SUPPORTING INFORMATION FOR

Octahedral Gyroscope Like Molecules Consisting of Rhenium Rotators Within Cage Like Dibridgehead Diphosphine Stators: Syntheses, Substitution Reactions, Structures, and Dynamic Properties

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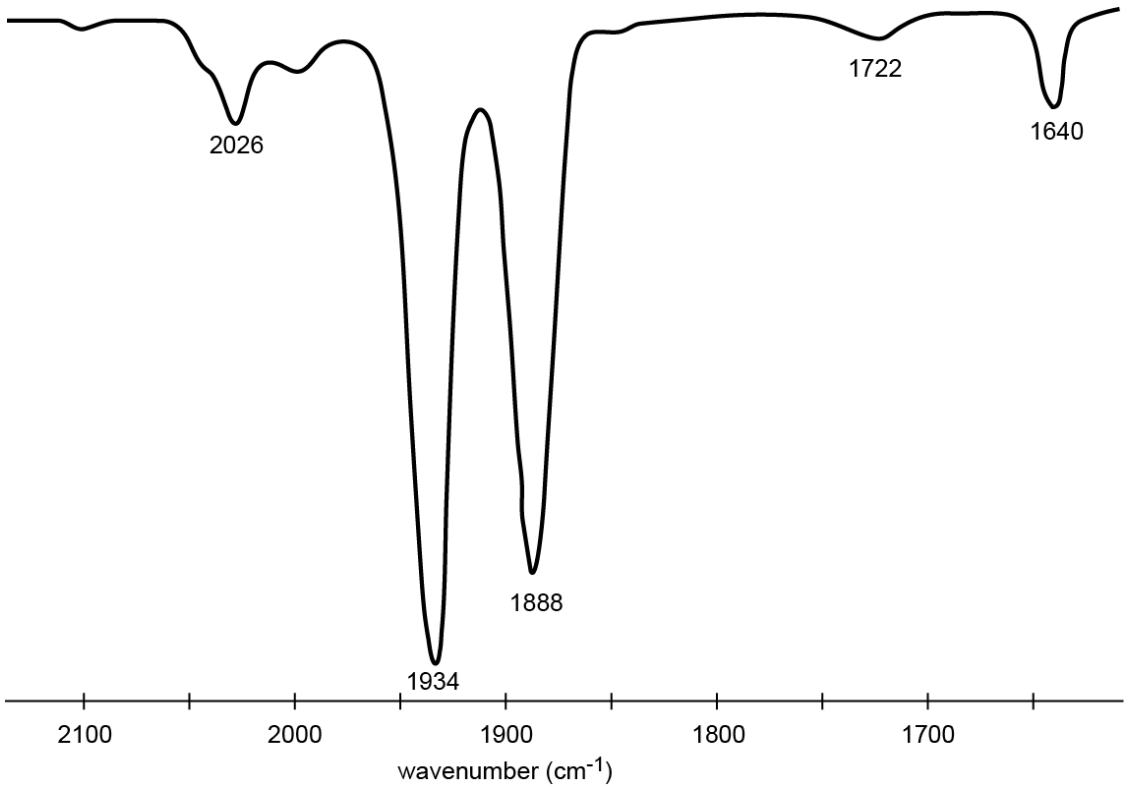

Figure s1. IR spectrum of **2a** (ν_{CO} and adjacent region).

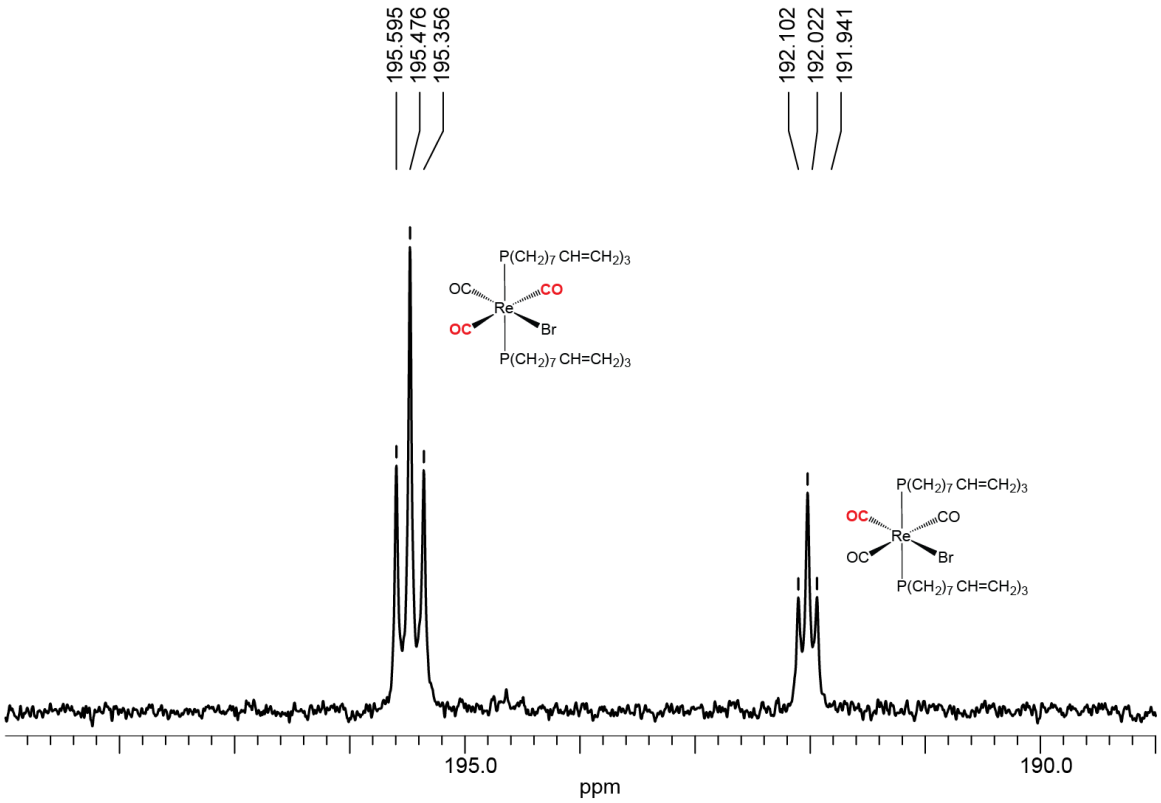

Figure s2. The CO $^{13}C\{^{1}H\}$ NMR signals of **3b**.

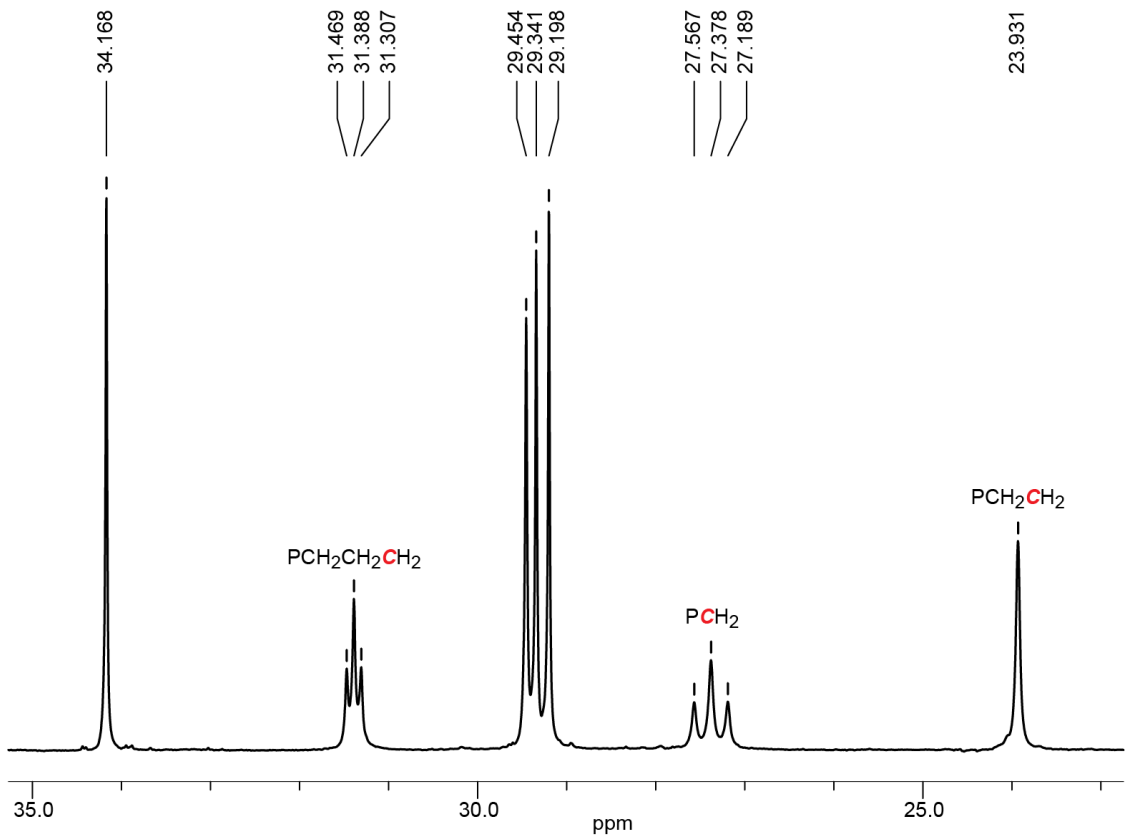

Figure s3. The CH_2 $^{13}C\{^1H\}$ NMR signals of **2b**, illustrating the two virtual triplets found with *mer,trans*-$Re(CO)_3(X)(P((CH_2)_mCH{=}CH_2)_3)_2$.

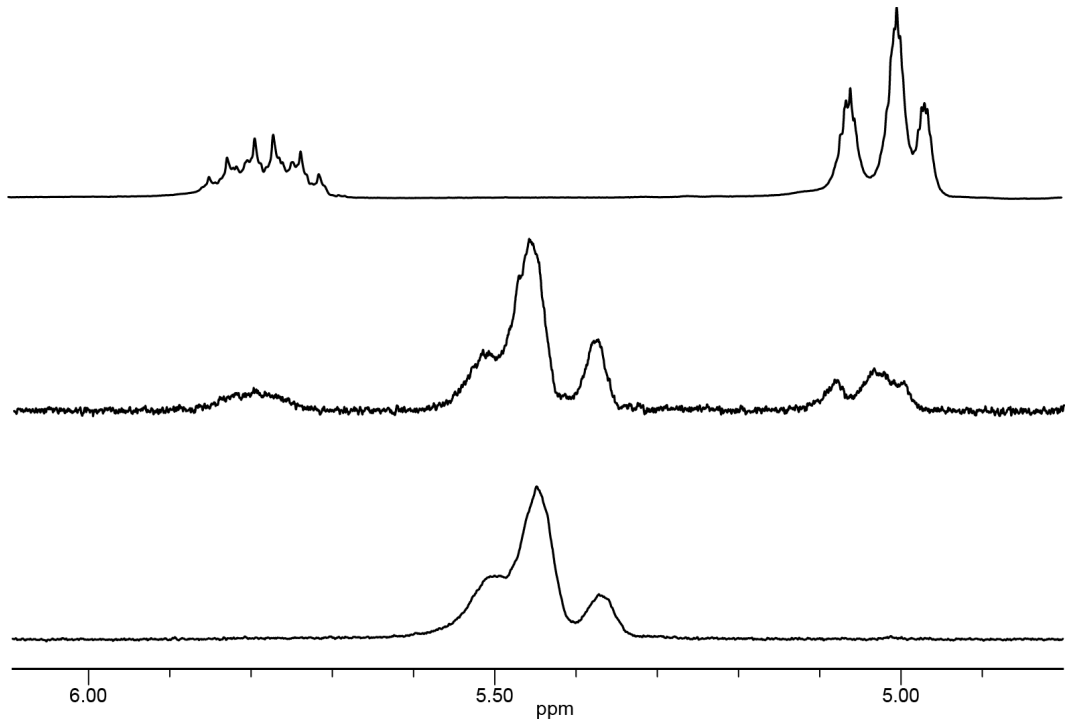

Figure s4. Representative ^1H NMR spectra (=CH region) showing the stages of ring closing metathesis. Top: the terminal $CH{=}CH_2$ signals of **2c**. Middle: partial conversion to **5*c**. Bottom: the CH=CH signals (*Z*/*E*) of **5*c**.

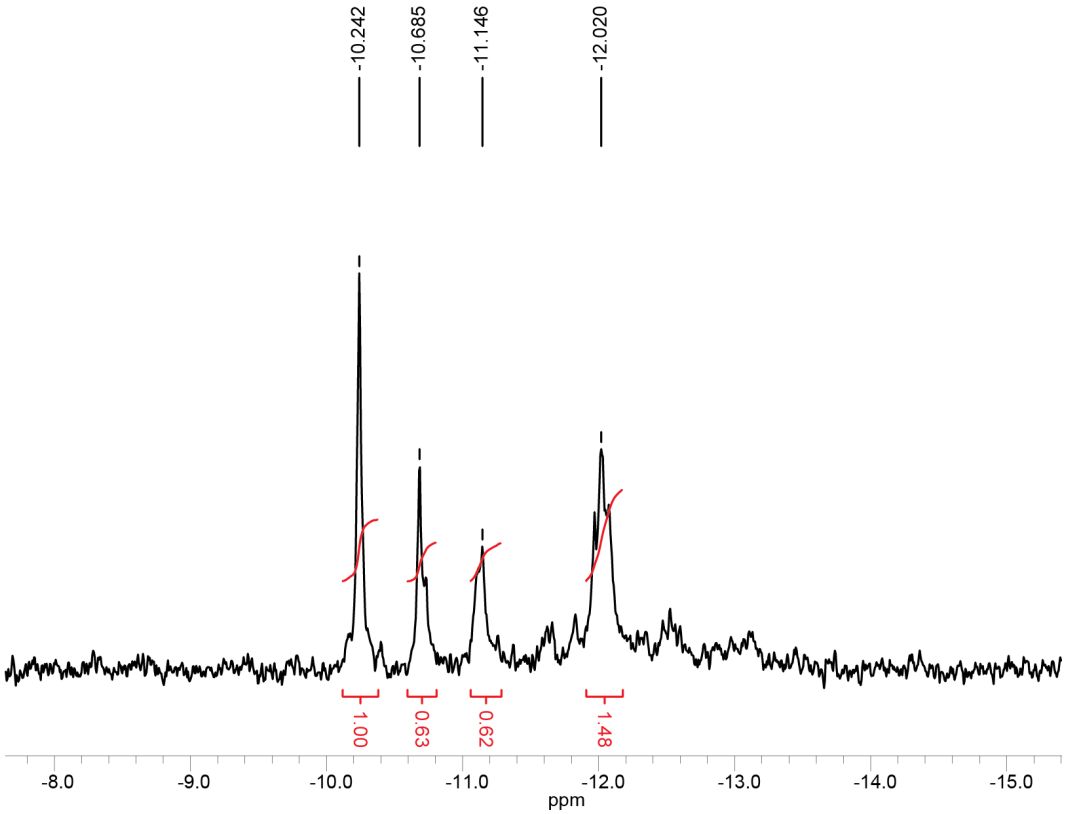

Figure s5. The $^{31}P\{^{1}H\}$ NMR spectrum of crude **6*c** reflecting the possible geometric (*EEE*, *EEZ*, *EZZ*, *ZZZ*) and constitutional (**6'c**) isomers of the major product *mer*,*trans*-$Re(CO)_3(Br)(P((CH_2)_8CH{=}CH(CH_2)_8)_3P)$ (**6c**).

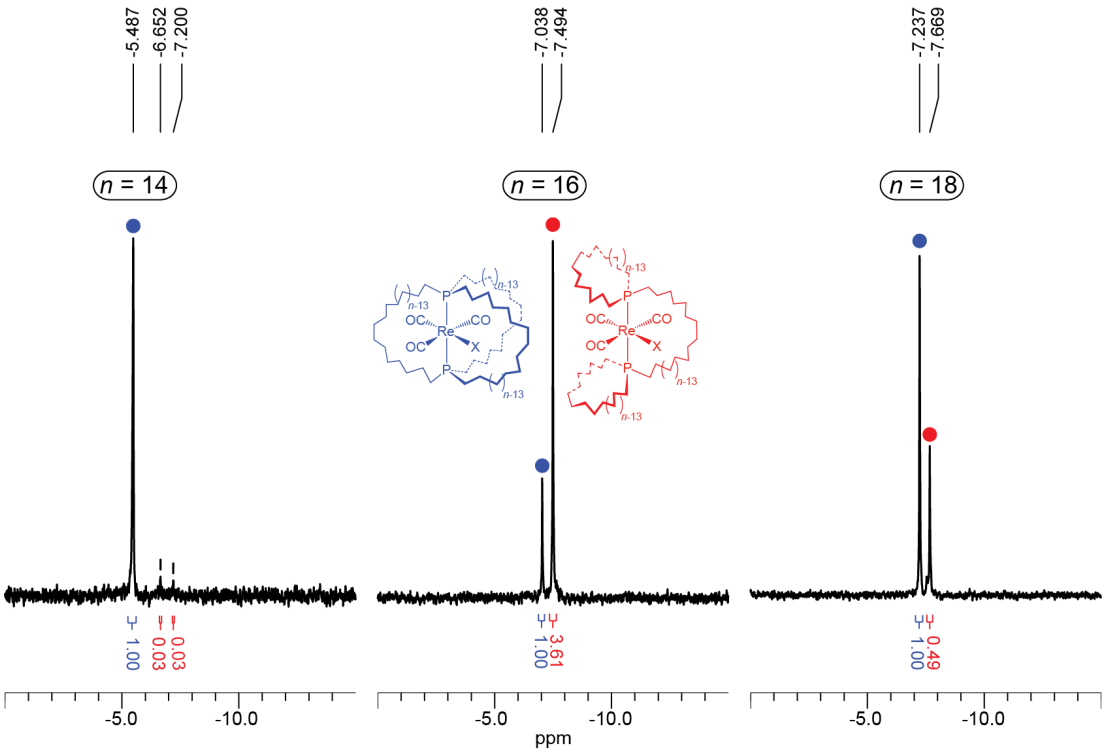

Figure s6. $^{31}P\{^{1}H\}$ NMR spectra of the crude mixtures **7*a** (left), **7*b** (middle), and **7*c** (right).

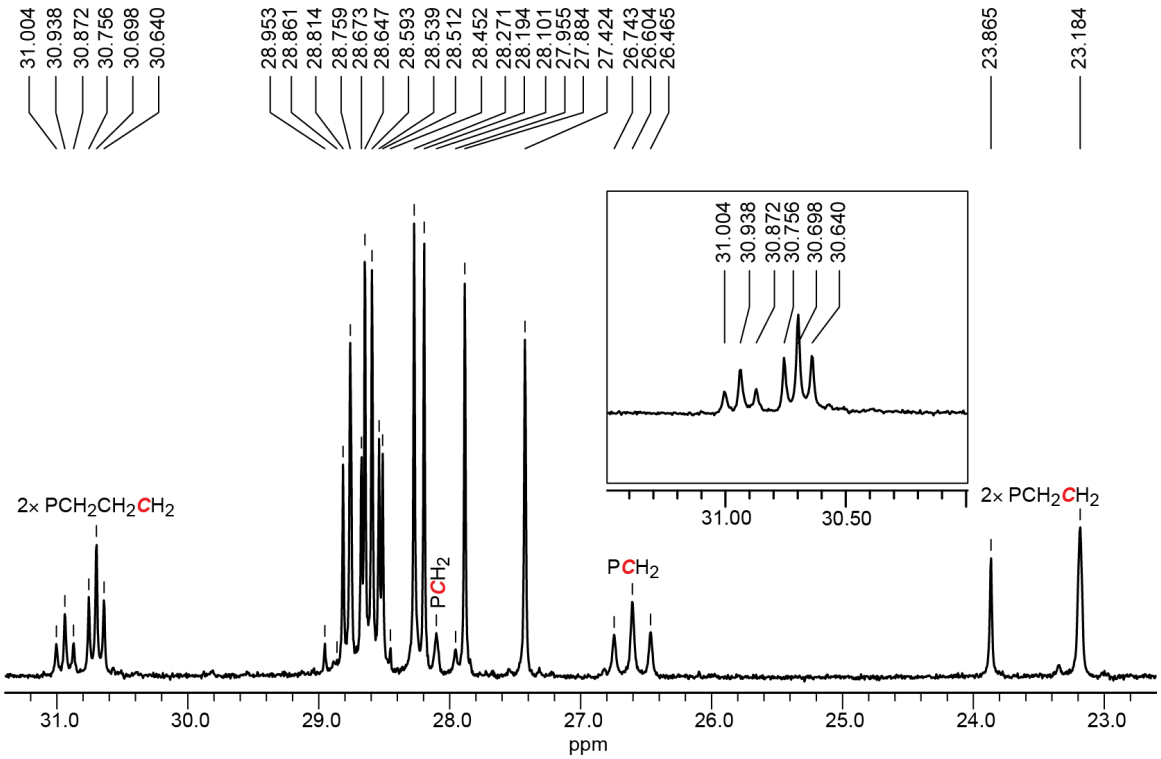

Figure s7. The CH_2 $^{13}C\{^1H\}$ NMR signals of **7'c**, illustrating two sets of peaks (ca. 2:1) including four virtual triplets (2 $P\underline{C}H_2$, 2 $PCH_2CH_2\underline{C}H_2$).

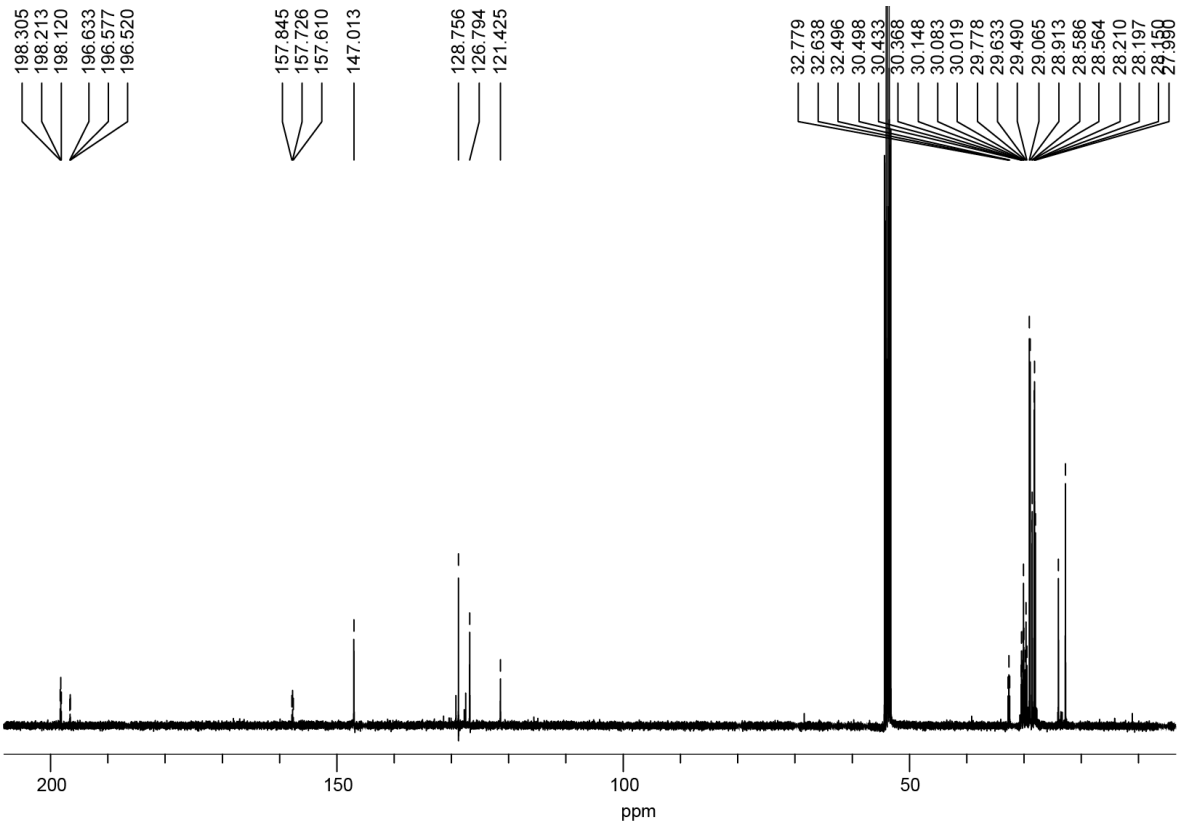

Figure s8. The $^{13}C\{^1H\}$ NMR spectrum of the phenyl complex **12a**.

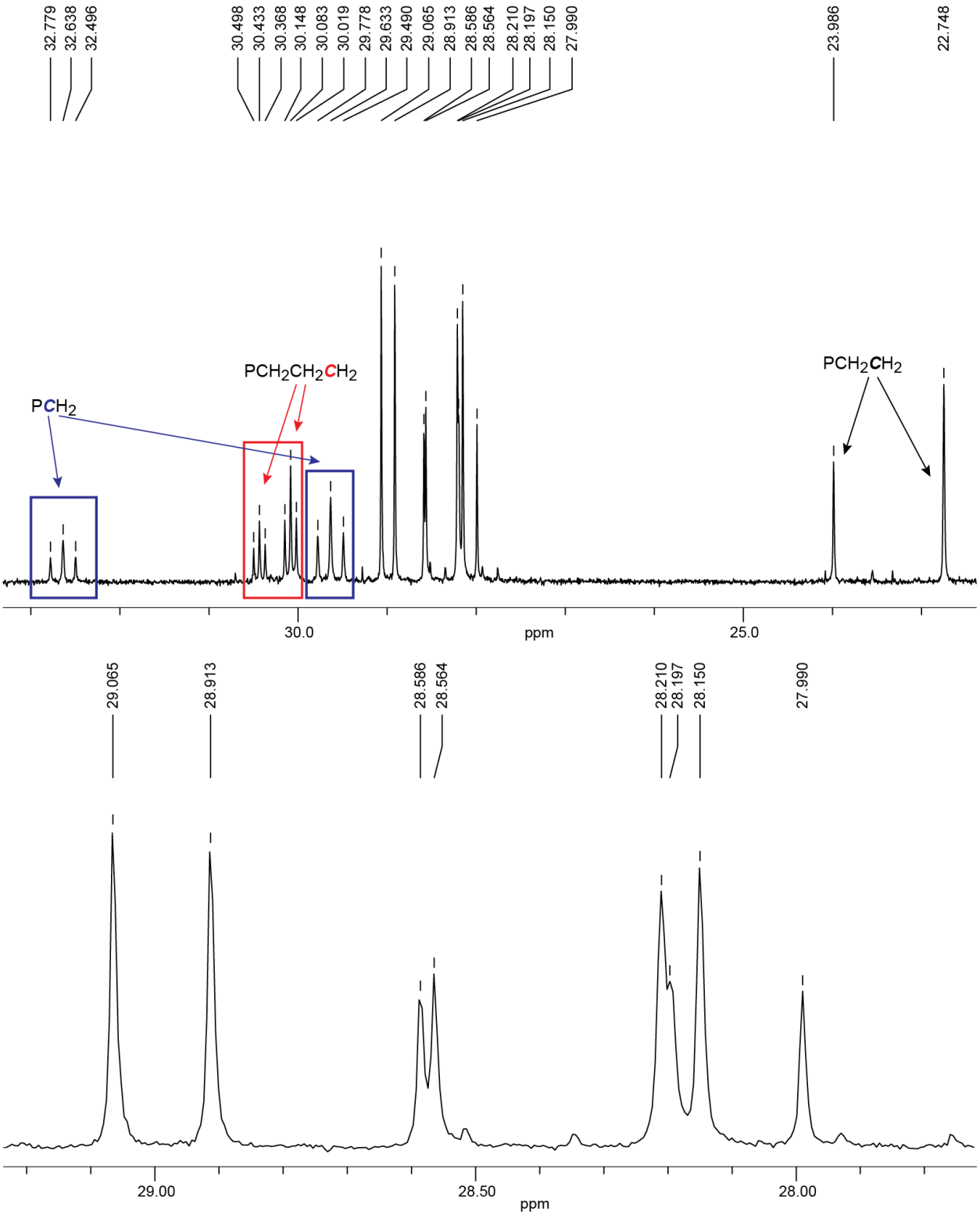

Figure s9. The CH_2 $^{13}C\{^1H\}$ NMR signals of the phenyl complex **12a**, illustrating two sets of peaks (ca. 2:1) including four virtual triplets (2 P$\underline{C}H_2$, 2 $PCH_2CH_2\underline{C}H_2$).

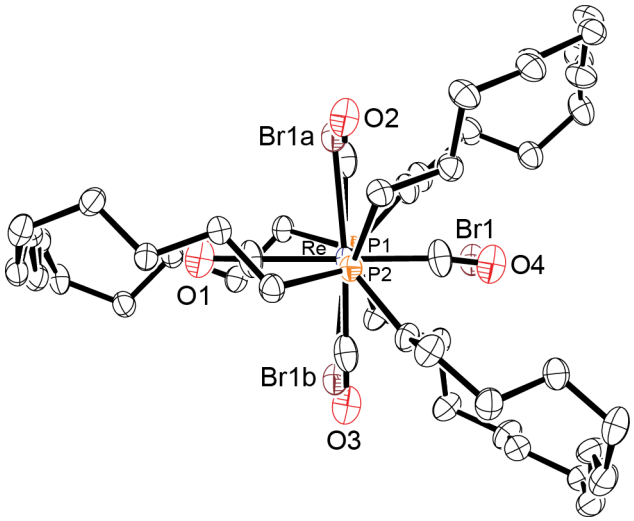

Figure s10. View of **8a** with the P-Re-P axis perpendicular to the plane of the paper and showing the disordered bromide and carbonyl ligands.

Table s1. Thermal properties (°C).

Complex	TGA mass loss (onset)	DSC (T_i/T_e/T_p/T_c/T_f)[a]	mp °C[b] capillary
7a	282	33.33/40.77/41.95/43.45/49.18[c] 187.44/188.71/190.55/ 191.98/192.90[c] 194.33/195.93/200.87/205.17/207.86[c]	230 (>180)[d]
8a	277	209.62/216.57/224.10/232.73/235.68[c] 235.96/237.18/246.10/251.51/253.70[c] 266.73/271.28/275.42/278.52/279.76[c]	254 (>180)[d]
8'a	-	-	70
9a	316	151.35/173.72/176.44/179.24/193.05[c] 289.28/313.78/317.64/318.61/319.39[c]	278 (>265)[d]
11a	264	-	225 (>173)[d]
12a	-	-	200 (>172)[d]
13a	200	74.41/81.23/148.43/197.41/199.37[e]	175 (>149)[d]

[a]Cammenga, H. K.; Epple, M. Basic Principles of Thermoanalytical Techniques and Their Applications in Preparative Chemistry. *Angew. Chem., Int. Ed.* **1995**, *34*, 1171-1187; Grundlagen der Thermischen Analysetechniken und ihre Anwendungen in der präparativen Chemie. *Angew. Chem.* **1995**, *107*, 1284-1301. The T_e values best represent the temperature of the phase transition or exotherm. [b]Conventional melting point apparatus. [c]Endotherm. [d]Gradual darkening without melting above this temperature. [e]Exotherm.

Table s2. Summary of crystallographic data.[a]

	7a	**8a**	**12a**·THF	**13a**
empirical formula	$C_{45}H_{84}ClO_3P_2Re$	$C_{45}H_{84}BrO_3P_2Re$	$C_{55}H_{97}O_4P_2Re$	$C_{46}H_{87}O_3P_2Re$
formula weight	956.71	1001.17	1070.47	936.30
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1$	$P2_1/n$
unit cell dimensions:				
a [Å]	13.5740(3)	13.6121(3)	18.8338(1)	13.6068(2)
b [Å]	17.5266(5)	17.4912(2)	29.0773(2)	17.5243(5)
c [Å]	20.0597(3)	20.1795(4)	22.0132(2)	20.1568(4)
α [°]	90	90	90	90
β [°]	96.773(2)	97.285(1)	112.83(3)	97.266(1)
γ [°]	90	90	90	90
V [Å^3]	4739.02(19)	4765.79(15)	11111.14(14)	4767.78(18)
Z	4	4	8	4
ρ_{calc} [Mg/m^{-3}]	1.341	1.395	1.280	1.304
μ [mm^{-1}]	2.723	3.490	2.285	2.651
F(000)	2000	2072	4512	1968
crystal size [mm^3]	0.20 × 0.20 × 0.20	0.20 × 0.20 × 0.20	0.20 × 0.20 × 0.10	0.10 × 0.10 × 0.10
Θ limit [°]	1.55 to 27.49	2.07 to 27.51	1.00 to 27.51	2.32 to 27.48
index range (h, k, l)	−17, 17; −20, 22; −26, 26	−17, 17; −22, 18; −26, 26	−24, 24; −37, 37; −28, 28	−17, 17; −21, 22; −26, 26
reflections collected	17693	18598	50315	18925
independent reflections	10858	10885	50315	10924
R(int)	0.0195	0.0205	0.0000	0.0317
completeness to Θ	99.8 (27.49)	99.2 (27.51)	99.6 (27.51)	99.8 (27.48)
data/restraints/parameters	10858/0/470	10885/15/457	50315/1/2234	10924/0/479
goodness-of-fit on F^2	1.003	1.038	1.013	0.994
R indices (final) [$I > 2\sigma(I)$]				
R_1	0.0310	0.0318	0.0383	0.0337
wR_1	0.0788	0.0756	0.0853	0.0678
R indices (all data)				
R_2	0.0519	0.0508	0.0560	0.0754
wR_2	0.0919	0.0846	0.0991	0.0791
largest diff. peak and hole [eÅ^{-3}]	2.874 and −1.262	1.129 and −1.648	0.874 and −0.977	0.776 and −1.034

[a]Data common to all structures: T = 173.15 K; λ = 0.71073 Å; diffractometer = Nonius KappaCCD.

Table s3. Key crystallographic angles (°).

	7a	**8a**[a]	**12a**(1)[b]	**12a**(2)[b]
P-Re-P	171.99(2)	173.12(3)	169.89(5)	174.45(5)
O<u>C</u>-Re-<u>C</u>O$_{cis}$	89.64/89.17(13)	89.33/90.83(17)	87.65/87.35(2)	87.10/90.25(2)
O<u>C</u>-Re-<u>C</u>O$_{trans}$	178.80(12)	179.84(19)	174.96(2)	176.89(2)
O<u>C</u>-Re-X$_{cis}$[c]	90.08/91.11(9)	90.88/88.96(13)	89.89/95.14(2)	90.32/92.36(2)
O<u>C</u>-Re-X$_{trans}$[c]	179.72(10)	179.65(11)	175.47(2)	177.08(2)
Re-C-O	178.9(3)/179.4(3)/179.0(3)	179.6(4)/175.8(5)/177.8(4)	174.8(5)/175.1(5)/177.0(6)	176.1(5)/177.7(5)/174.8(5)
P-Re-<u>C</u>O	89.58(8)/93.80(10)/90.37(8)	88.58(13)/93.88(10)/91.45(12)	94.49(16)/86.51(15)/94.11(16)	91.26(17)/94.90(15)/87.35(17)
	91.01(10)/94.19(10)/89.21(8)/	90.86(13)/92.97(10)/89.09(12)	88.41(16)/91.45(15)/95.69(16)	89.60(16)/90.62(15)/92.05(16)
P-Re-X[c]	86.14(3)	86.40(2)	82.29(13)	86.54(12)
	85.87(3)	86.75(2)	88.04(13)	87.97(12)
C[d]-P-P-C[d]	25.28	25.16	−26.29	−18.98
C[e]-P-P-C[e]	22.09	22.63	−18.55	−15.61
C[f]-P-P-C[f]	22.56	22.07	−24.17	−22.98
C[g]-P-P-<u>C</u>O(1)	46.11/−23.55	46.87/−24.81	44.18/−68.34	−9.70/9.25
C[g]-P-P-<u>C</u>O(2)	11.37/13.91	14.08/11.08	6.77/−25.28	−47.67/24.66
C[g]-P-P-<u>C</u>O(3)	−25.74/47.82	−21.34/43.97	−38.89/12.65	−78.31/62.66
C[g]-P-P-X[c]	70.40/−48.31//−48.39/70.95[h]	71.45/−48.82//−48.26/70.34[h]	54.78/−81.03//−59.03/34.87[h]	17.93/−33.59//−102.86/83.82[h]

	12a(3)[b]	**12a**(4)[b]	**13a**[a]
P-Re-P	169.44(4)	168.98(4)	173.38(3)
O<u>C</u>-Re-<u>C</u>O$_{cis}$	87.08/88.05(3)	88.01/86.68(2)	89.74/90.57(17)
O<u>C</u>-Re-<u>C</u>O$_{trans}$	174.13(2)	173.66(2)	179.45(14)
O<u>C</u>-Re-X$_{cis}$[c]	95.09/90.04(2)	96.34/89.28(2)	88.62/91.07(17)
O<u>C</u>-Re-X$_{trans}$[c]	175.01(2)	173.20(2)	178.34(16)
Re-C-O	175.4(5)/176.1(5)/175.7(5)	175.3(5)/175.8(5)/176.0(5)	177.4(5)/179.5(4)/179.0(5)
P-Re-<u>C</u>O	88.95(16)/88.38(15)/96.83(16)	87.21(16)/90.05(15)/97.45(16)	91.60(10)/93.63(10)/86.82(10)
	88.00(16)/95.54(15)/93.10(16)	88.18(16)/95.49(15)/92.38(15)	89.24(10)/92.94(10)/86.61(10)
P-Re-X[c]	87.72(13)	88.00(13)	88.79(10)
	82.49(13)	82.56(13)	90.56(10)
C[d]-P-P-C[d]	−23.20	32.71	25.17
C[e]-P-P-C[e]	−22.00	35.25	22.48
C[f]-P-P-C[f]	−24.91	30.47	21.59
C[g]-P-P-<u>C</u>O(1)	8.90/32.09	75.37/−44.90	70.88/−48.39//−47.68/69.23[h]
C[g]-P-P-<u>C</u>O(2)	−39.62/14.66	44.27/11.57	14.11/11.02
C[g]-P-P-<u>C</u>O(3)	−71.79/49.75	3.12/38.39	−23.00/45.48
C[g]-P-P-X[c]	32.12/−54.16//−84.32/61.14[h]	88.08/−52.81//−30.77/61.24[h]	47.66/−26.10

[a]Values for the dominant $Re(CO)_3(X)$ rotamer. [b]Values for the four independent molecules of **12a** in the unit cell. [c]X = Cl, Br, CH_3, or C_{ipso} [d]First methylene chain for which the carbonyl ligand (**7a**, **8a**, **12a**) or the methyl ligand (**12a**) occupies the macrocycle "hole". [e]Second methylene chain. [f]Third methylene chain. [g]Torsion angles between the ligand and the nearest methylene chain (first carbon atom of macrocycle). [h]Two methylene chains are equally spaced from the ligand, so the angles for both chains are given (four angles total).

■ REFERENCES

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(s2) (a) Structural characterization of *mer,trans*-$Re(CO)_3(Br)(PPh_2OMe)_2$: Carballo, R.; García-Fontán, S.; Vázquez-López, E. M.; Losada-González, P; Rodríguez-Seoane, P. Crystal structure of *mer-trans*-bromo-tricarbonyl-bis(diphenylmethylphosphinite)rhenium(I), $[ReBr(CO)_3\{PPh_2(OMe)\}_2$ (I) and its carbon tetrachloride solvate, $[ReBr(CO)_3\{PPh_2(OMe)\}_2 \cdot 2CCl_4$ (II). *Z. Kristallogr.* **1998**, *213*, 379-381. (b) For a closely related *fac* complex, see: Carbillo, R.; Castiñeiras, A.; García-Fontán, S.; Losada-González, P; Abram, U.; Vázquez-López, E. M. Synthesis, structure and reactivity of bromo- and aquatricarbonylrhenium(I) phosphinite and phosphonite derivatives. *Polyhedron* **2001**, *20*, 2371-2383.

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