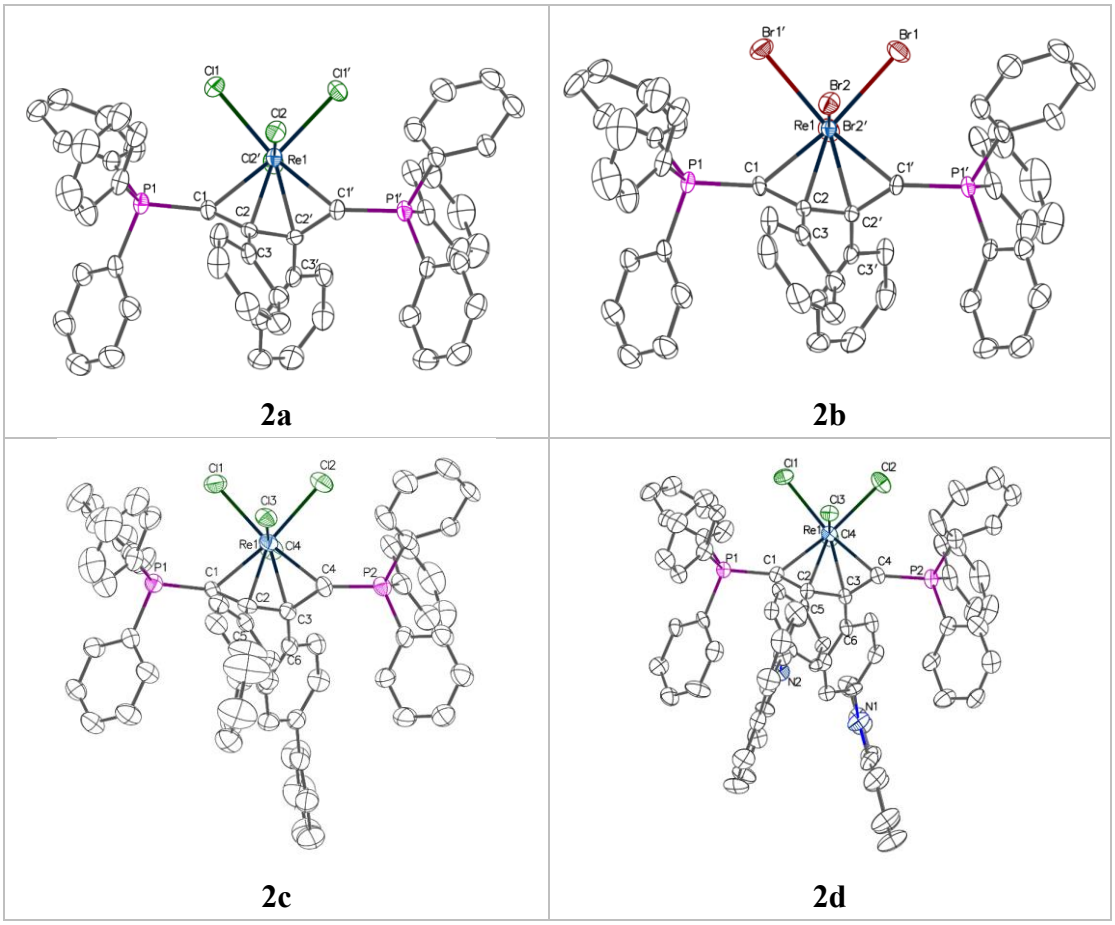
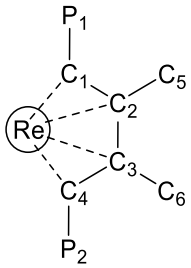


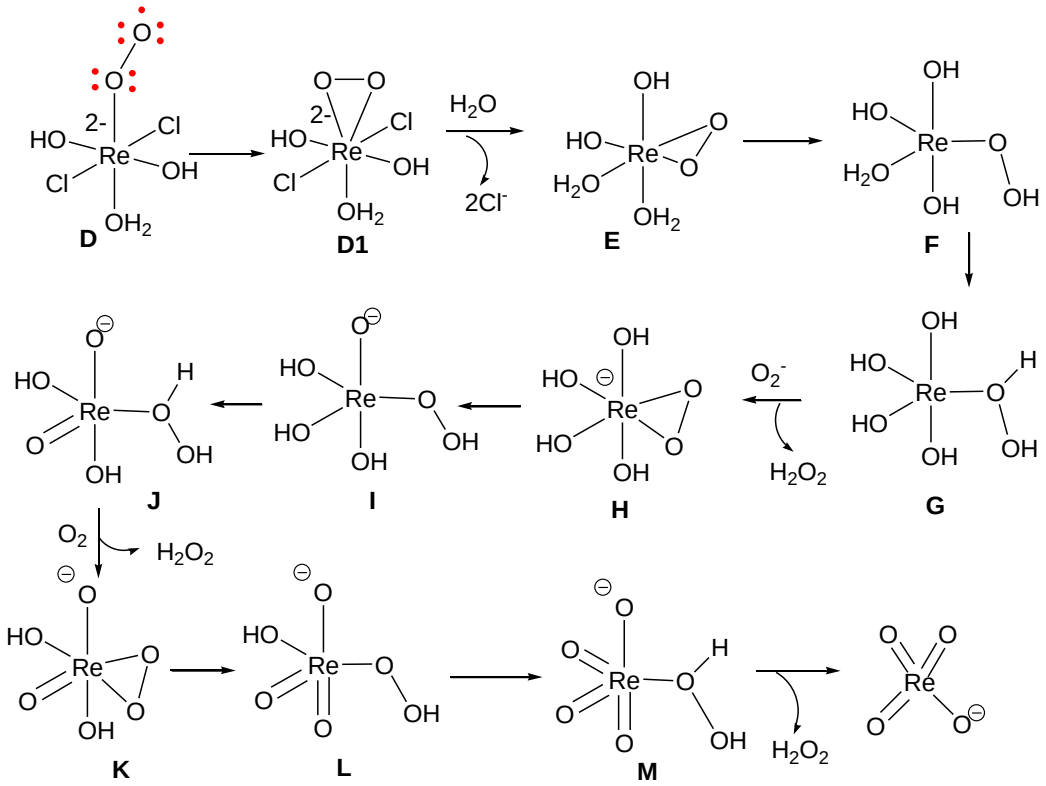
Figure S2. The crystal structures of the complexes **2a-d** (ellipsoids at the 40% probability level), presented with an orientation different from that in the main text. The hydrogen atoms are omitted for clarity.

Table S2. Selected bond lengths [Å] and angles [°] for the η^4-diene complexes **2a-d.**

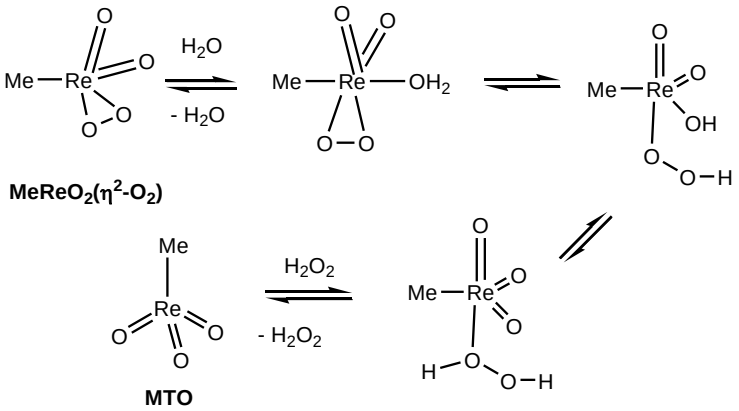


Compound	*M-C1*	*M-C2*	*M-C3*	*M-C4*	*C1-C2*	*C2-C3*	*C3-C4*	*C1-P1*
2a	2.193(3)	2.150(3)	2.151(3)	2.193(3)	1.457(4)	1.487(6)	1.457(4)	1.787(3)
2b	2.204(3)	2.159(3)	2.159(3)	2.204(3)	1.461(5)	1.478(6)	1.461(5)	1.786(3)
2c	2.207(4)	2.164(4)	2.145(4)	2.209(5)	1.454(6)	1.483(6)	1.458(6)	1.794(4)
2d	2.196(8)	2.131(8)	2.165(8)	2.204(8)	1.451(9)	1.509(9)	1.464(10)	1.789(8)
	C4-P2	C2-C5	C3-C6	C1-C2-C3-C4	C1-M-C4		C2-M-C3	
2a	1.787(3)	1.493(4)	1.493(4)	125.9(4)	101.82(16)		40.46(17)	
2b	1.786(3)	1.486(5)	1.486(5)	126.1(4)	101.46(18)		40.04(18)	
2c	1.783(5)	1.478(6)	1.502(6)	126.4(4)	101.57(16)		40.27(16)	
2d	1.773(7)	1.514(9)	1.455(9)	126.4(6)	102.2(3)		41.1(3)	

3. Proposed mechanisms for ReO_4^- production from intermediate D.



Scheme S1. A proposed mechanism for ReO_4^- production from intermediate **D**. The key transformation is the reaction of peroxo complexes $L_nM(O_2)$ with water (H_2O) to give $L_nM(=O)$ and H_2O_2. It is noted that the reaction of $MeReO_2(\eta^2\text{-}O_2)$ with H_2O to give $MeReO_3$ (MTO) and H_2O_2 have been confirmed experimentally and verified computationally (Scheme S2).[6]



Scheme S2. Equilibrium between $MeReO_3$ (MTO) and $MeReO_2(\eta^2\text{-}O_2)$ in the presence of H_2O_2 and H_2O.

4. Computational studies.

General Procedures

All of the calculations were performed using the Gaussian 09 software (rev. D.01),[7] and based on density functional theory with either the restricted B3LYP-D3(BJ) functional (for all singlet species) or otherwise the unrestricted B3LYP-D3(BJ) functional (for all non-singlet species).[8] The basis set def2-TZVP was used to describe all atom[9] with the corresponding effective core potential for Re atom.[10] Solvation effect was also considered using the PCM solvation model with dichloromethane as the solvent.[11] Vibrational frequency of each structure was calculated to confirm that all optimized structures are indeed either a local minimum (with zero imaginary frequencies) or a saddle point (with only one imaginary frequency) of the PES, and to give free energies at standard conditions. Intrinsic reaction coordinate (IRC) calculations[12] were performed to confirm that the transition state connects to two relevant local minima. All reported relative free energies and electronic energies (in parentheses) are in kcal/mol. Optimized structures were visualized and represented by CYLview20.[13]

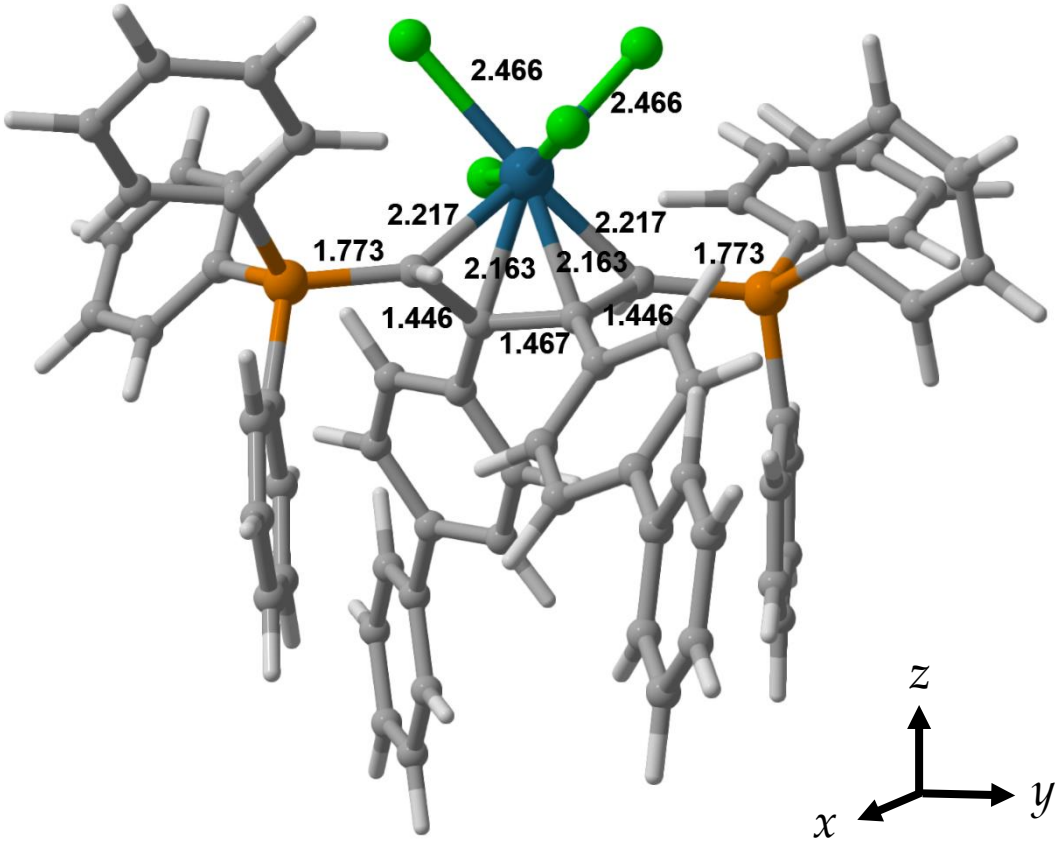


Figure S3. Selected bond distances (in Å) in optimized structure of **2c**. The results clearly show that the diene is symmetrically bound to Re and the complex has an C2 symmetry. The C2 axis coincides with the *z*-axis.

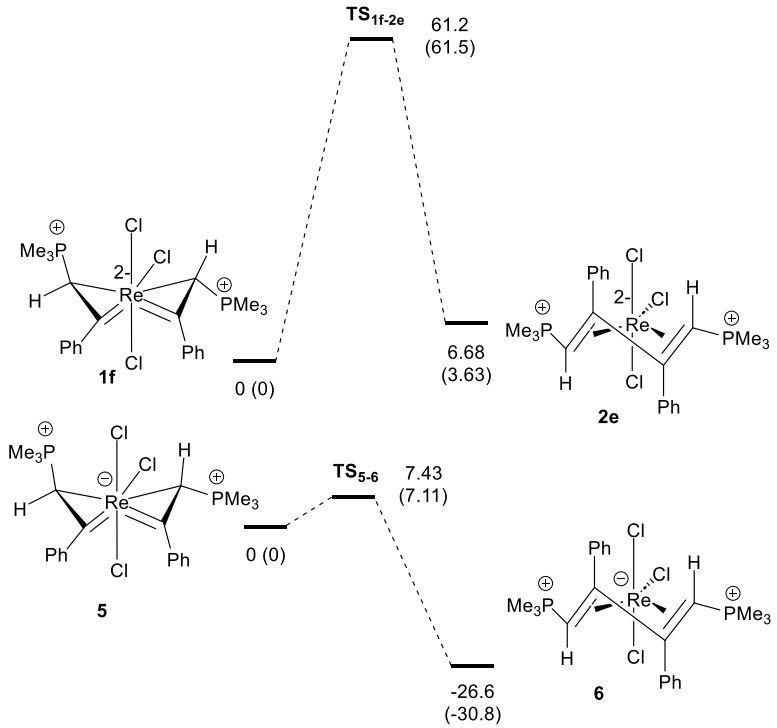
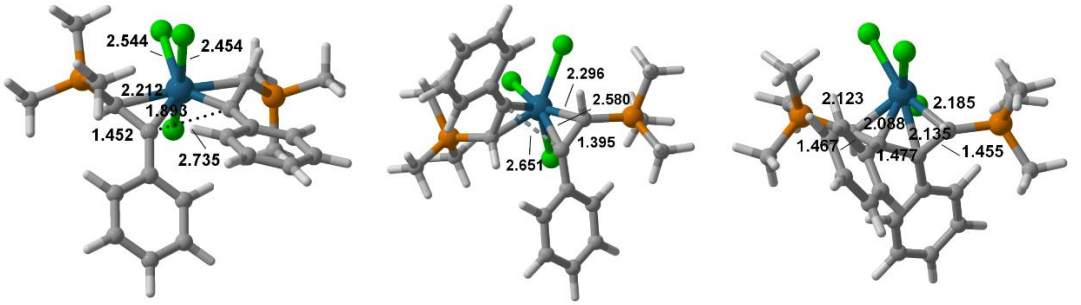
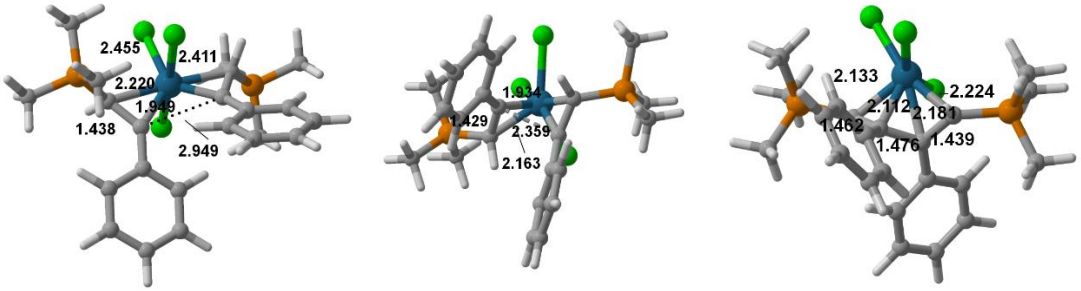


Figure S4. Calculated energy profiles for the coupling reactions of the bi(metallacycloprop-1-ene) complexes **1f** and **5**. The relative free energies and electronic energies (in parentheses) are given in kcal/mol. The computational results reveal that oxidation can indeed promote the carbene coupling reaction both kinetically and thermodynamically.



1f **$TS_{1f\text{-}2e}$** **2e**



5 **$TS_{5\text{-}6}$** **6**

Figure S5. DFT-optimized structures and their selected structural parameters (Å) for species in Figure 3.

5. Cartesian Coordinates of Calculated Structures

58
Structure 1f −2998.848291 a.u.

Re	−0.00008100	0.86417400	0.00008800
C	−2.12891200	0.70838500	−0.57962200
C	−1.24609600	−0.44469900	−0.56326600
C	−1.39613200	−1.74395400	−1.17039300
C	−2.66637600	−2.30679800	−1.36710700
C	−2.81088200	−3.56600300	−1.93002400
C	−1.68771500	−4.27911100	−2.33772500
C	−0.42105000	−3.72023300	−2.18160800
C	−0.27547600	−2.47175500	−1.60155000
C	2.12885500	0.70886500	0.57963600
C	1.24631500	−0.44442500	0.56325200
C	1.39662600	−1.74358600	1.17051300
C	2.66696900	−2.30624100	1.36711400
C	2.81171900	−3.56529100	1.93031400
C	1.68870700	−4.27841700	2.33841200
C	0.42194700	−3.71973600	2.18235800
C	0.27612500	−2.47142400	1.60200200
P	−3.49332500	0.94494300	0.49782500
C	−5.03479900	0.85681100	−0.44555300
C	−3.50992100	2.57371700	1.26438300
C	−3.57762200	−0.31573400	1.78057400
P	3.49310700	0.94580600	−0.49793100
C	3.50944000	2.57476000	−1.26412400
C	5.03472000	0.85765200	0.44522100
C	3.57740100	−0.31460100	−1.78094400
Cl	−0.00044800	3.40818000	0.00049200
Cl	0.52647700	1.13571700	−2.38164200
Cl	−0.52684400	1.13481300	2.38190100
H	−2.36119000	1.12811200	−1.56176900
H	−3.54324400	−1.74887100	−1.07202900
H	−3.79919900	−3.98742200	−2.06112200
H	−1.79879200	−5.25861800	−2.78435500
H	0.45423200	−4.26332800	−2.51411700
H	0.70265200	−2.03289200	−1.48239300
H	2.36116600	1.12851200	1.56181100
H	3.54372000	−1.74829500	1.07172700
H	3.80010800	−3.98656600	2.06133800
H	1.79997800	−5.25778600	2.78529500
H	−0.45321200	−4.26284800	2.51516100
H	−0.70207200	−2.03270300	1.48288700
H	−5.88541600	1.03896000	0.21090200
H	−5.01618600	1.61787000	−1.22537300
H	−5.13925900	−0.12177200	−0.91076100
H	−2.62311600	2.68280600	1.88308200
H	−3.48952000	3.32635800	0.47711500
H	−4.41396600	2.69178700	1.86157100
H	−3.70640400	−1.29459800	1.32150800
H	−2.65350900	−0.29539700	2.35312400
H	−4.42359700	−0.10735000	2.43522200
H	3.48929700	3.32721800	−0.47667200
H	4.41329600	2.69298400	−1.86156800
H	2.62244100	2.68398400	−1.88252200
H	5.88522200	1.03998800	−0.21132900
H	5.01614900	1.61858100	1.22516600
H	5.13934100	−0.12099600	0.91025400
H	2.65329000	−0.29417000	−2.35349100
H	4.42338200	−0.10607800	−2.43554200
H	3.70620200	−1.29355600	−1.32207600

58
TS 1f−2e −2998.750279 a.u.

Re	−0.11808200	−0.77704100	−0.26497300
C	−1.26746900	0.62833400	0.88440200
C	−1.22892100	0.71690000	−0.55608000
C	−1.80252600	1.64353500	−1.49610200
C	−2.50859200	2.75895800	−1.01503600
C	−3.06401300	3.68120900	−1.88677900
C	−2.92275400	3.51203800	−3.26148000
C	−2.21798900	2.41673800	−3.75363700
C	−1.66255600	1.49055000	−2.88447300
C	1.60008800	0.47461800	−1.13196500
C	1.29983100	1.37293500	−0.10765100
C	2.00432200	1.56421500	1.15893000
C	3.01372700	0.76266800	1.72914000
C	3.62374800	1.09120900	2.93008700
C	3.23550500	2.23129700	3.62826700
C	2.22907600	3.03714900	3.10677200
C	1.63184700	2.70462600	1.89787100
P	−2.74100500	0.18232400	1.76997000
C	−3.35842300	1.64203700	2.64132900
C	−2.43379200	−1.04505000	3.04753100
C	−4.05602800	−0.37456300	0.67765200
P	3.15331900	−0.38051200	−1.54206000
C	3.16713600	−0.65332000	−3.32449500
C	4.59652200	0.65809900	−1.21582500
C	3.42990600	−1.99775100	−0.78335400
Cl	−1.57661500	−2.71661000	0.12415700
Cl	0.89123100	−1.46669700	1.80328200
Cl	−0.17860700	−1.58178500	−2.55147600
H	−0.69679800	1.35133400	1.46419100
H	−2.59279000	2.90602000	0.05188800
H	−3.60226300	4.53549300	−1.49693500
H	−3.35630300	4.23111300	−3.94433300
H	−2.10351200	2.28425400	−4.82183800
H	−1.12471800	0.63575700	−3.26453700
H	1.17218200	0.69228700	−2.11132500
H	3.31276000	−0.15073800	1.24601300
H	4.39697500	0.44792600	3.33232000
H	3.70956400	2.48387600	4.56829400
H	1.91326800	3.92585300	3.63920500
H	0.85651500	3.33369300	1.48031300
H	−3.67509900	2.40156800	1.92930000
H	−4.20615500	1.36240000	3.26671300
H	−2.56781100	2.04854000	3.27113600
H	−1.65055600	−0.67320400	3.70681400
H	−3.34685000	−1.21431900	3.61842600
H	−2.09673600	−1.96450000	2.57610800
H	−4.93688700	−0.61814200	1.27090800
H	−4.29759700	0.42436400	−0.02215000
H	−3.71971400	−1.25333600	0.13307900
H	2.31868200	−1.27845000	−3.59428700
H	3.08058900	0.30604400	−3.83359300
H	4.10062400	−1.13425200	−3.61586600
H	4.47384800	1.59568000	−1.75676100
H	4.69623600	0.87340900	−0.15633900
H	5.49066500	0.14643000	−1.57222000
H	2.71298800	−2.69974000	−1.20766700
H	4.44302800	−2.33524500	−1.00266000
H	3.27521200	−1.95857900	0.29177800

58
Structure 2e −2998.842506 a.u.
Re -0.05100700 -1.09620100 -0.13029300
C -1.17584300 0.20644100 1.11304000
C -0.59363600 0.91762500 -0.03090000
C -1.23875800 1.83129100 -0.99973000
C -2.40779300 1.52139200 -1.69800300
C -2.98730500 2.43410400 -2.56855100
C -2.39795400 3.67682100 -2.77967700
C -1.21572800 3.98902400 -2.11797300
C -0.64458900 3.07592800 -1.23960700
C 1.35799900 0.24636700 -1.12316900
C 0.87117600 0.81266100 0.12594900
C 1.60337200 1.40377200 1.25758800
C 2.86928600 0.98442600 1.68151400
C 3.51780900 1.60025100 2.74194300
C 2.91188300 2.64974500 3.42572300
C 1.64810700 3.07231300 3.03142600
C 1.00781600 2.45969900 1.96172500
P -2.89320000 -0.04012800 1.46711000
C -3.66444500 1.54161300 1.87614800
C -2.94279000 -1.07857100 2.93515700
C -3.92169600 -0.81859700 0.20348400
P 2.96472900 -0.30032000 -1.59218500
C 2.81404200 -0.76152800 -3.32631900
C 4.23642900 0.98238000 -1.50850700
C 3.55853100 -1.76281900 -0.72316700
Cl -1.37702300 -3.11694000 0.34830400
Cl 1.16780300 -1.83196500 1.87824800
Cl -0.91747000 -1.40460500 -2.38805600
H -0.70928100 0.39174000 2.08490800
H -2.82920000 0.53586300 -1.60500400
H -3.89084200 2.16479500 -3.10113500
H -2.84660900 4.38585900 -3.46332300
H -0.73678900 4.94597300 -2.28334100
H 0.27542500 3.32686700 -0.72878900
H 0.90205500 0.64951200 -2.02840500
H 3.34735400 0.14502600 1.20622200
H 4.49601500 1.24863400 3.04480200
H 3.41693700 3.12762100 4.25503300
H 1.16042500 3.88757000 3.55113800
H 0.03135700 2.80991200 1.65673500
H -3.62185700 2.18987800 1.00148700
H -4.70375800 1.38933100 2.16661700
H -3.11973800 2.00830200 2.69599400
H -2.34840600 -0.62141400 3.72462200
H -3.97244000 -1.19328700 3.27156600
H -2.52044800 -2.04856300 2.67679400
H -4.66482600 -1.43434000 0.70922400
H -4.43195000 -0.05902600 -0.38232600
H -3.30694500 -1.44983000 -0.43317700
H 1.99010500 -1.46738600 -3.42688000
H 2.59882300 0.12263200 -3.92475300
H 3.74211600 -1.21672800 -3.66932200
H 3.89464800 1.84735300 -2.07597600
H 4.40498400 1.28119600 -0.47679700
H 5.16582200 0.60929400 -1.93875100
H 3.02343700 -2.62923100 -1.10968900
H 4.62585700 -1.88368300 -0.90758400
H 3.35508600 -1.69610800 0.34280000

58
Structure 5 −2998.652670 a.u.
Re 0.00000300 0.81828100 0.00014000
C -2.17504600 0.72492200 -0.43253300
C -1.36481000 -0.45673300 -0.55750800
C -1.57807700 -1.69211800 -1.22314800
C -2.87996300 -2.09024500 -1.59012200
C -3.09165000 -3.28968200 -2.24198800
C -2.00724300 -4.10739600 -2.55735400
C -0.70992400 -3.72316100 -2.21868000
C -0.49480600 -2.53385100 -1.55177500
C 2.17495400 0.72541500 0.43251400
C 1.36484600 -0.45636100 0.55750500
C 1.57840800 -1.69178200 1.22315100
C 2.88038100 -2.08966200 1.58998500
C 3.09237300 -3.28903500 2.24190800
C 2.00817500 -4.10693300 2.55746400
C 0.71076200 -3.72292200 2.21893400
C 0.49535100 -2.53367100 1.55198500
P -3.47140500 0.98646800 0.74367600
C -3.34136600 2.58299800 1.55789600
C -5.04399700 1.01999900 -0.14207600
C -3.56837500 -0.34198400 1.95243700
P 3.47111500 0.98685300 -0.74393700
C 3.34093300 2.58327700 -1.55835800
C 5.04391500 1.02048900 0.14144300
C 3.56780300 -0.34173100 -1.95258100
Cl 0.00000800 3.27314900 0.00008800
Cl 0.41188600 0.91972100 -2.37287500
Cl -0.41258900 0.91951800 2.37293400
H -2.47866500 1.16151100 -1.38794500
H -3.71336800 -1.44271900 -1.36144600
H -4.09414000 -3.58960700 -2.51505300
H -2.17322400 -5.04433400 -3.07242600
H 0.12657800 -4.35828300 -2.47635600
H 0.50499100 -2.22419200 -1.29167700
H 2.47854500 1.16226500 1.38781800
H 3.71364700 -1.44199400 1.36119700
H 4.09496000 -3.58874100 2.51486500
H 2.17438500 -5.04381200 3.07257000
H -0.12561200 -4.35815700 2.47675900
H -0.50455300 -2.22422300 1.29203300
H -3.32231400 3.35805100 0.79305100
H -4.20521700 2.72922900 2.20595100
H -2.42119200 2.62781600 2.13259000
H -5.84465000 1.27419700 0.55237300
H -4.99963100 1.77381700 -0.92754900
H -5.25226700 0.04944100 -0.58856500
H -2.66098100 -0.36276400 2.54930300
H -4.43126400 -0.17502700 2.59654600
H -3.68607100 -1.29037000 1.42974100
H 2.42062000 2.62804300 -2.13283700
H 3.32207900 3.35843800 -0.79361800
H 4.20462600 2.72940700 -2.20664400
H 5.84441900 1.27452700 -0.55323800
H 4.99977400 1.77446000 0.92678300
H 5.25224200 0.05000700 0.58807000
H 3.68550500 -1.29007500 -1.42981100
H 2.66029700 -0.36249200 -2.54928100
H 4.43058900 -0.17491700 -2.59686400

58
TS 5-6 −2998.641331
Re 0.00887800 −1.05594300 −0.40838500
C −1.16277200 −0.16927200 1.17937000
C −0.95703900 0.57467600 −0.02358300
C −1.22750800 1.90657300 −0.45160200
C −1.54461300 2.88269200 0.51489000
C −1.72909200 4.20115500 0.14355900
C −1.61715400 4.56930700 −1.19630200
C −1.31612300 3.61480500 −2.16362700
C −1.11720400 2.29324800 −1.80056200
C 1.52410200 0.38438900 −1.11259100
C 1.37594100 0.40063200 0.27893800
C 1.73619300 1.20995800 1.37055100
C 1.57481000 0.80370300 2.71771400
C 1.91667400 1.65168800 3.75576000
C 2.43617100 2.91918500 3.49673200
C 2.62178600 3.33119000 2.17601100
C 2.28228600 2.49741000 1.12922400
P −2.80942700 −0.70113000 1.63377700
C −3.49851700 0.55884700 2.72456100
C −2.76441700 −2.22888200 2.57268900
C −3.88712700 −0.80556200 0.20243200
P 3.02859200 −0.21414000 −1.87714200
C 2.84484300 −0.07899500 −3.65663500
C 4.40281700 0.82183500 −1.34952300
C 3.42643000 −1.91161300 −1.45710400
Cl −1.38590200 −3.05338400 −0.46632200
Cl 1.18038000 −2.39144200 1.25437800
Cl −0.57581100 −1.01107800 −2.73851400
H −0.62275300 0.12268700 2.07887400
H −1.60489400 2.59741600 1.55560600
H −1.95636500 4.94634400 0.89376400
H −1.76742700 5.60105800 −1.48532900
H −1.23995800 3.90354000 −3.20328600
H −0.91186400 1.54197900 −2.54816500
H 1.10731800 1.18339100 −1.73025400
H 1.23291800 −0.19943200 2.92390500
H 1.79359200 1.31863800 4.77830300
H 2.70407100 3.57537000 4.31388900
H 3.02659700 4.31331300 1.96819300
H 2.40668300 2.82960600 0.10760400
H −3.64302900 1.48586700 2.17375500
H −4.46115300 0.21332000 3.10154300
H −2.82609300 0.73265200 3.56357100
H −2.10921600 −2.09035900 3.43235000
H −3.77089500 −2.46195400 2.91911900
H −2.38142500 −3.02895100 1.94576700
H −4.89300400 −1.05680700 0.53736800
H −3.90381500 0.16611400 −0.29069500
H −3.52049900 −1.56285600 −0.48461800
H 1.99860800 −0.68764000 −3.97037600
H 2.66260000 0.95993600 −3.92818600
H 3.75724000 −0.42613500 −4.14015600
H 4.21098500 1.85574700 −1.63187500
H 4.50814500 0.75634700 −0.26754300
H 5.32063700 0.47992500 −1.82756900
H 4.41012300 −2.14725000 −1.86246100
H 3.42950000 −2.03368900 −0.37565400
H 2.68700400 −2.58397600 −1.88967200

58
Structure 6 −2998.701749 a.u.
Re −0.10678200 −1.09812900 −0.44885800
C −1.22059700 −0.06664800 1.04981900
C −0.57559400 0.87566900 0.13731800
C −1.14209100 2.00575600 −0.62967700
C −2.32589700 1.93467300 −1.36617200
C −2.81835600 3.04777800 −2.03102800
C −2.12761100 4.25467600 −1.98676300
C −0.93535900 4.33441400 −1.27795900
C −0.44756800 3.22027200 −0.60693400
C 1.42627300 0.42011900 −0.98791200
C 0.87844300 0.69197500 0.31480000
C 1.54928500 0.95652400 1.59930700
C 2.78352700 0.41314300 1.96554000
C 3.39054500 0.75622000 3.16396200
C 2.77315400 1.64932100 4.03353200
C 1.54210000 2.19411600 3.69025500
C 0.93933000 1.85284800 2.48712500
P −2.96352600 −0.25705400 1.40625200
C −3.53069100 1.27620500 2.16160000
C −3.05639300 −1.58175500 2.61529900
C −4.07560000 −0.66488100 0.04985900
P 3.07366600 0.04712900 −1.54782800
C 2.93382100 0.01066700 −3.33987500
C 4.22712300 1.35771200 −1.10737500
C 3.75112200 −1.54468200 −1.05517300
Cl −1.52379000 −3.02881200 −0.47224200
Cl 1.21214700 −2.30865900 1.10723200
Cl −0.88816600 −0.70318800 −2.66980700
H −0.72434200 −0.18571800 2.01283600
H −2.83585400 0.99306200 −1.47385300
H −3.73368100 2.96639900 −2.60241900
H −2.50973600 5.12039500 −2.51124800
H −0.38255600 5.26408600 −1.24485500
H 0.47878900 3.29352900 −0.05373400
H 0.96729300 0.98453600 −1.79500700
H 3.26717100 −0.30965600 1.33285800
H 4.34527800 0.31775900 3.42262100
H 3.24795700 1.91733700 4.96793900
H 1.05228600 2.89472100 4.35370400
H −0.00765500 2.30300000 2.22361200
H −3.45421400 2.08308700 1.43366800
H −4.56782100 1.16744400 2.47763800
H −2.90701500 1.50628000 3.02436700
H −2.42723900 −1.34195400 3.47097900
H −4.08835900 −1.69920400 2.94355600
H −2.70757100 −2.50265900 2.15024700
H −4.93259200 −1.18088000 0.48272100
H −4.42426600 0.23772500 −0.44294000
H −3.58115600 −1.32528600 −0.65831300
H 2.19224200 −0.73371400 −3.62648000
H 2.61706700 0.98804500 −3.70051100
H 3.89882800 −0.24265900 −3.77632000
H 3.83820600 2.30267100 −1.48549300
H 4.33552000 1.42015000 −0.02696600
H 5.19620000 1.15466900 −1.56255900
H 4.72599300 −1.65164000 −1.53129400
H 3.86250200 −1.62848100 0.02058800
H 3.08853800 −2.33747200 −1.39689700

```
121
Structure 2c -5072.402895 a.u.
Re    0.00000000    0.00000000    2.08672300
C    -1.24133900    1.15855200    0.66050700
C    0.00000000    0.73340300    0.05215800
C    1.00768800    1.48004500   -0.72969200
C    1.45680600    2.77168800   -0.44528000
C    2.35334900    3.41734200   -1.27952800
C    2.86258800    2.79576000   -2.42508700
C    2.43820500    1.49205100   -2.69520500
C    1.53226900    0.85191600   -1.86639800
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6. NMR and MS spectra

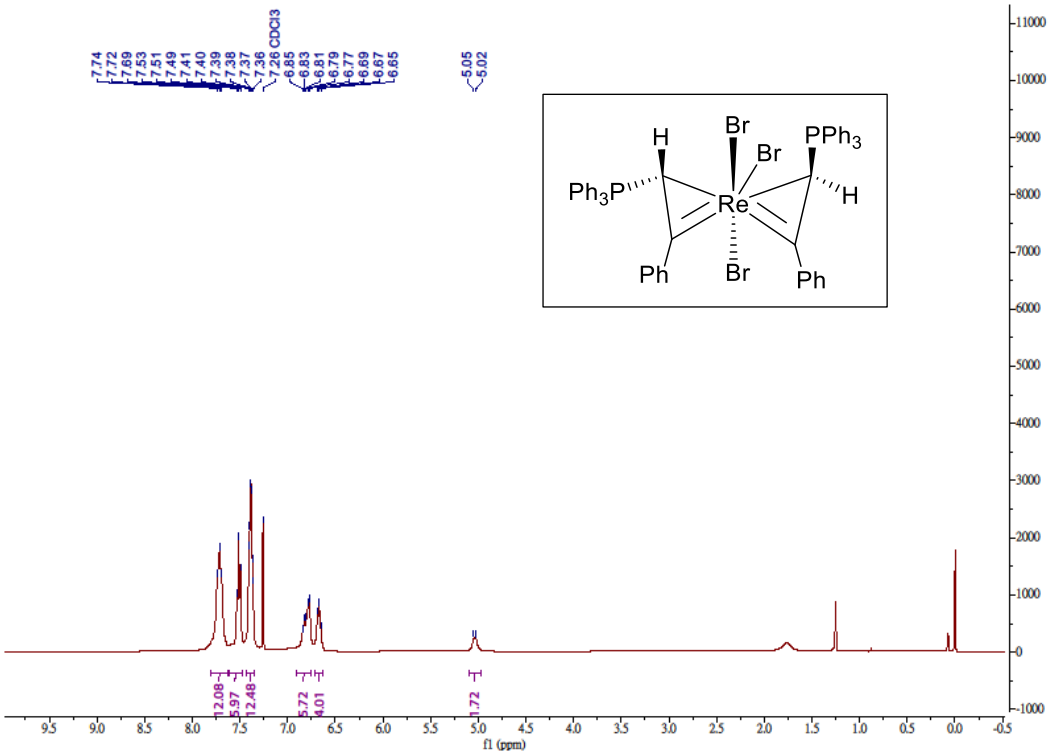


Figure S6. The ^{1}H NMR spectrum of **1b** in $CDCl_3$ at 400 MHz.

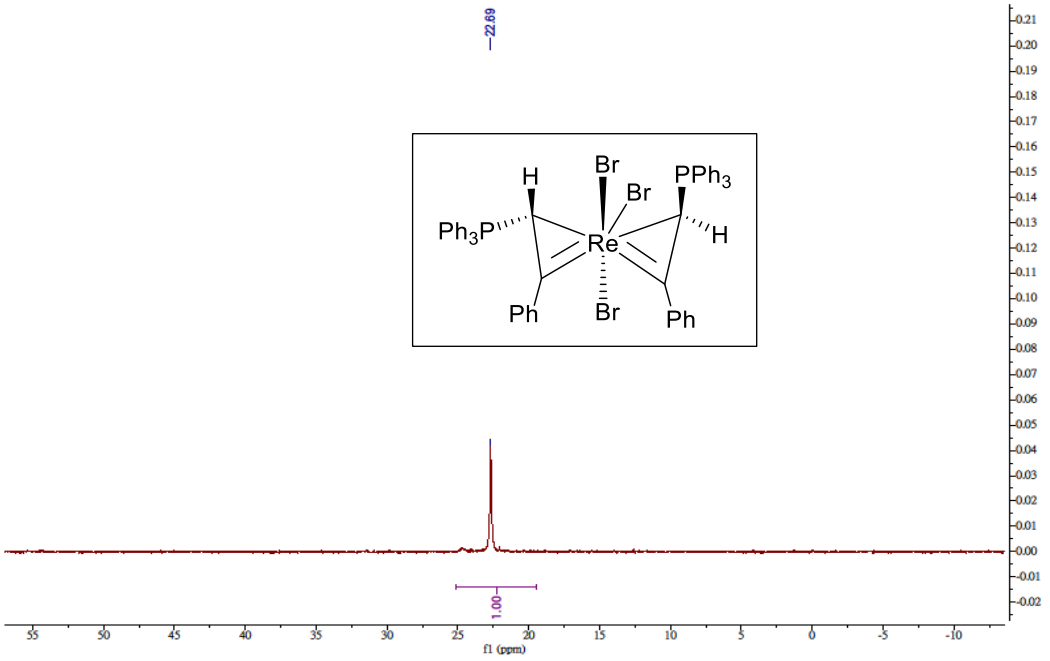


Figure S7. The $^{31}P\{^{1}H\}$ NMR spectrum of **1b** in $CDCl_3$ at 243 MHz.

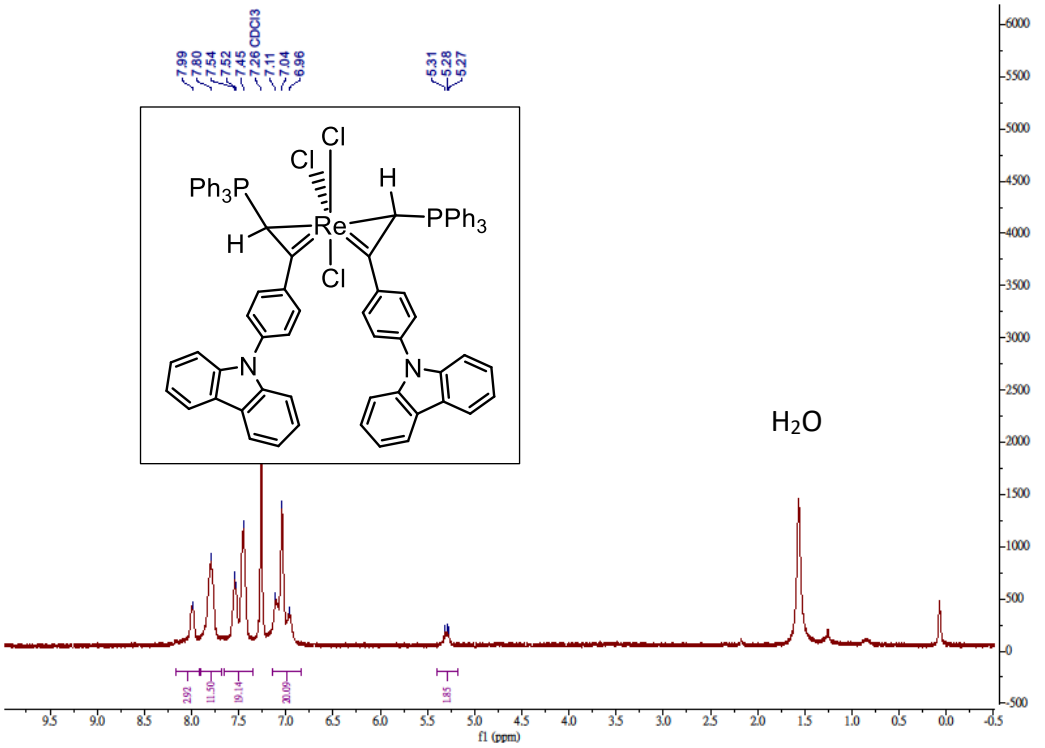


Figure S8. The ^{1}H NMR spectrum of the complex **1d** in $CDCl_3$ at 400 MHz.

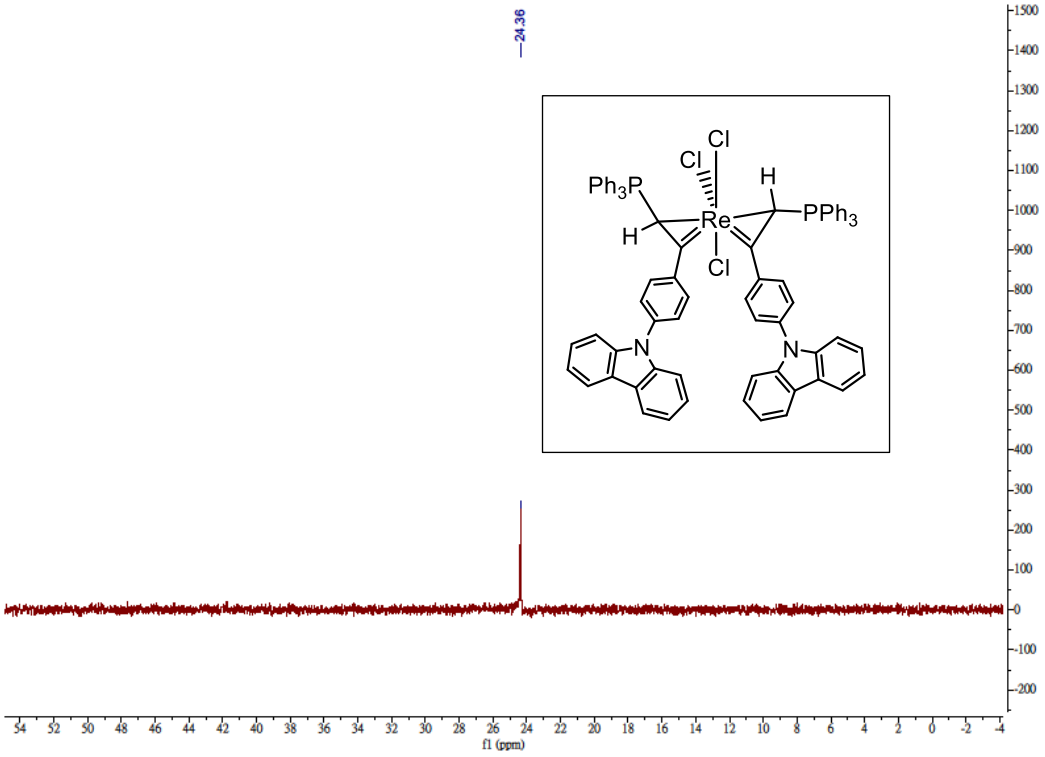


Figure S9. The $^{31}P\{^{1}H\}$ NMR spectrum of the complex **1d** in $CDCl_3$ at 162 MHz.

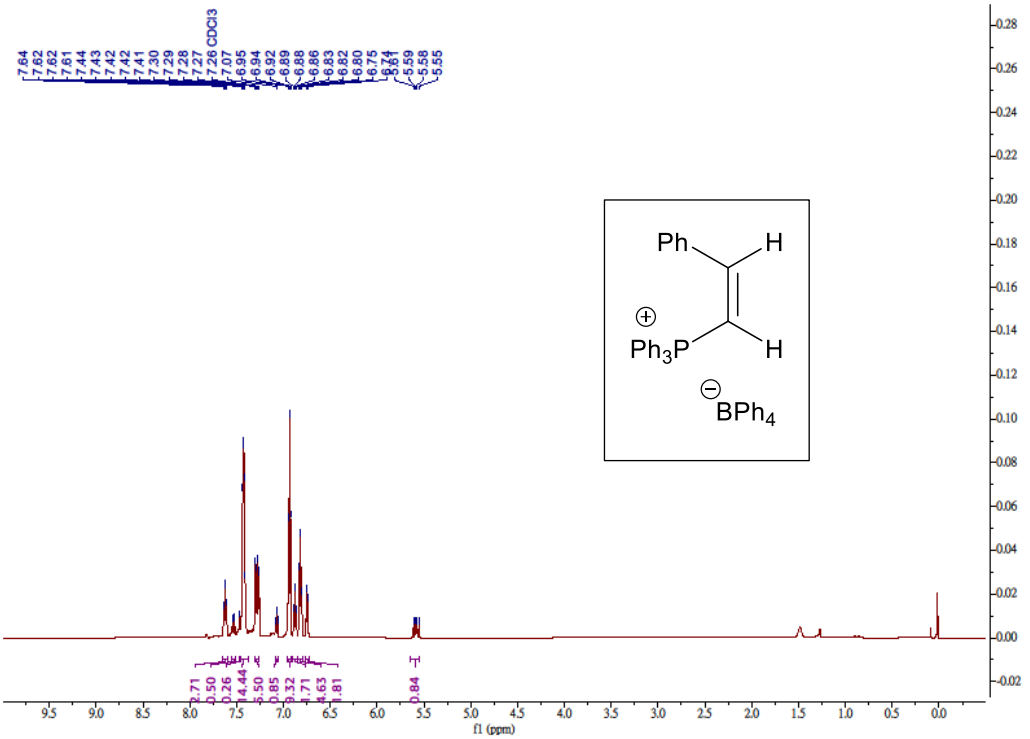


Figure S10. The ^{1}H NMR spectrum of **3a[BPh$_4$]** in $CDCl_3$ at 600 MHz.

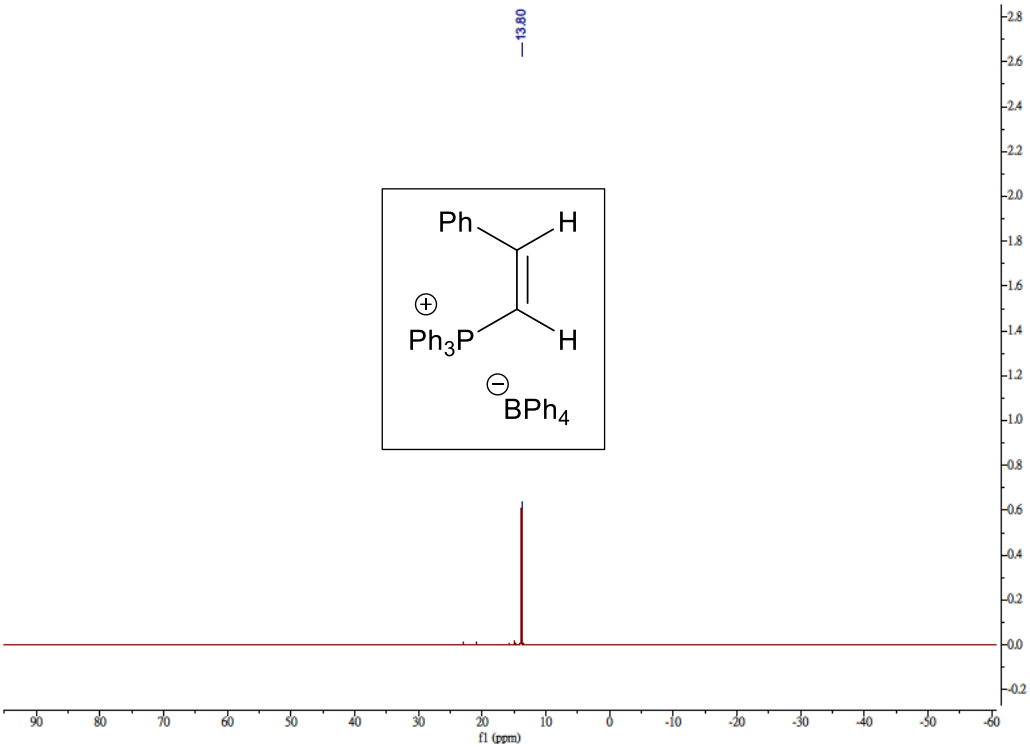


Figure S11. The $^{31}P\{^{1}H\}$ NMR spectrum of **3a[BPh$_4$]** in $CDCl_3$ at 243 MHz.

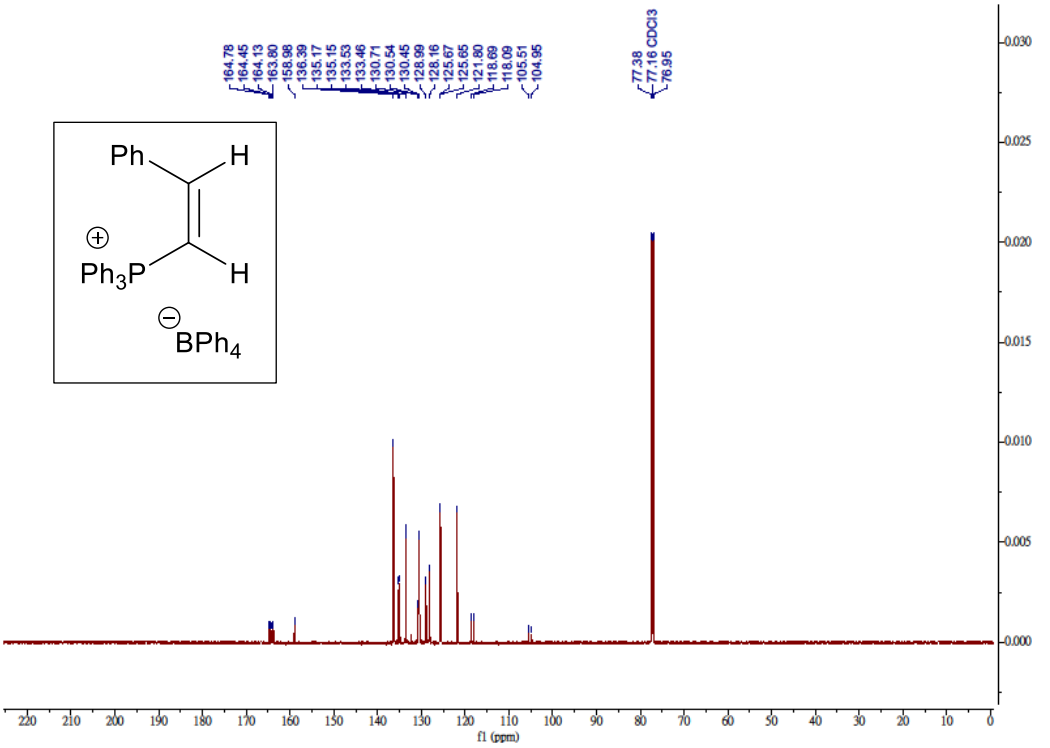


Figure S12. The $^{13}C\{^{1}H\}$ NMR spectrum of **3a[BPh$_4$]** in $CDCl_3$ at 151 MHz.

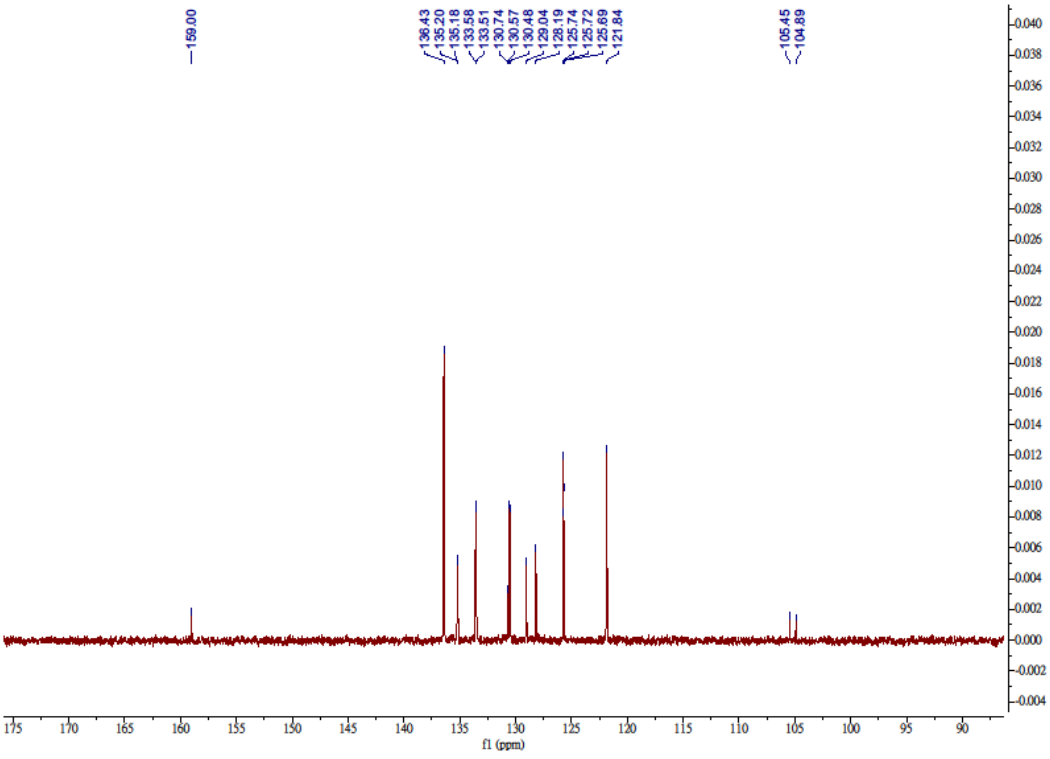


Figure S13. The DEPT-135 NMR spectrum of **3a[BPh$_4$]** in $CDCl_3$ in 151 MHz.

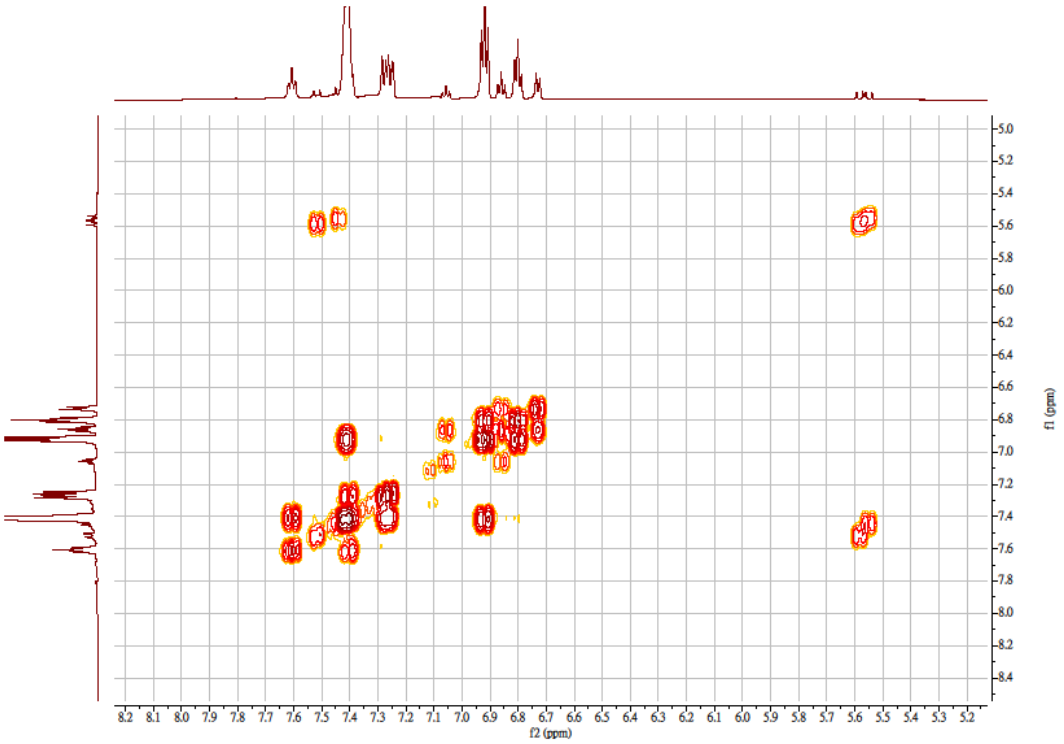


Figure S14. The ^{1}H-^{1}H COSY NMR spectrum of **3a[BPh$_4$]** in $CDCl_3$.

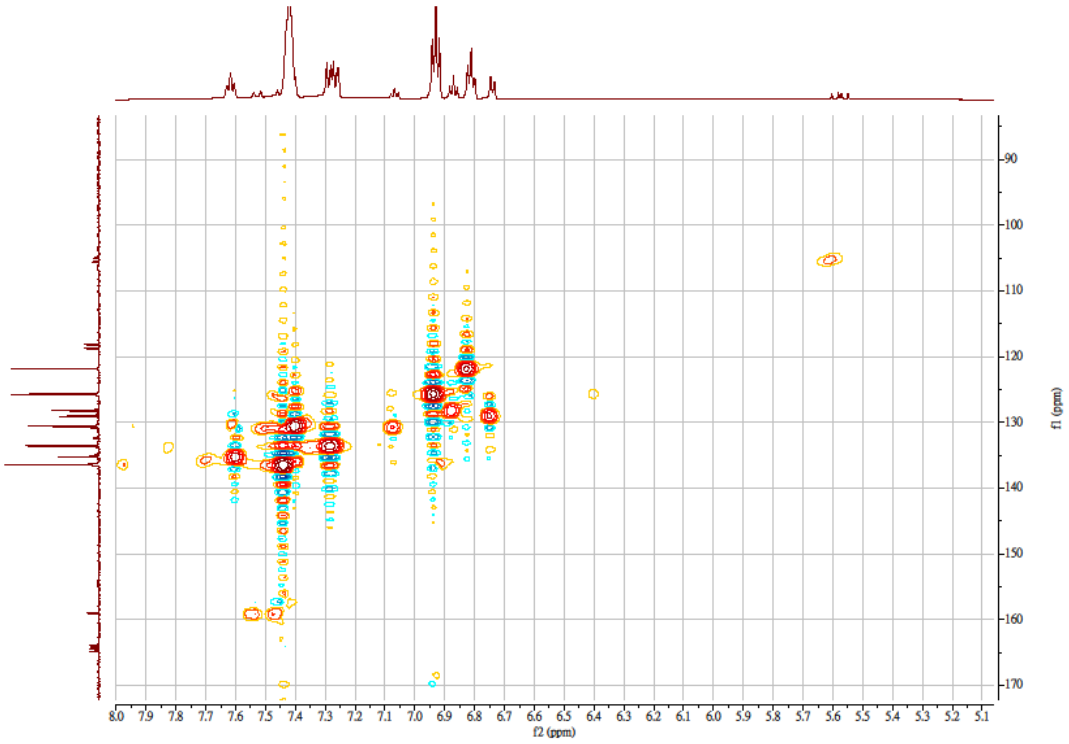


Figure S15. The ^{13}C-^{1}H HSQC NMR spectrum of **3a[BPh$_4$]** in $CDCl_3$.

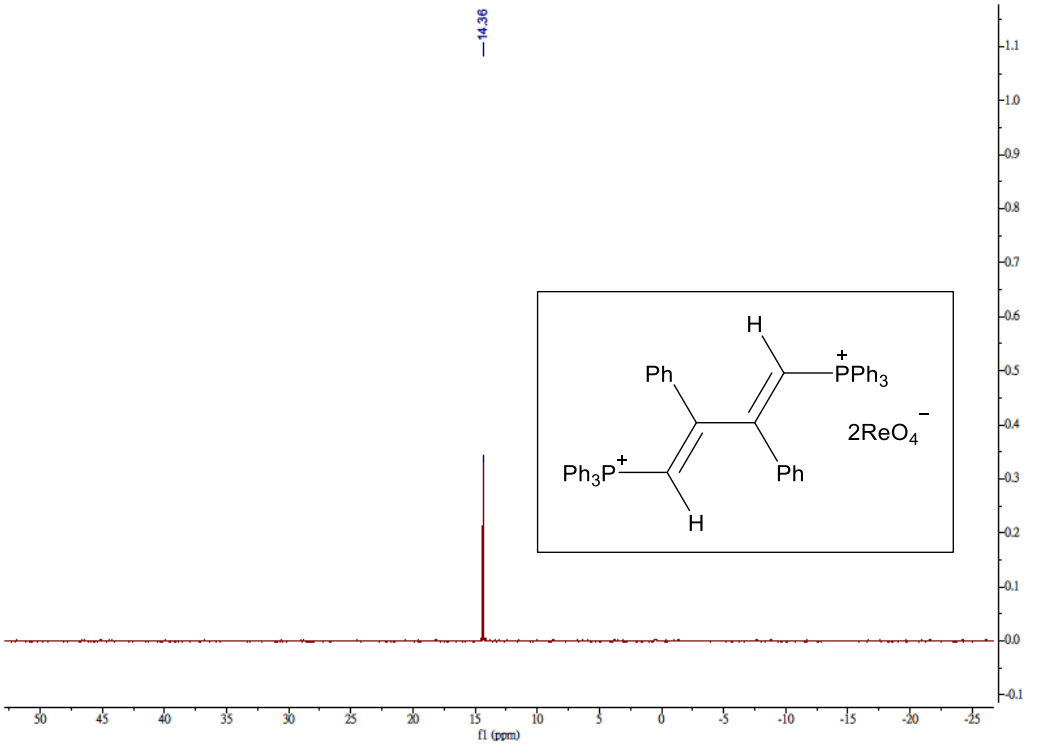


Figure S16. The $^{31}P\{^{1}H\}$ NMR spectrum of **4a(ReO$_4$)$_2$** in CD_2Cl_2 at 243 MHz.

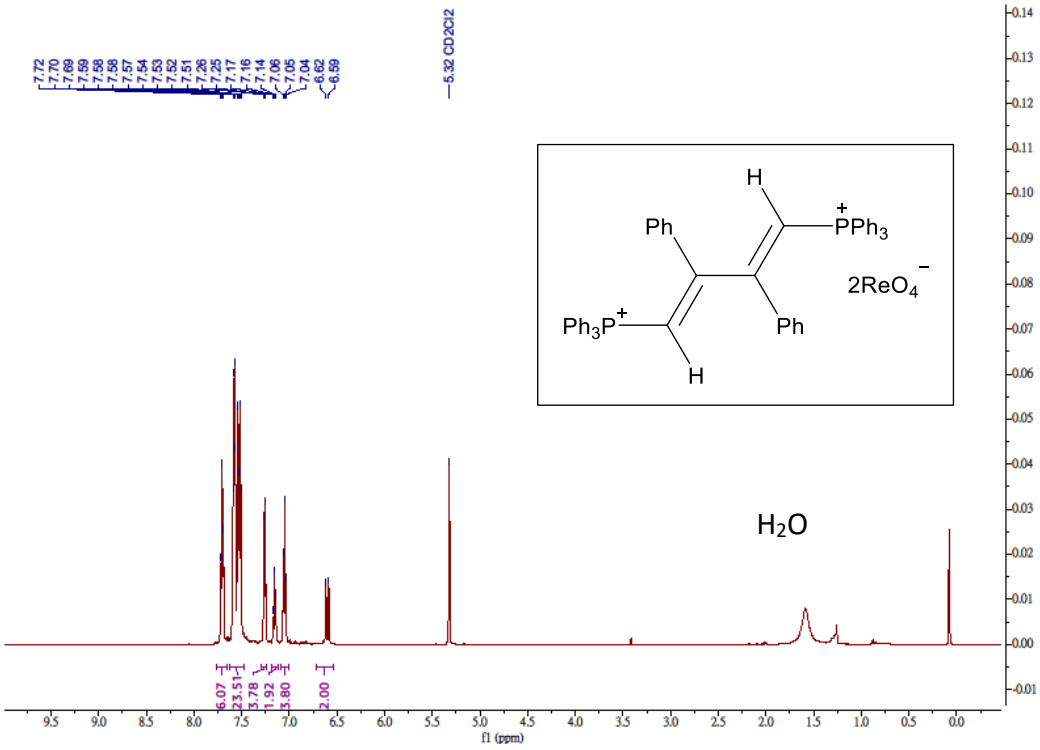


Figure S17. The ^{1}H NMR spectrum of **4a(ReO$_4$)$_2$** in CD_2Cl_2 at 600 MHz.

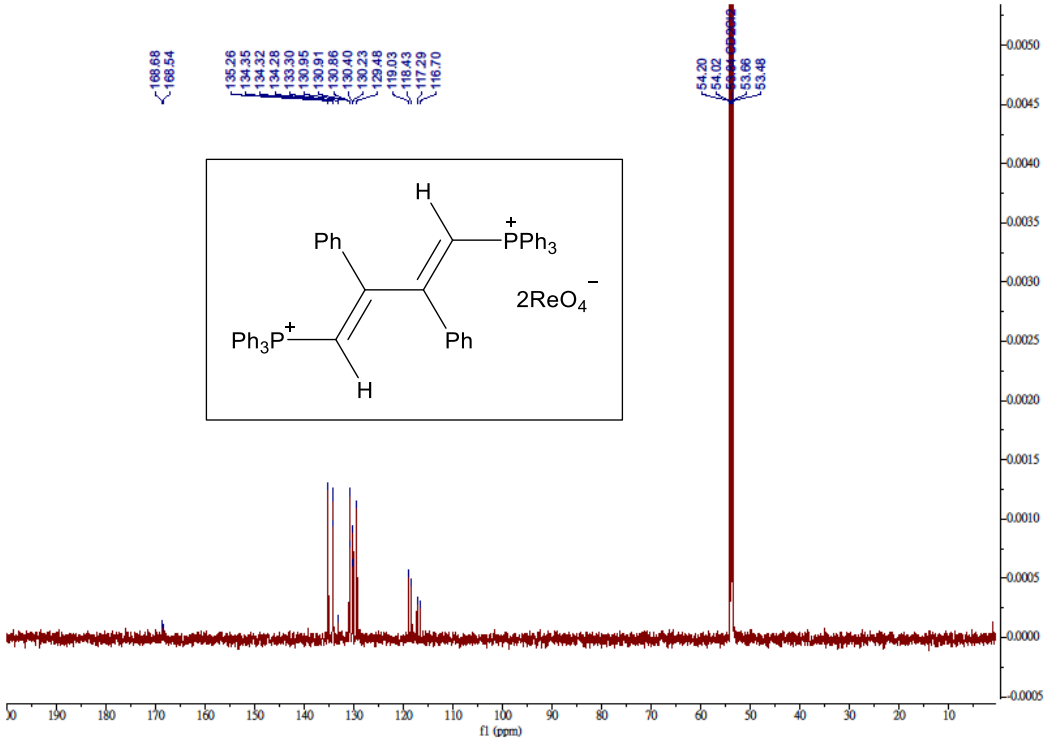
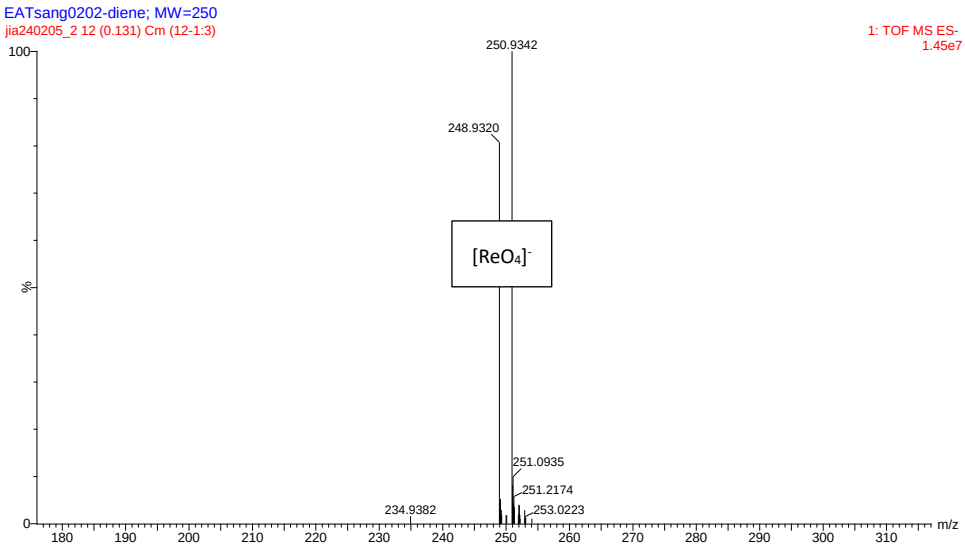


Figure S18. The $^{13}C\{^{1}H\}$ NMR spectrum of **4a[ReO$_4$]$_2$** in CD_2Cl_2 at 101 MHz.



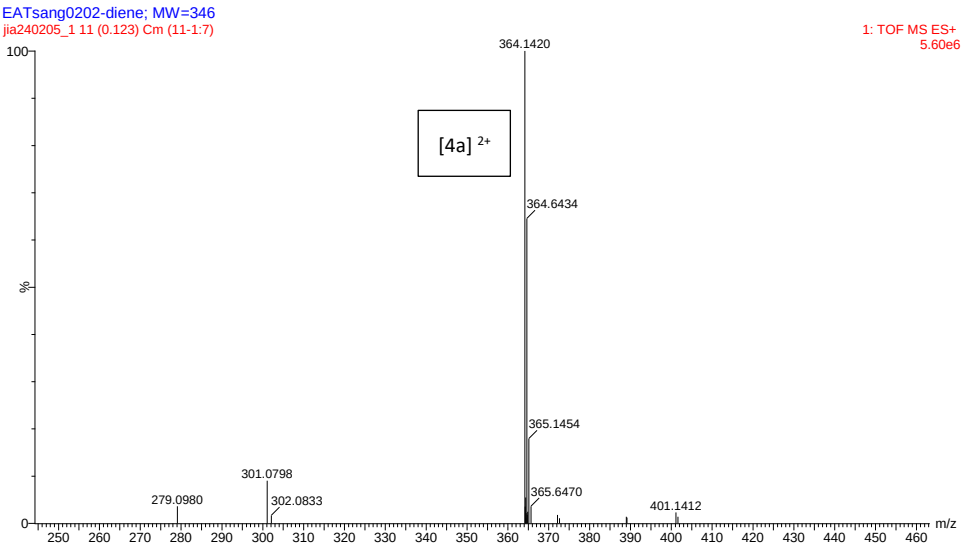


Figure S19. The mass spectra of **4a[ReO$_4$]$_2$** in negative (top) and positive (below) modes. Calculated m/z: ReO_4^-, 250.9360; 1/2[$(Ph_3P)CH{=}C(Ph)\text{-}C(Ph){=}CH(PPh_3)$]$^{2+}$ (1/2[$C_{52}H_{42}P_2$]$^{2+}$, **4a**/2), 364.1375.

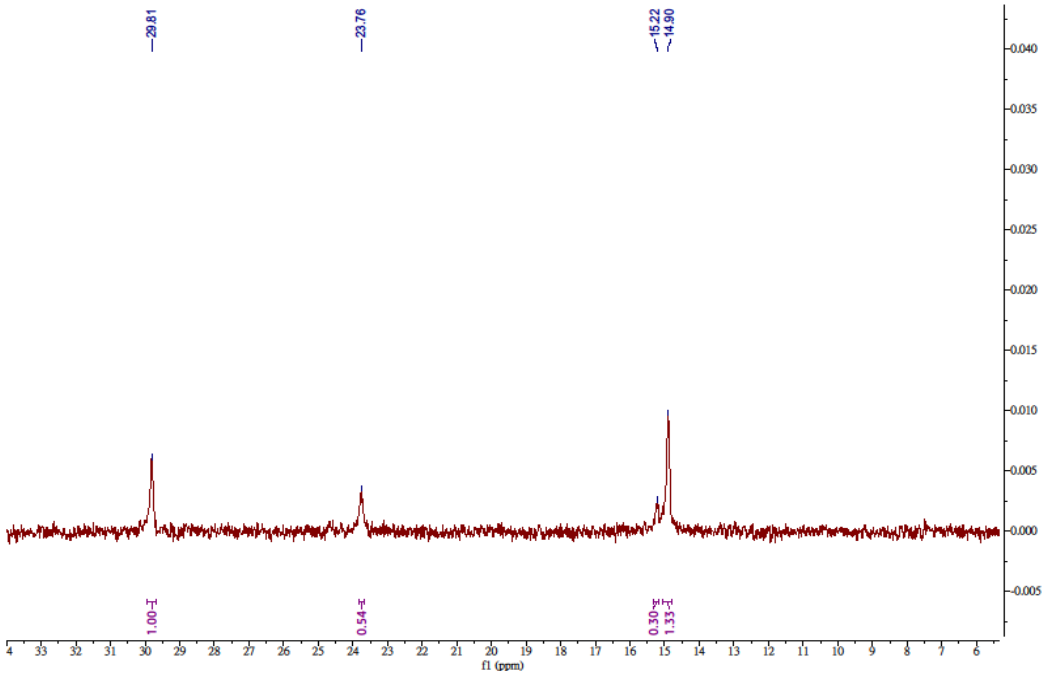


Figure S20. The in-situ $^{3\ 31}P\{^{1}H\}$ NMR spectrum of complex **1a** in $CDCl_3$ after stored under air at room temperature for 14 days. Peak assignments: 29.81, $Ph_3P{=}O$; 23.76, unreacted **1a**, 15.22, $[Ph_3PCH{=}CPh\text{-}CPh{=}CHPPh_3]^{2+}$ (**4a**); 14.90, cis-$[PhCH{=}CHPPh_3]^{+}$ (**3a**).

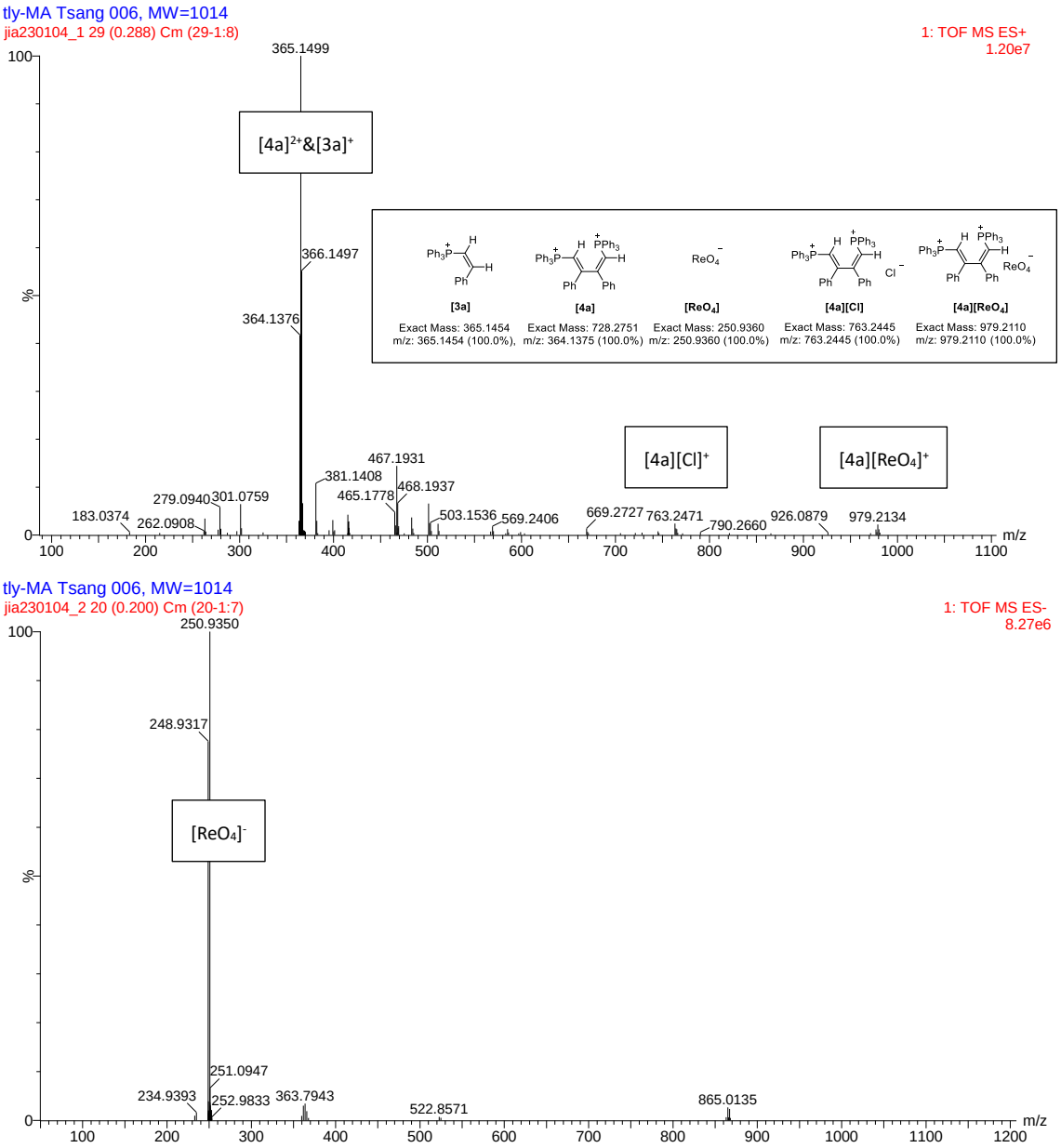


Figure S21. The mass spectra of a $CDCl_3$ solution of the complex **1a** stored under air at room temperature for 14 days in positive (top) and negative (below) modes. Calculated m/z: ReO_4^-, 250.9345; $1/2[(Ph_3P)CH{=}C(Ph)\text{-}C(Ph){=}CH(PPh_3)]^{2+}$ ($1/2[C_{52}H_{42}P_2]^{2+}$, **4a**/2), 364.1375; $[Ph_3PCH{=}CHPh]^+$ ($C_{26}H_{22}P^+$, **3a**), 365.1454; [**4a**·Cl]$^+$, 763.2445; [**4a**·ReO_4]$^+$, 979.2110.

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