

Supporting Information

Mechanochemical strategy for oxidative addition: remarkable yields and stereoselectivity in the halogenation of organometallic Re(I) complexes

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1. Experimental Section

The experiments were carried out in a Retsch MM400 mill at a frequency of 30 Hz using a 10 mL stainless steel or tungsten carbide milling jar and a single ball made of the same material (7 or 10 mm). ^1H and ^{13}C NMR spectra were recorded on a Varian MERCURY plus-300 or plus-400 spectrometer (300 or 400 MHz). Chemical shift (δ) are given in parts per million. The molecular weight was determined using high-resolution mass spectra (HRMS). FT-IR spectra were collected using a Fourier Diagform-Infrared Attenuated Total Reflection PerkinElmer UATR Two spectrometer in the range 400 cm^{-1} to 4000 cm^{-1} . Room temperature Powder X-Ray Diffraction (PXRD) patterns were collected in the 20 range from 3° to 30° on a Bruker D2 phaser X-ray diffractometer using a $\text{Cu}-K_\alpha(\lambda=1.54 \text{ \AA})$ source equipped with a LinxEye detector and a nickel filter. The X-ray tube was operating at the power setting of 30 kV and 10 mA power. Data analysis was carried out using the Panalytical X'pert Highscore Plus program. Solid-state NMR ^{13}C experiments were performed on a Varian VNMRS 400 MHz spectrometer using a 7.5 mm zirconia rotor spinning at 5.5 KHz. X-ray diffraction data was obtained on Bruker D8 single-crystal X-ray diffractometer equipped with a MoK_α X-ray source and a graphite monochromator. Multi-scan absorption correction (SADABS) was applied. Structures were solved by direct methods and refined using SHELX-97 software.

Table S1. Representative yields of $\text{CpRe}(\text{CO})_2\text{X}_2$ and $\text{Cp}^*\text{Re}(\text{CO})_2\text{X}_2$ (%), no. of steps) with respect to **1** or **1*** in published solution syntheses.

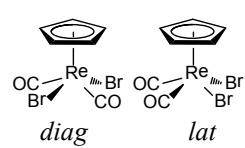
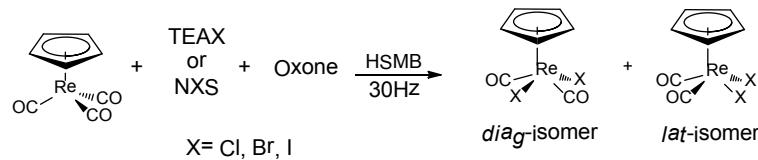
Compound	Steps	Yield	References
	5	<i>diag</i> - (70%, only 5 th step)	F. W. B. Einstein, A. H. Klahn-Oliva, D. Sutton, K. G. Tyres, <i>Organometallics</i> , 1986 , 5, 53
	4	<i>lat</i> - yield not given	F. W. B. Einstein, A. H. Klahn-Oliva, D. Sutton, K. G. Tyres, <i>Organometallics</i> , 1986 , 5, 53
	3	Mixture (<i>diag/lat</i>) 13% only 3 rd step	B. M. Handwerker, K. E. Garrett, K. L. Nagle, G. L. Geoffroy. <i>Organometallics</i> , 1990 , 9, 1562
	2	<i>diag/lat</i> (24%, 28%, overall yield)	A. C. Filippou, B. Lungwitz, G. Kociok-Kohn, I. Hinz. <i>J. Organomet. Chem.</i> 1996 , 524, 133.
	3	Mixture (<i>diag/lat</i>) yield not given	C. F. Barrientos-Penna, A. H. Klahn-Oliva, D. Sutton. <i>Organometallics</i> 1985 , 4, 367
	3	<i>diag/lat</i> (11%, 42%, only 3 rd step)	N. E. Kolobova, Z. P. Valueva, E. I. Kazimirchuk, V. G. Andrianov. Y. T. Struchkov. <i>Izv. Akad. Nauk SSSR, Ser. Khim.</i> 1984 , 920.
	2	Mixture (<i>diag/lat</i>) overall yield 61%	A. C. Filippou, B. Lungwitz, G. Kociok-Kohn, I. Hinz. <i>J. Organomet. Chem.</i> 1996 , 524, 133.
	1	Mixture (<i>diag/lat</i>) 55%	A. N. Nesmeyanov, N. E. Kolobova, Y. V. Makarov, K. N. Anisimov, <i>Izv. Akad. Nauk SSSR, Ser. Khim.</i> 1969 , 1826
	1	<i>diag/lat</i> (39%/13%)	R. B King, R. H Reimann, D. J. Darensbourg, <i>J. Organomet. Chem.</i> , 1975 , 93, C23
	1	<i>diag/lat</i> (38%/13%)	R. B King, R. Reimann, <i>Inorg. Chem.</i> , 1976 , 15, 179.

Table S1. (Contd.) Representative yields of $\text{CpRe}(\text{CO})_2\text{X}_2$ and $\text{Cp}^*\text{Re}(\text{CO})_2\text{X}_2$ (%), no. of steps) with respect to **1** or **1*** in published solution syntheses.

	3	<i>diag/lat</i> (39% 13%, only for 3 rd step)	N. E. Kolobova, Z. P. Valueva, E. I. Kazimirchuk, V. G. Andrianov, Y. T. Struchkov. <i>Izv. Akad. Nauk SSSR, Ser. Khim.</i> 1984 , 920.
	3	Mixture (<i>diag/lat</i>) yield not given	C. F. Barrientos-Penna, A. H. Klahn-Oliva, D. Sutton. <i>Organometallics</i> 1985 , 4, 367
	2	<i>diag-</i> (30%, only 2 nd step)	D. F. Dong, J. K. Hoyano, W. A. G. Graham, <i>Can. J. Chem.</i> , 1981 , 59, 1455
	2	<i>lat</i> yield not given	F. W. B. Einstein, A. H. Klahn-Oliva, D. Sutton, K. G. Tyres, <i>Organometallics</i> , 1986 , 5, 53
	1	<i>diag/lat</i> (35% 26%)	N. E. Kolobova, Z. P. Valueva, E. I. Kazimirchuk, <i>Izv. Akad. Nauk SSSR, Ser. Khim.</i> 1981 , 408.
	4	<i>diag-</i> (90%, only 4 th step)	W. A. Herrmann, R. A. Fischer, E. Herdtweck. <i>Organometallics</i> , 1989 , 8, 2821.
	3	<i>diag-</i> (16%, overall yield)	F. W. B. Einstein, A. H. Klahn-Oliva, D. Sutton, K. G. Tyres, <i>Organometallics</i> , 1986 , 5, 53
	3	<i>diag</i> Yield not provided	C. Leiva, A. H. Klahn, F. Godoy, A. Toro, V. Manriquez, O. Wittke, D. Sutton. <i>Organometallics</i> , 1999 , 18, 339.
	2	<i>lat-</i> (70%, only 2 nd step)	A. H. Klahn, C. Manzur, A. Toro, M. Moore. <i>J. Organomet. Chem.</i> 1996 , 516, 51.
	2	<i>lat-</i> (25%, overall yield)	F. W. B. Einstein, A. H. Klahn-Oliva, D. Sutton, K. G. Tyres, <i>Organometallics</i> , 1986 , 5, 53
	2	<i>lat-</i> (37%, overall yield)	G. Díaz, A. H. Klahn, C. Manzur, <i>Polyhedron</i> , 1988 , 7, 2743
	3	Mixture (<i>diag/lat</i>) yield not given	C. F. Barrientos-Penna, A. H. Klahn-Oliva, D. Sutton <i>Organometallics</i> 1985 , 4, 367
	3	<i>diag-</i> (overall yield 18%)	F. W. B. Einstein, A. H. Klahn-Oliva, D. Sutton, K. G. Tyres, <i>Organometallics</i> , 1986 , 5, 53
	2	<i>diag/lat</i> (27%, 39%) overall yield	F. Zobi, B. Spingler, R. Alberto <i>Eur. J. Inorg. Chem.</i> 2008 , 4205.
	2	<i>lat-</i> (overall yield 29%)	F. W. B. Einstein, A. H. Klahn-Oliva, D. Sutton, K. G. Tyres, <i>Organometallics</i> , 1986 , 5, 53
	1	<i>diag/lat</i> (3.9%, 36.6%)	C. M. Nunn, A. H. Cowley, S. W. Lee. M. G. Richmond. <i>Inorg. Chem.</i> , 1990 , 29, 2105.
	1	Mixture (<i>diag/lat</i>) yield not given	Y.-X. He, D. Sutton. <i>J. Organomet. Chem.</i> 1997 , 538, 49.
	1	<i>diag/lat</i> (25%, 29%)	G. Díaz, A. H. Klahn, C. Manzur, <i>Polyhedron</i> , 1988 , 7, 2743
	1	<i>diag/lat</i> (9%, 19%)	A. J. Rest. et al. <i>Inorg. Chim. Acta</i> , 1997 , 259, 137.
	2	Mixture (<i>diag/lat</i>) yield not given	J. K. Hoyano, W. A. G. Graham, <i>J. Chem. Soc. Chem. Commun.</i> , 1982 , 27
	2	<i>lat-</i> (overall yield 32%)	F. W. B. Einstein, A. H. Klahn-Oliva, D. Sutton, K. G. Tyres, <i>Organometallics</i> , 1986 , 5, 53
	1	<i>diag/lat</i> (11%, 51%)	F. W. B. Einstein, A. H. Klahn-Oliva, D. Sutton, K. G. Tyres, <i>Organometallics</i> , 1986 , 5, 53
	1	<i>diag/lat</i> (8%, 26%)	G. Díaz, A. H. Klahn, C. Manzur, <i>Polyhedron</i> , 1988 , 7, 2743

Table S2. Effect of the halogen source on halogenation of **1**.^[a]



Entry	Source	% conv ^[b]	% <i>diag:lat</i> ^[b]
1	Et ₄ N ⁺ Cl ⁻	90	17:83
2	Et ₄ N ⁺ Br ⁻	99	54:44
3	Et ₄ N ⁺ I ⁻	99	91:9
4	NCS	65	33:67
5	NBS	99	53:47
6	NIS	33	82:18

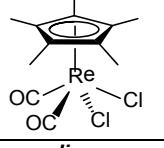
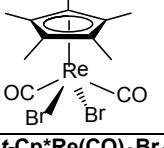
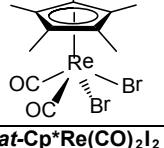
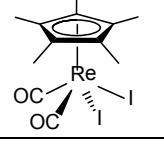
[a] Reaction conditions: Oxone (2 eq.); AX_n (2 eq.), 30 min milling. [b] determined using ¹H NMR.

2. Synthesis of compounds CpRe(CO)₂X₂ and Cp^{*}Re(CO)₂X₂

A mixture of **1** or **1*** (100 mg, 0.298 mmol or 0.246 mmol respectively), oxone (2 equiv) and halide source (2 equiv) was milled using a tungsten carbide ball (10 mm) in a tungsten carbide jar (10 mL) for 30 min at a frequency of 30 Hz in Retsch MM400 mixer mill. (Same results were obtained using stainless steel milling assemblies). After that, the reaction mixture was purified by column chromatography on silica gel (hexane : ethyl acetate ratios from 20:1 to 1:1) to separate the *diag*- and *lat*-isomers.

3. Spectroscopic data for compounds CpRe(CO)₂X₂ and Cp^{*}Re(CO)₂X₂

<i>lat</i> -CpRe(CO) ₂ Cl ₂	<p>FTIR-ATR ν_{max} 3081, 2923, 2036, 1954 cm⁻¹. ¹H-NMR (300 MHz, acetone-d₆) δ 6.55 ppm. ¹³C-NMR (75 MHz, acetone-d₆) δ 98.5, 201.9 ppm. HRMS: Calculated for C₇H₅Cl₂O₂ReNa [M+Na]: 400.9101; found: 400.9097.</p>
<i>diag</i> -CpRe(CO) ₂ Br ₂	<p>FTIR-ATR ν_{max} 3096, 2923, 2050, 1965 cm⁻¹. ¹H-NMR (400 MHz, CDCl₃) δ 5.76 ppm. ¹³C-NMR (75 MHz, CDCl₃) δ 94.0, 182.8 ppm. HRMS: Calculated for C₇H₄Br₂O₂Re [M-1H]: 466.8115; found: 466.8063.</p>
<i>lat</i> -CpRe(CO) ₂ Br ₂	<p>FTIR-ATR ν_{max} 3081, 2922, 2015, 1951 cm⁻¹. ¹H-NMR (400 MHz, acetone-d₆) δ 6.48 ppm. ¹³C-NMR (75 MHz, acetone-d₆) δ 97.4, 199.3 ppm. HRMS: Calculated for C₇H₄Br₂O₂Re [M-1H]: 466.8115; found: 466.8102.</p>
<i>diag</i> -CpRe(CO) ₂ I ₂	<p>FTIR-ATR ν_{max} 3095, 2019, 1972 cm⁻¹. ¹H-NMR (300 MHz, acetone-d₆) δ 6.11 ppm. ¹³C-NMR (75 MHz, acetone-d₆) δ 93.3, 182.6 ppm. HRMS: Calculated for C₇H₅I₂NaO₂Re [M+Na]: 584.7829; found: 584.7817.</p>

<i>lat-Cp[*]Re(CO)₂Cl₂</i> 	FTIR-ATR ν_{max} 2925, 2011, 1921 cm ⁻¹ . ¹H-NMR (300 MHz, CDCl ₃) δ 1.98 ppm. ¹³C-NMR (75 MHz, CDCl ₃) δ 10.4, 108.2, 204.0 ppm. HRMS: Calculated for C ₁₂ H ₁₅ Cl ₂ NaO ₂ Re [M+Na]: 470.9883; found: 470.9892.
<i>diag-Cp[*]Re(CO)₂Br₂</i> 	FTIR-ATR ν_{max} 2922, 2853, 2035, 1955 cm ⁻¹ . ¹H-NMR (300 MHz, CDCl ₃) δ 2.00 ppm. ¹³C-NMR (75 MHz, CDCl ₃) δ 10.5, 105.5, 186.6 ppm. HRMS: Calculated for C ₁₂ H ₁₅ Br ₂ NaO ₂ Re [M+Na]: 558.8863; found: 558.8861.
<i>lat-Cp[*]Re(CO)₂Br₂</i> 	FTIR-ATR ν_{max} 2923, 2009, 1926 cm ⁻¹ . ¹H-NMR (300 MHz, CDCl ₃) δ 2.06 ppm. ¹³C-NMR (75 MHz, CDCl ₃) δ 10.6, 107.0, 201.6 ppm. HRMS: Calculated for C ₁₂ H ₁₅ Br ₂ NaO ₂ Re [M+Na]: 558.8863; found: 558.8861.
<i>lat-Cp[*]Re(CO)₂I₂</i> 	FTIR-ATR ν_{max} 2917, 1999, 1924 cm ⁻¹ . ¹H-NMR (300 MHz, CDCl ₃) δ 2.23 ppm. ¹³C-NMR (75 MHz, CDCl ₃) δ 11.3, 104.8, 199.6 ppm. HRMS: Calculated for C ₁₂ H ₁₅ I ₂ NaO ₂ Re [M+Na]: 654.8611; found: 654.8590.

4. Fourier-transform infrared attenuated total reflectance (FTIR-ATR) spectra of compounds CpRe(CO)₂X₂ and Cp^{*}Re(CO)₂X₂

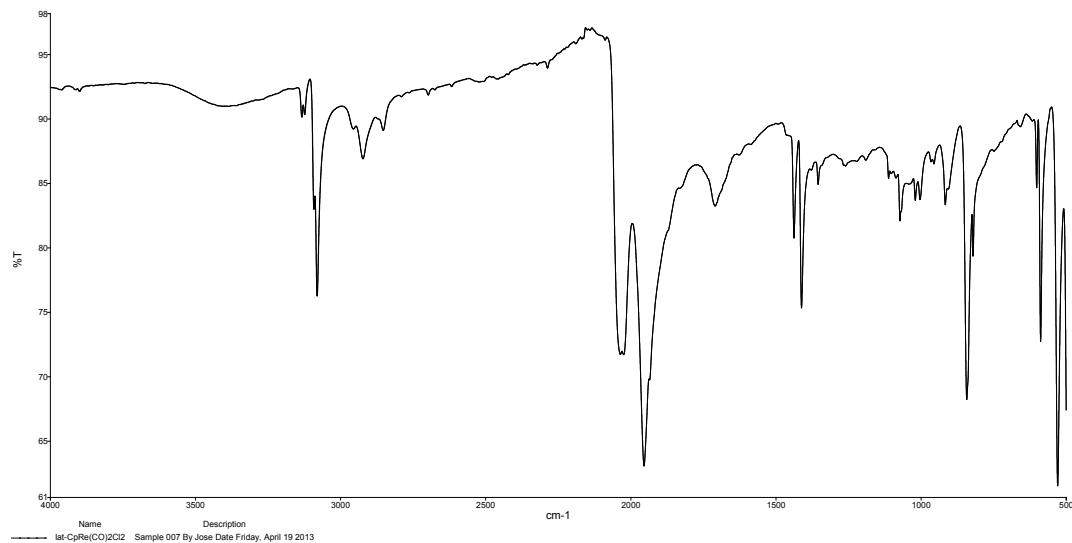


Figure S1. FTIR-ATR spectrum of *lat-CpRe(CO)₂Cl₂*

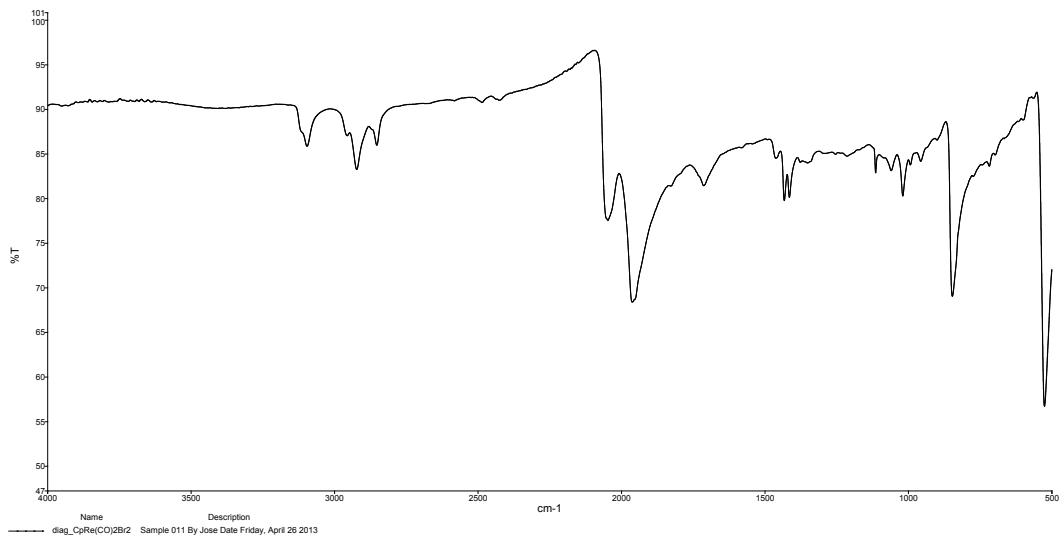


Figure S2. IR spectrum of *diag-2*

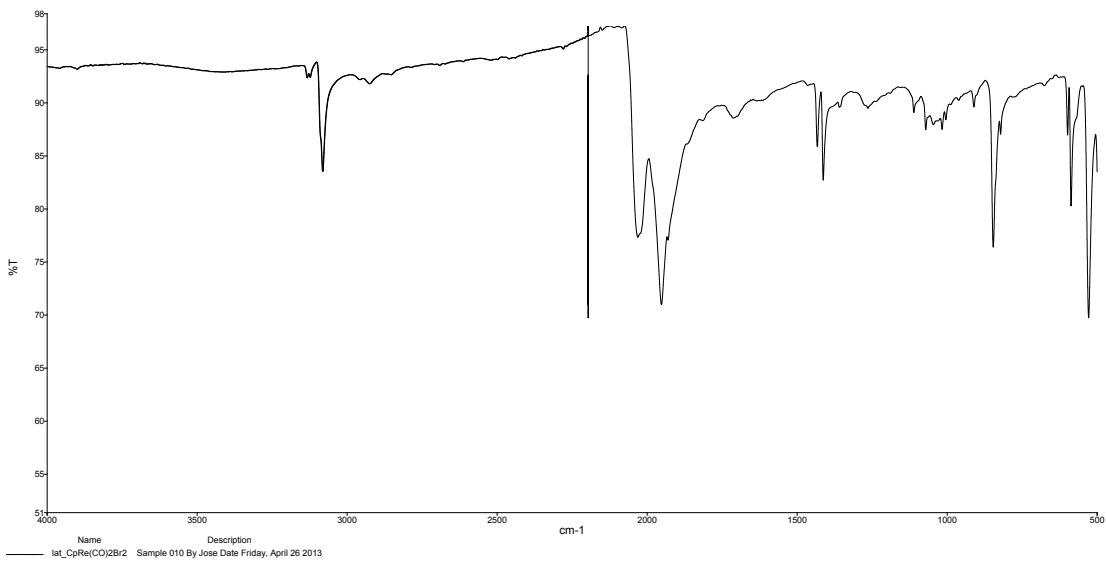


Figure S3. FTIR-ATR spectrum of *lat-2*

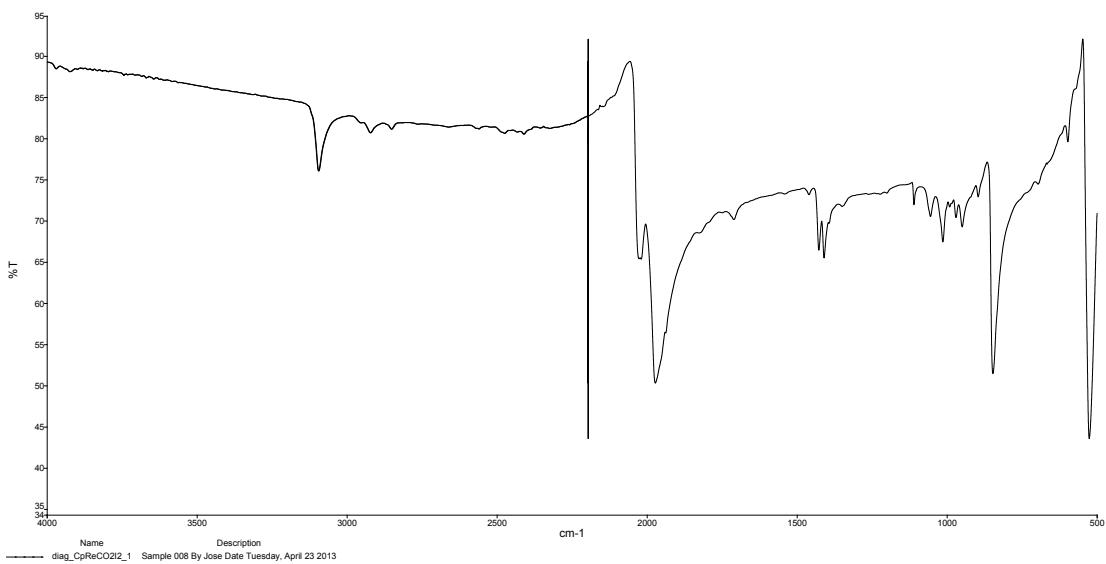


Figure S4. FTIR-ATR spectrum of *diag*-CpRe(CO)₂I₂

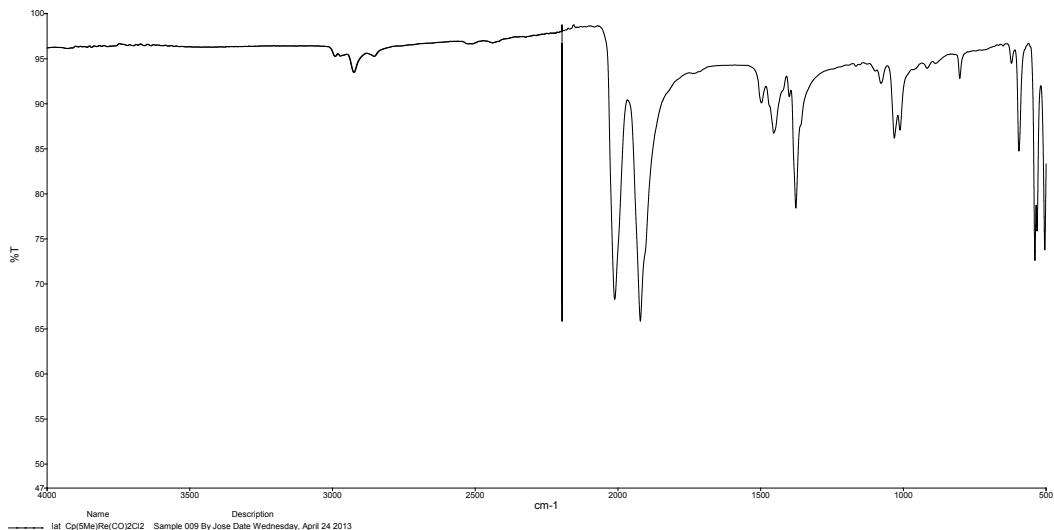


Figure S5. FTIR-ATR spectrum of *lat*-Cp^{*}Re(CO)₂Cl₂

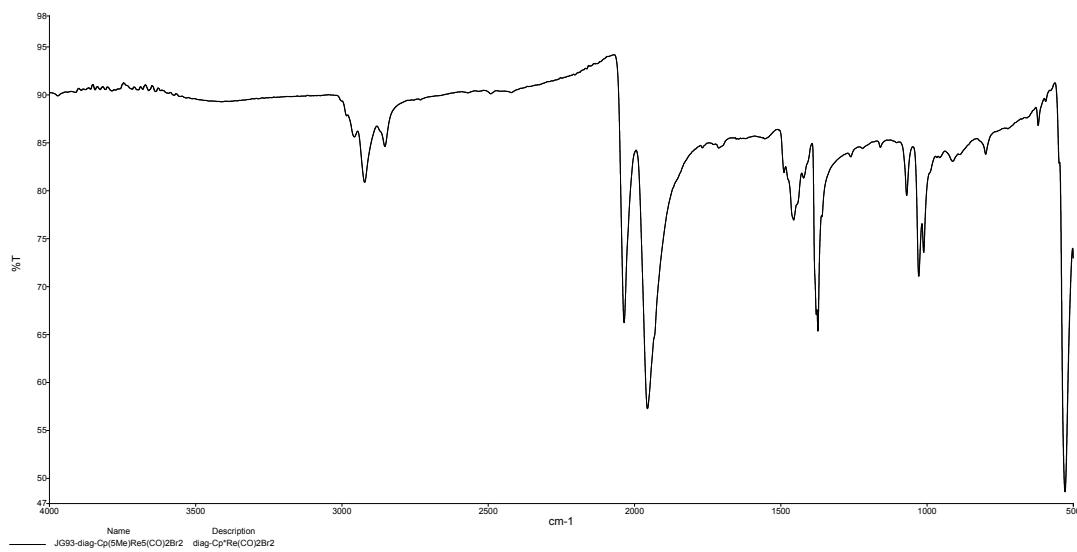


Figure S6. FTIR-ATR spectrum of *diag*-Cp*Re(CO)₂Br₂

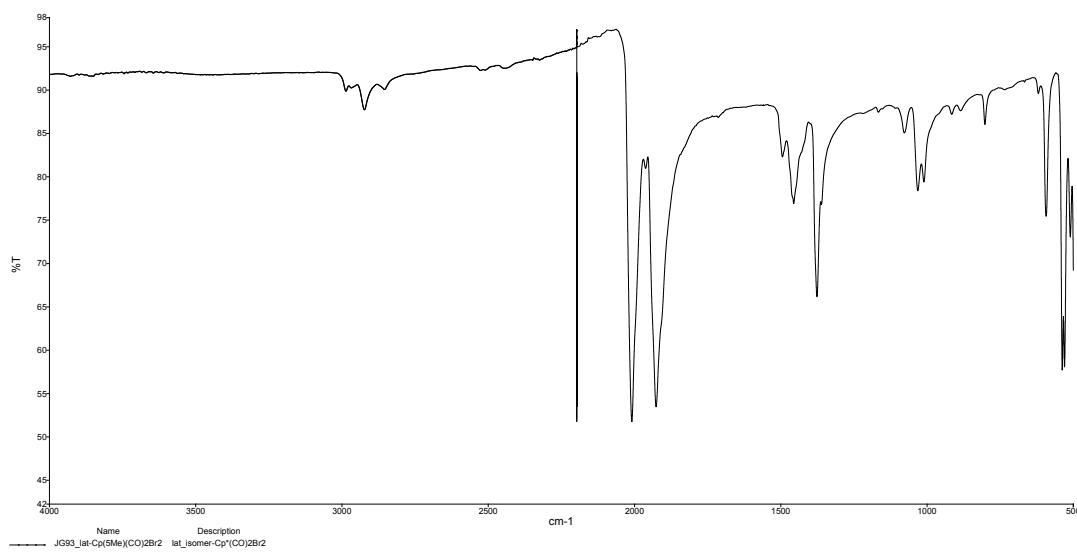


Figure S7. FTIR-ATR spectrum of *lat*-Cp*Re(CO)₂Br₂

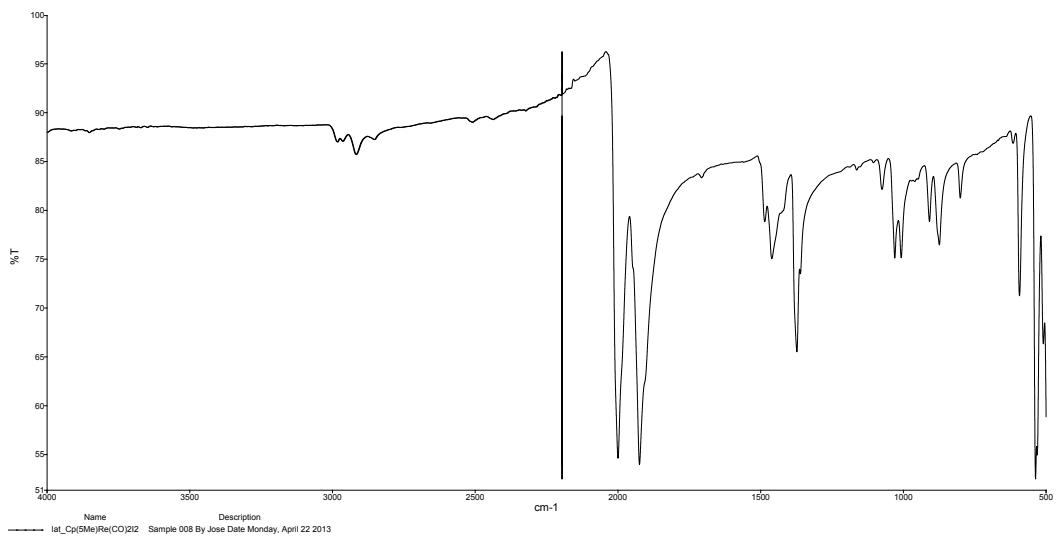


Figure S8. FTIR-ATR spectrum of *lat*-Cp*Re(CO)₂I₂

5. ^1H and ^{13}C NMR spectra of compounds $\text{CpRe}(\text{CO})_2\text{X}_2$ and $\text{Cp}^*\text{Re}(\text{CO})_2\text{X}_2$

lat- $\text{CpRe}(\text{CO})_2\text{Cl}_2$

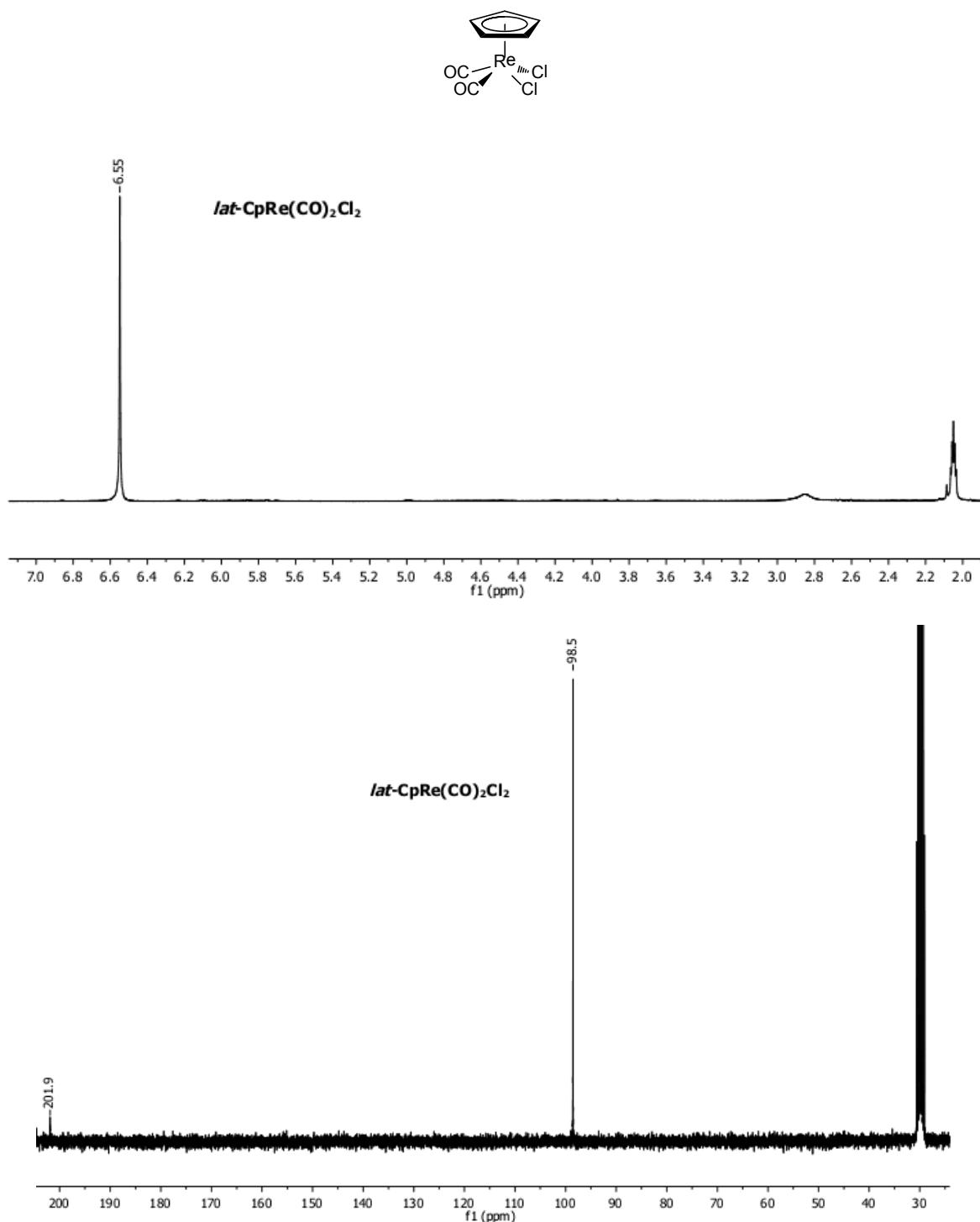


Figure S9. (Top) ^1H NMR spectrum, (bottom) ^{13}C NMR spectrum of *lat*- $\text{CpRe}(\text{CO})_2\text{Cl}_2$

diag-CpRe(CO)₂Br₂

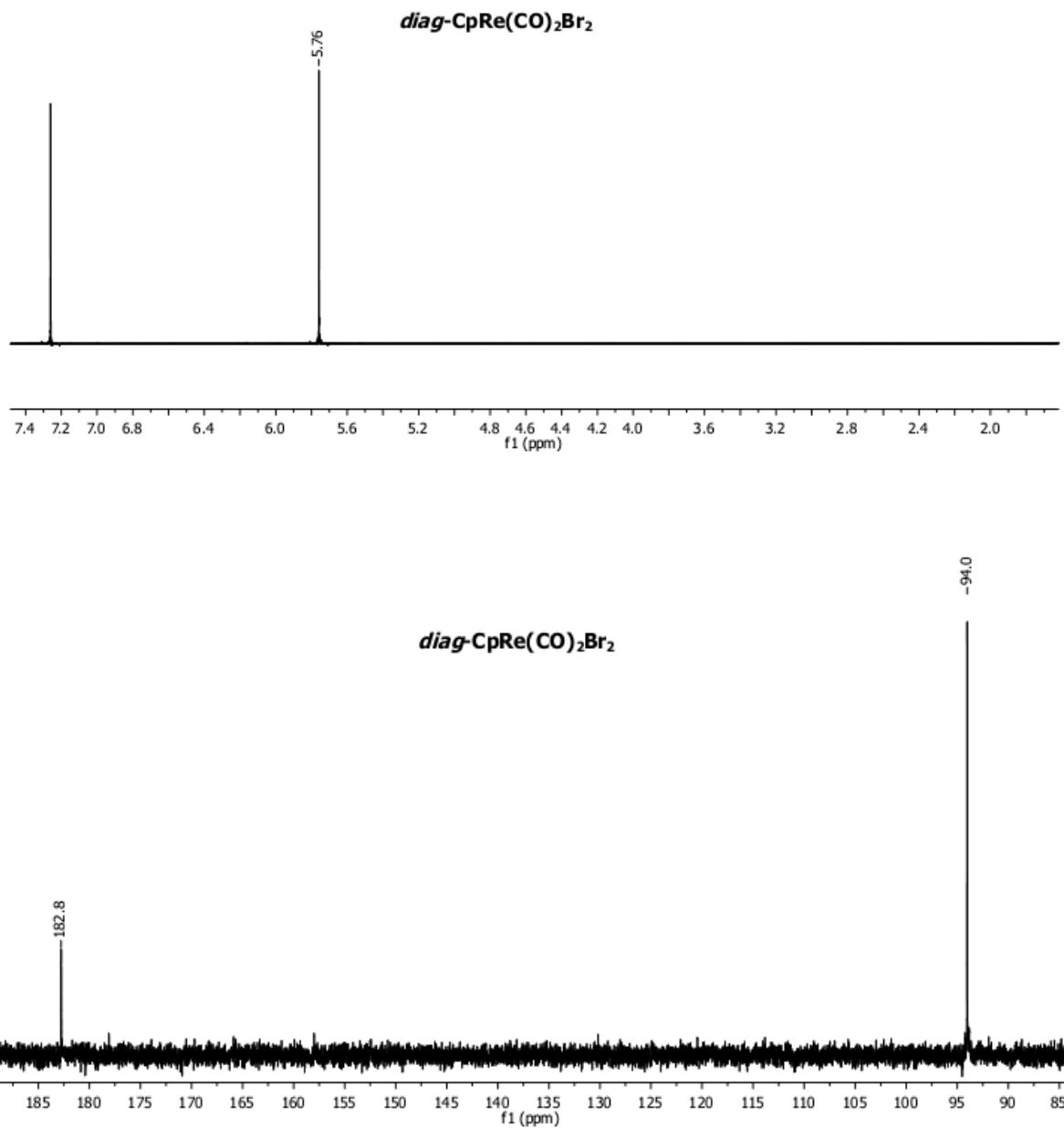
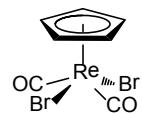
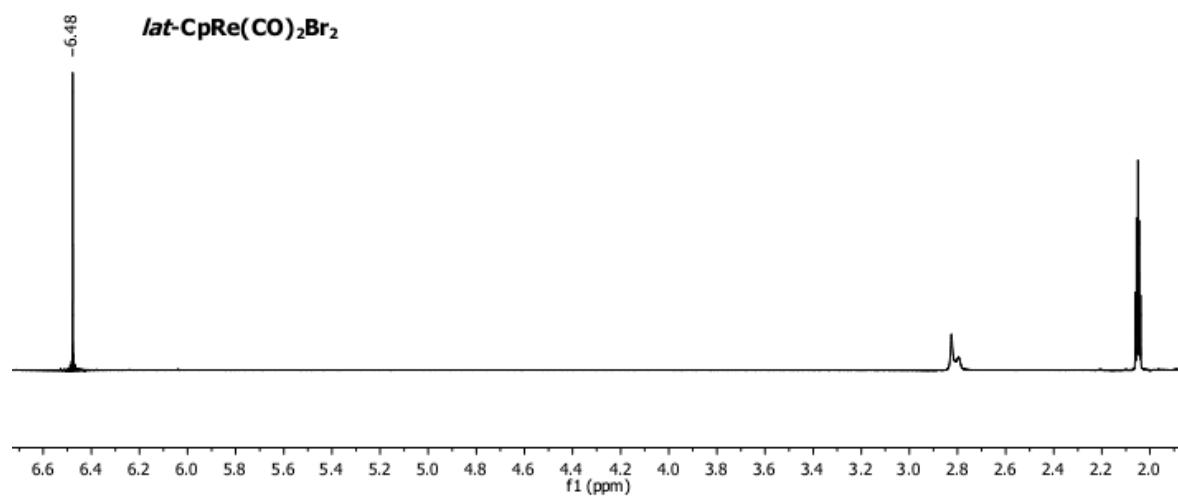
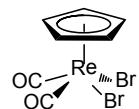


Figure S10. (Top) ¹H NMR spectrum, (bottom) ¹³C NMR spectrum of *diag-CpRe(CO)₂Br₂*

lat-CpRe(CO)₂Br₂



STANDARD CARBON PARAMETERS

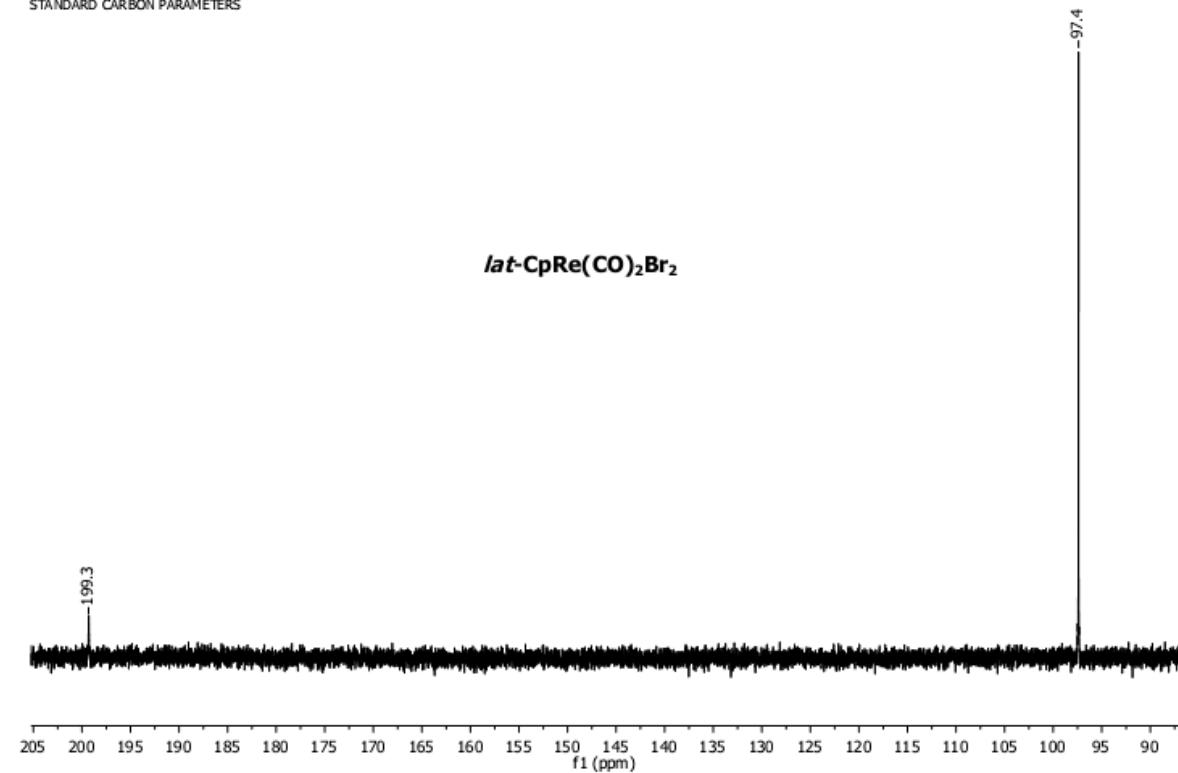


Figure S11. (Top) ¹H NMR spectrum, (bottom) ¹³C NMR spectrum of *diag*-CpRe(CO)₂Br₂

diag-CpRe(CO)₂I₂

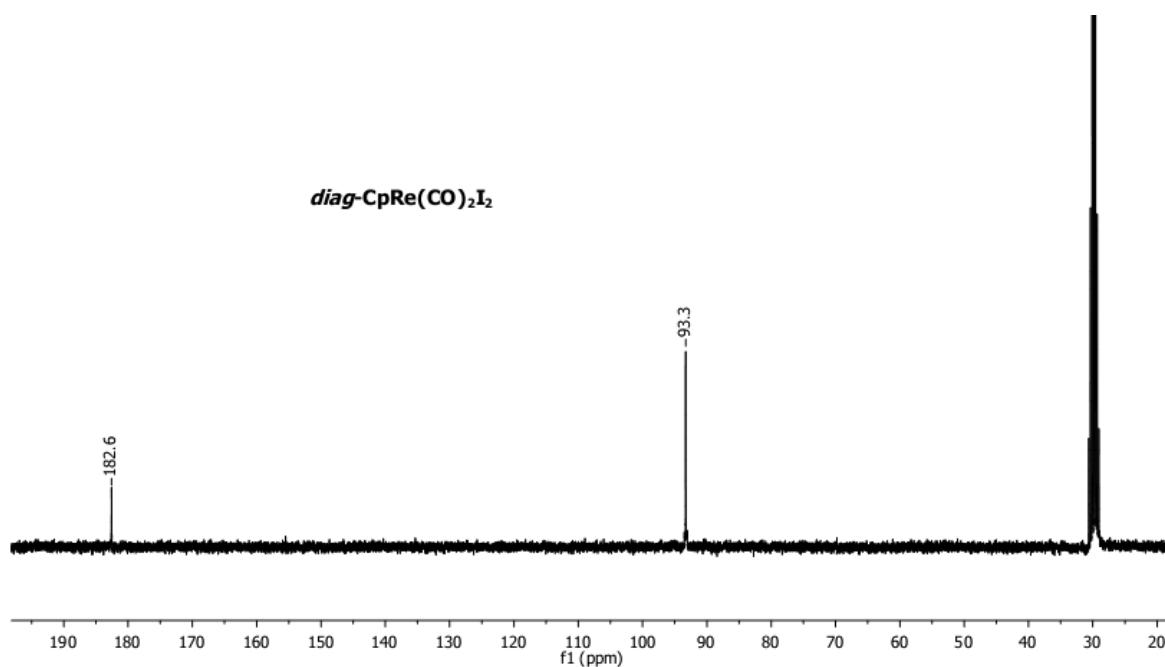
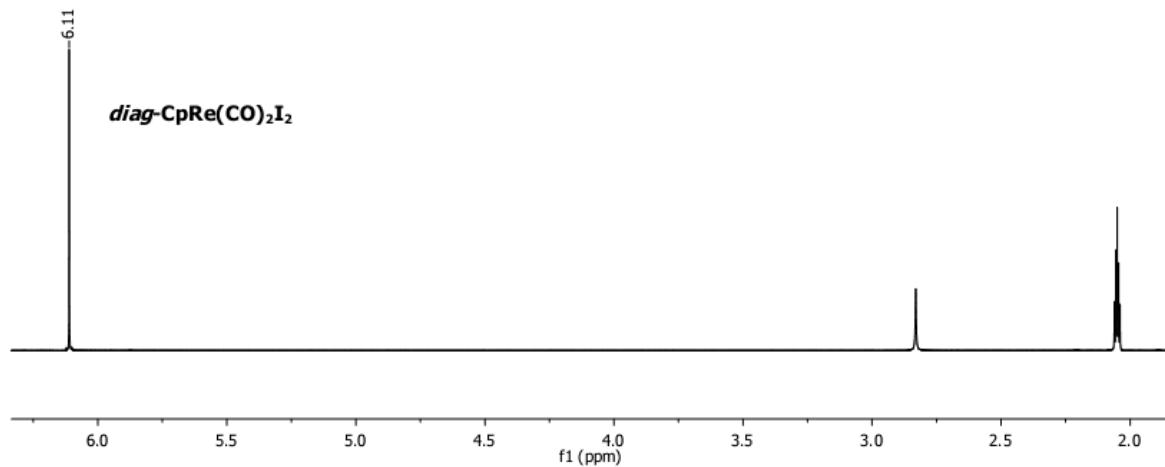
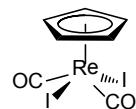


Figure S12. (Top) ¹H NMR spectrum, (bottom) ¹³C NMR spectrum of *diag*-CpRe(CO)₂I₂

lat-Cp*-Re(CO)₂Cl₂

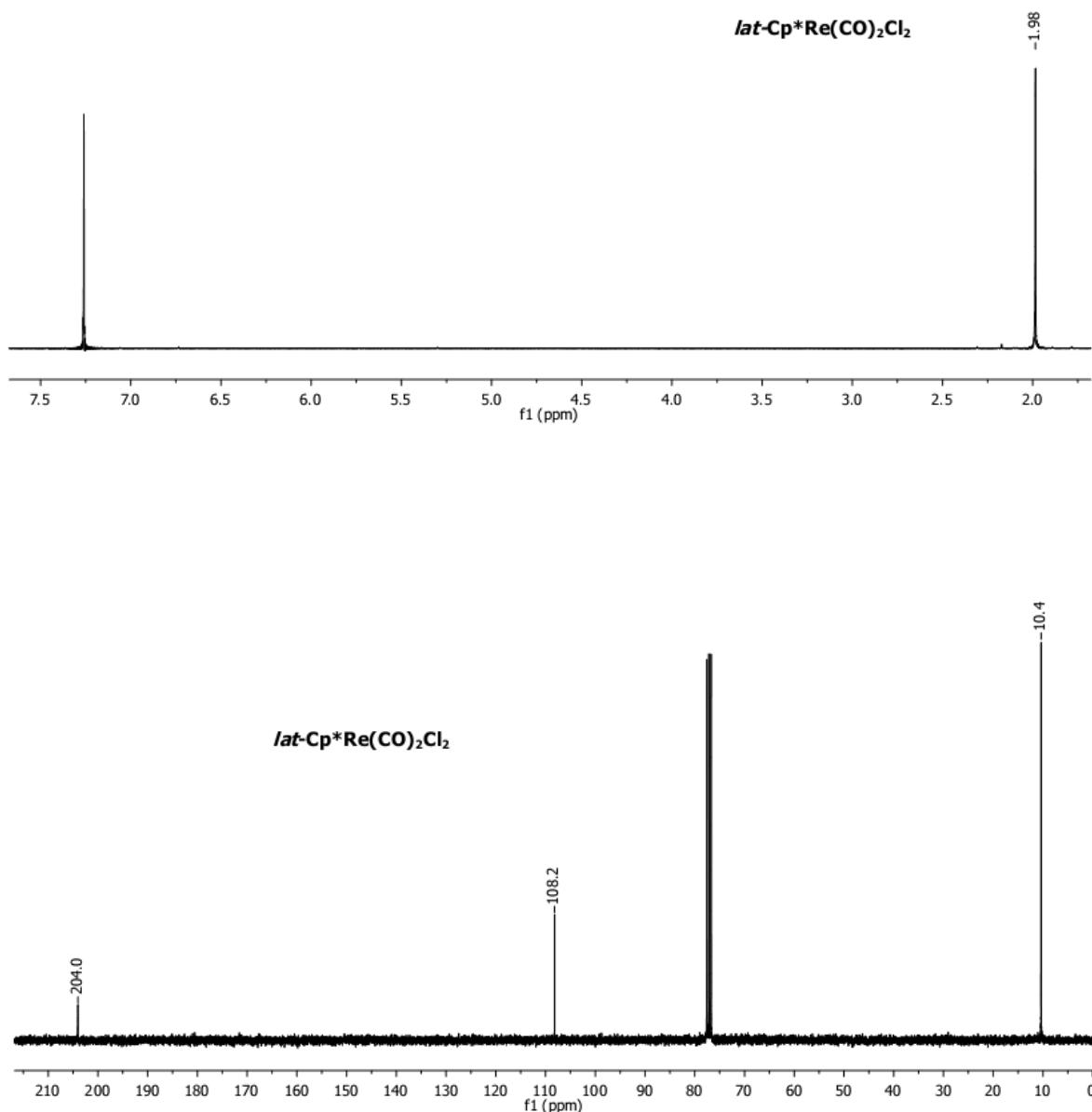
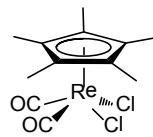
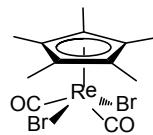
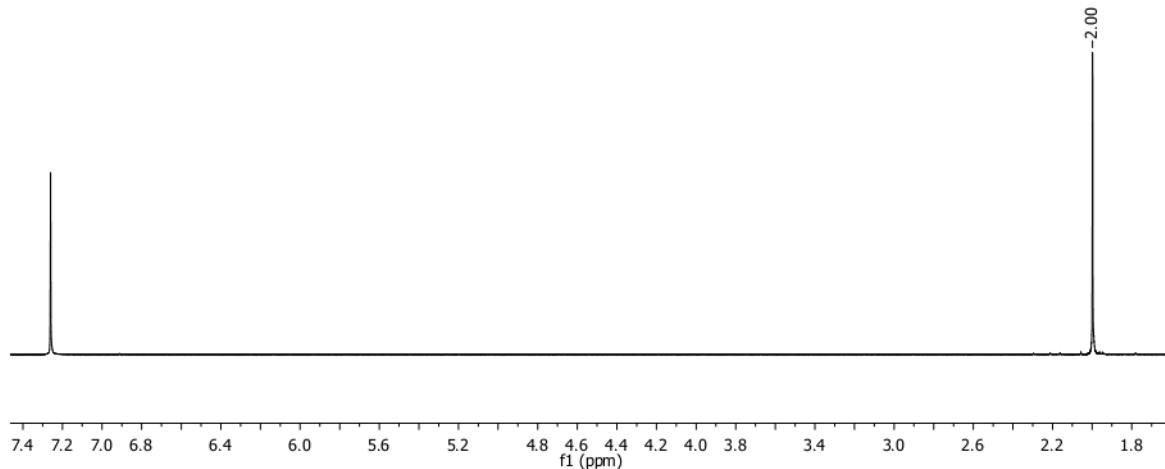


Figure S13. (Top) ¹H NMR spectrum, (bottom) ¹³C NMR spectrum of *lat*-Cp*-Re(CO)₂Cl₂

diag-Cp^{}Re(CO)₂Br₂*



diag-Cp^{}-Re(CO)₂Br₂*



diag-Cp^{}-Re(CO)₂Br₂*

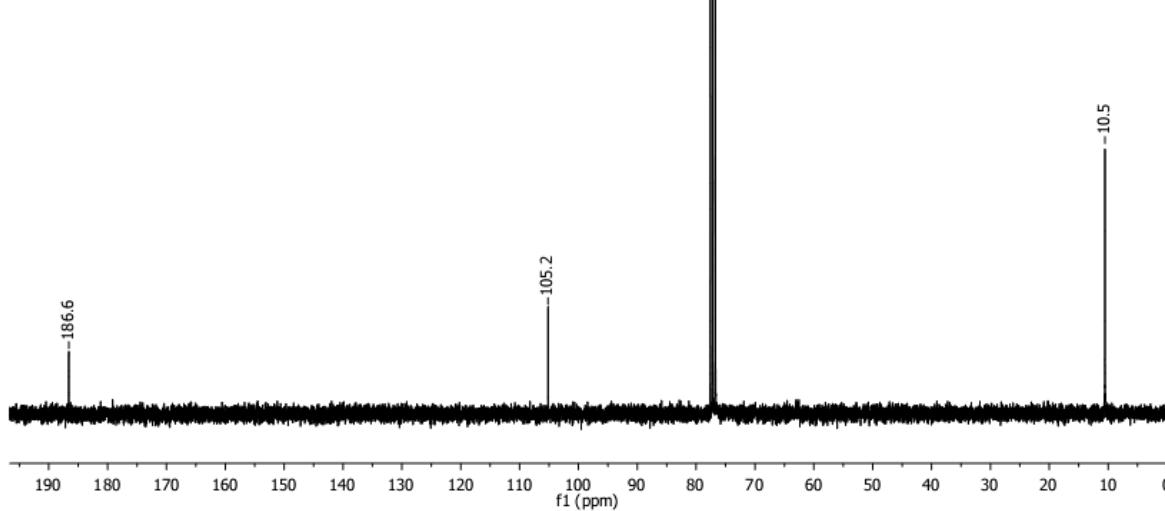


Figure S14. (Top) ¹H NMR spectrum, (bottom) ¹³C NMR spectrum of *diag-Cp^{*}-Re(CO)₂Br₂*

lat-Cp^{*}Re(CO)₂Br₂

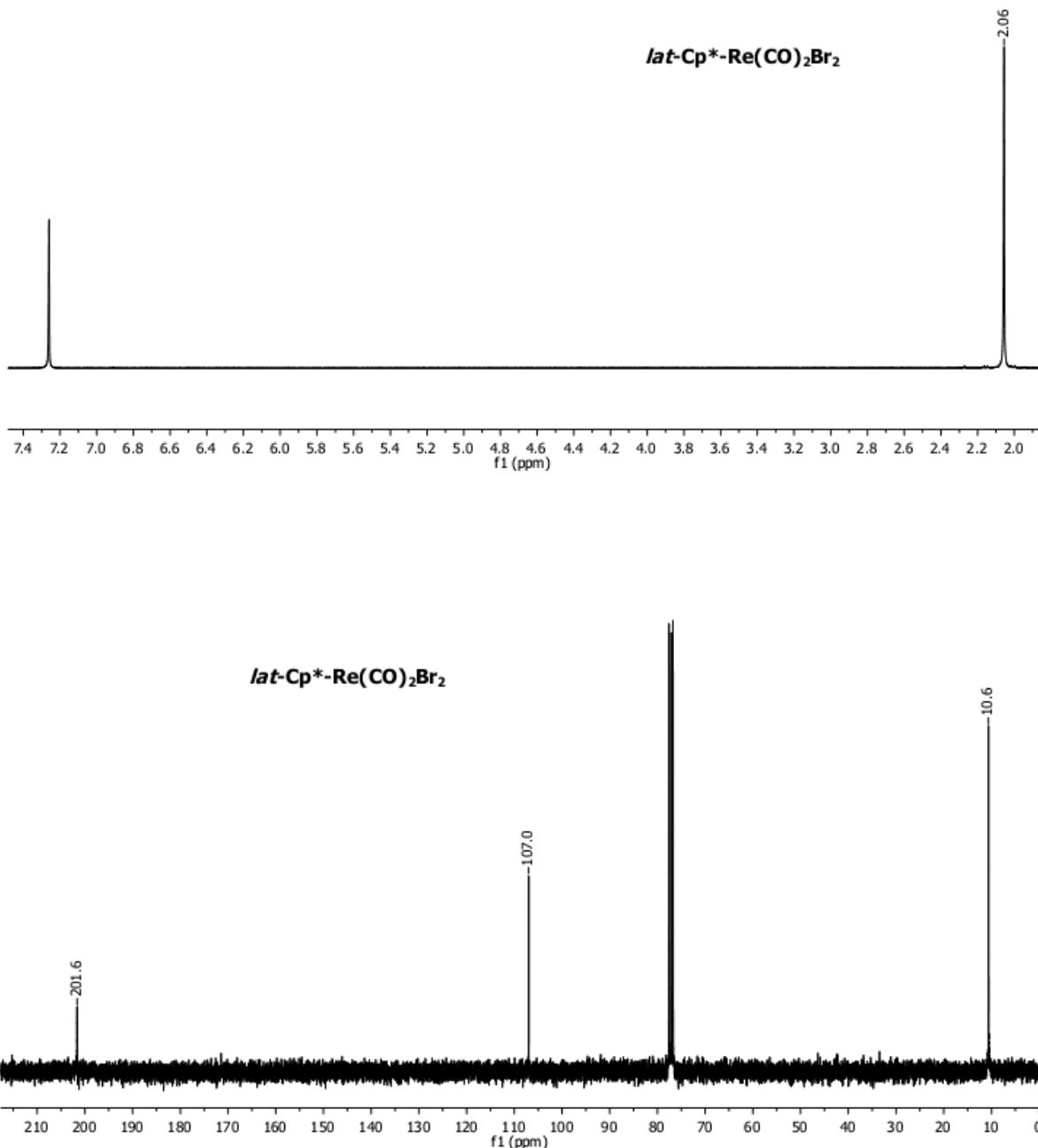
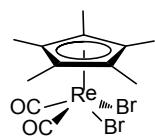


Figure S15. (Top) ¹H NMR spectrum, (bottom) ¹³C NMR spectrum of *lat*-Cp^{*}Re(CO)₂Br₂

*lat-Cp**Re(CO)₂I₂

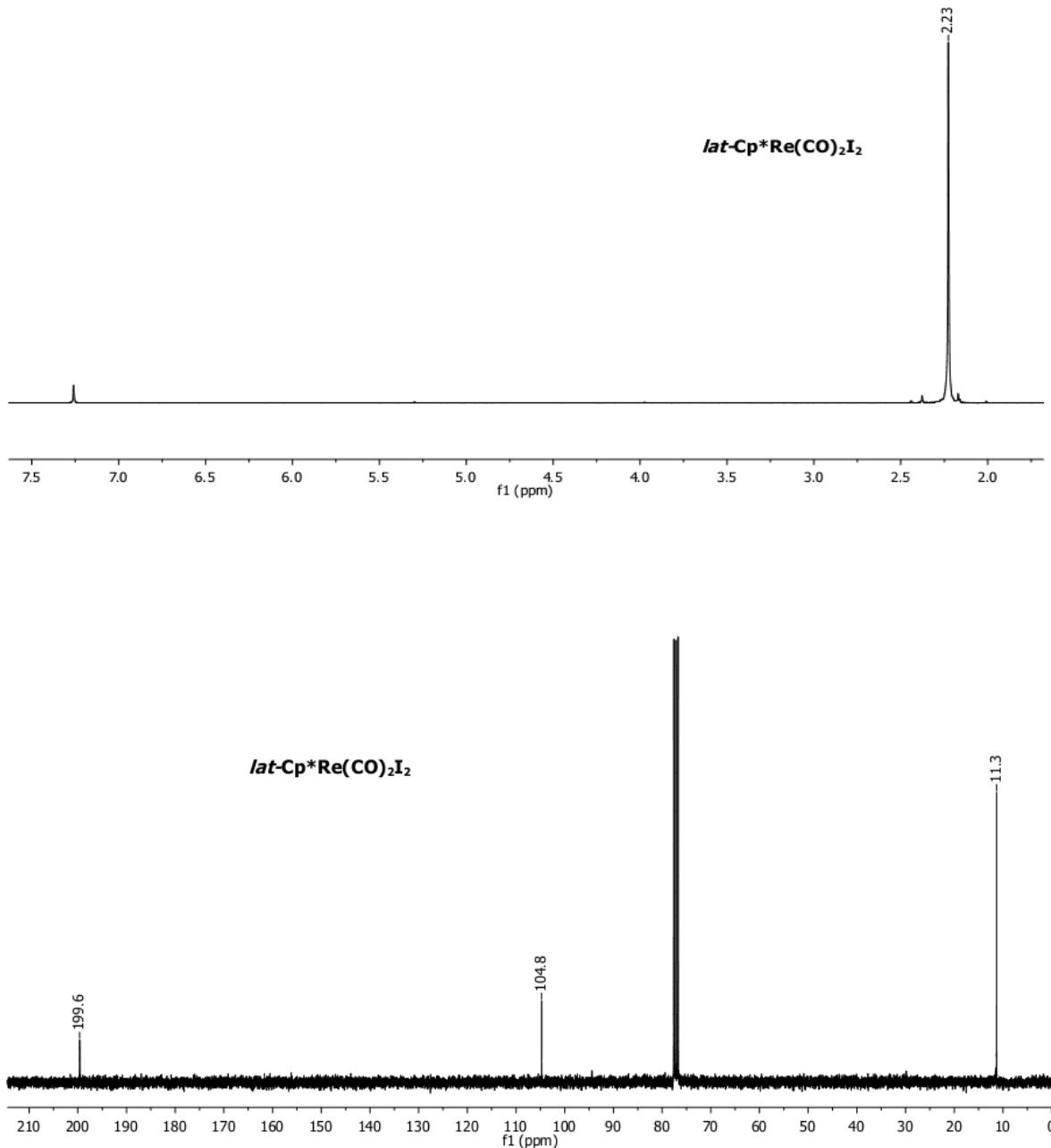
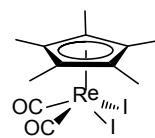


Figure S16. (Top) ¹H NMR spectrum, (bottom) ¹³C NMR spectrum of *lat-Cp**Re(CO)₂I₂

6. PXRD patterns of compounds $\text{CpRe}(\text{CO})_2\text{X}_2$ and $\text{Cp}^*\text{Re}(\text{CO})_2\text{X}_2$

lat- $\text{CpRe}(\text{CO})_2\text{Cl}_2$

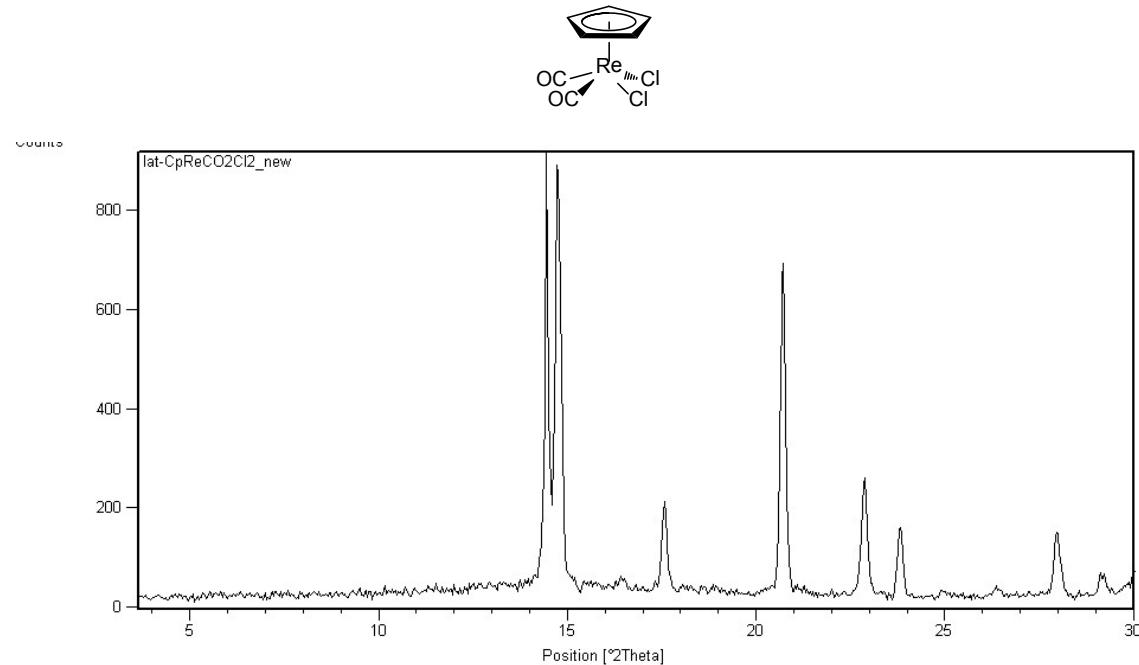


Figure S17. PXRD pattern of *lat*- $\text{CpRe}(\text{CO})_2\text{Cl}_2$

diag- $\text{CpRe}(\text{CO})_2\text{Br}_2$

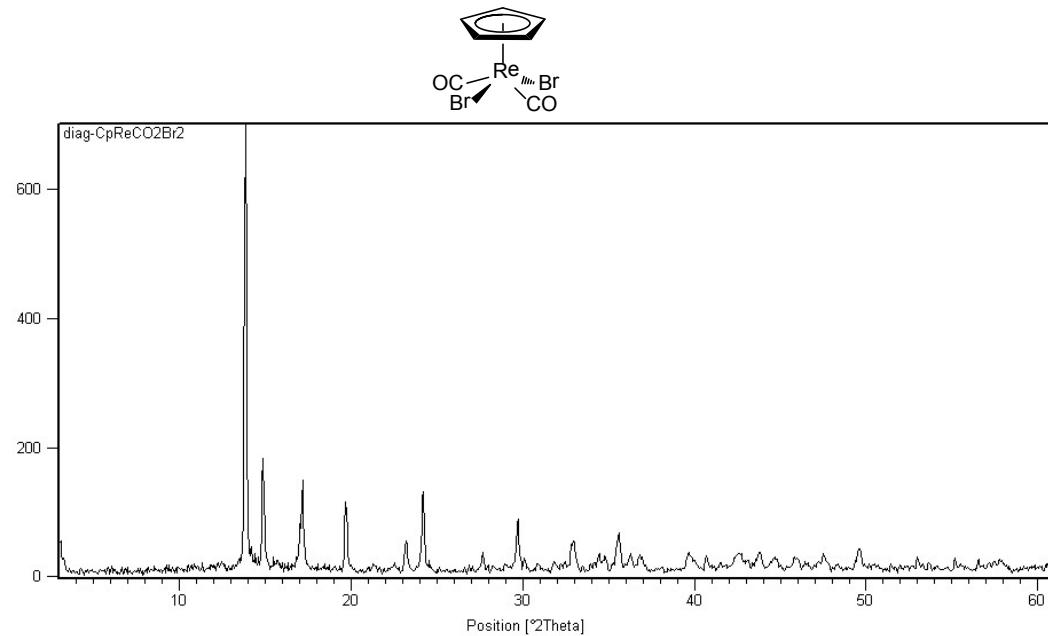


Figure S18. PXRD pattern of *diag*- $\text{CpRe}(\text{CO})_2\text{Br}_2$

lat-CpRe(CO)₂Br₂

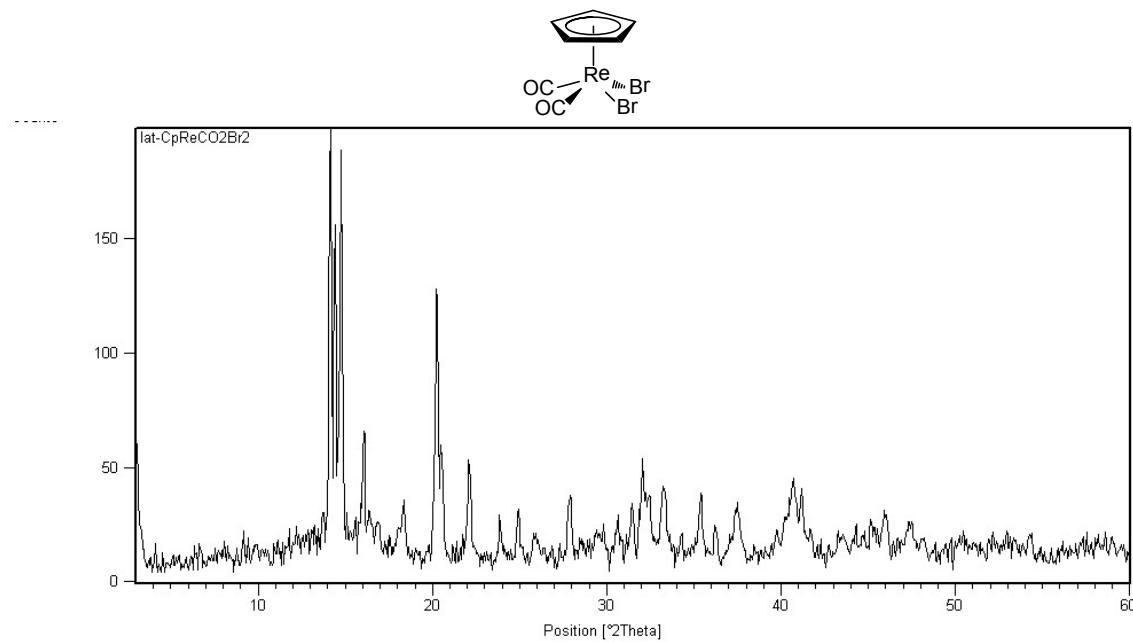


Figure S19. PXRD pattern of *lat*-CpRe(CO)₂Br₂

diag-CpRe(CO)₂I₂

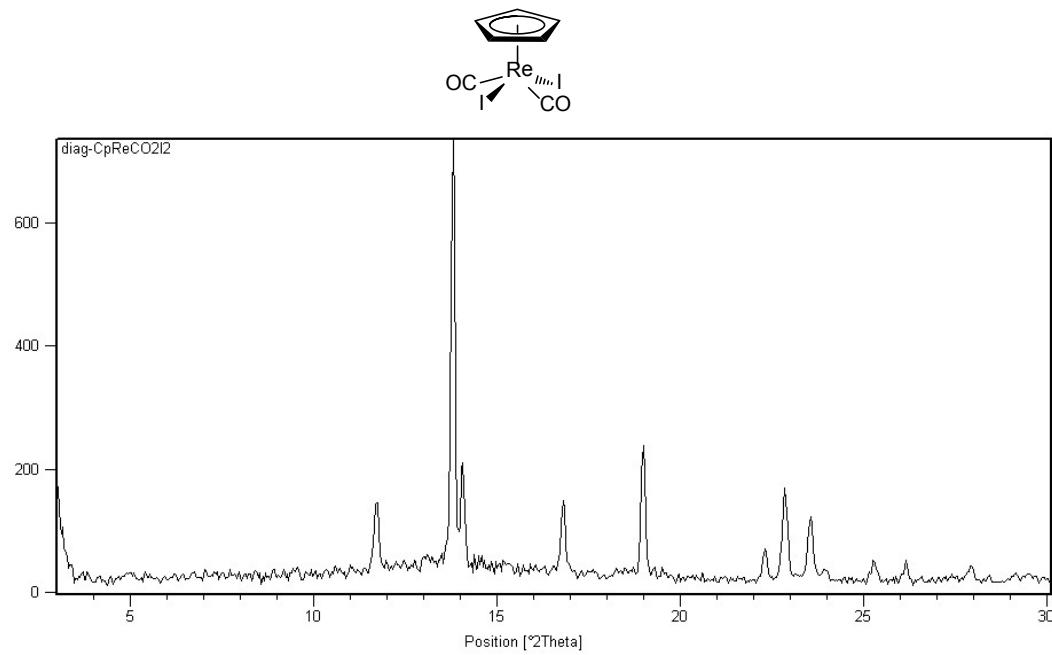


Figure S20. PXRD pattern of *diag*-CpRe(CO)₂I₂

lat-Cp^{*}Re(CO)₂Cl₂

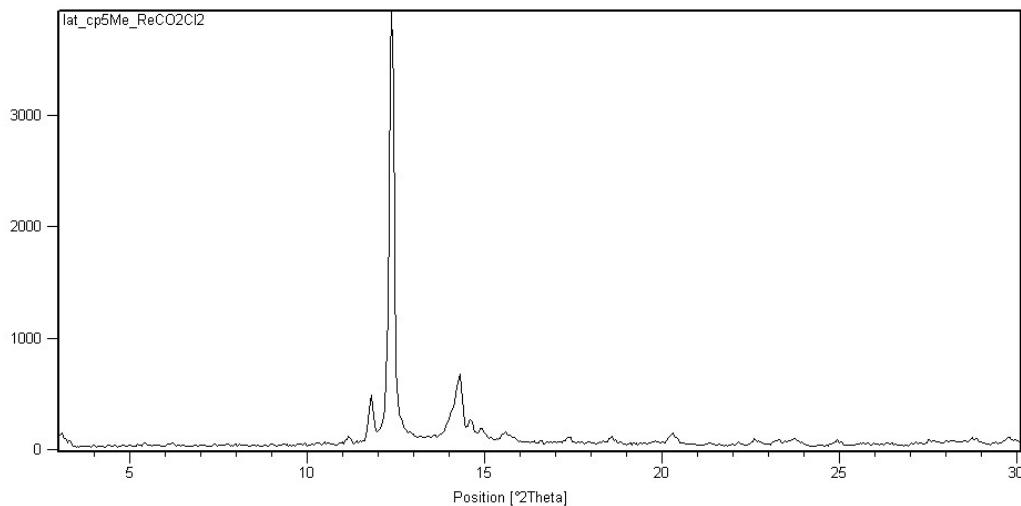
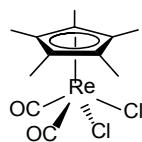


Figure S21. PXRD pattern of *lat*-Cp^{*}Re(CO)₂Cl₂

diag-Cp^{*}Re(CO)₂Br₂

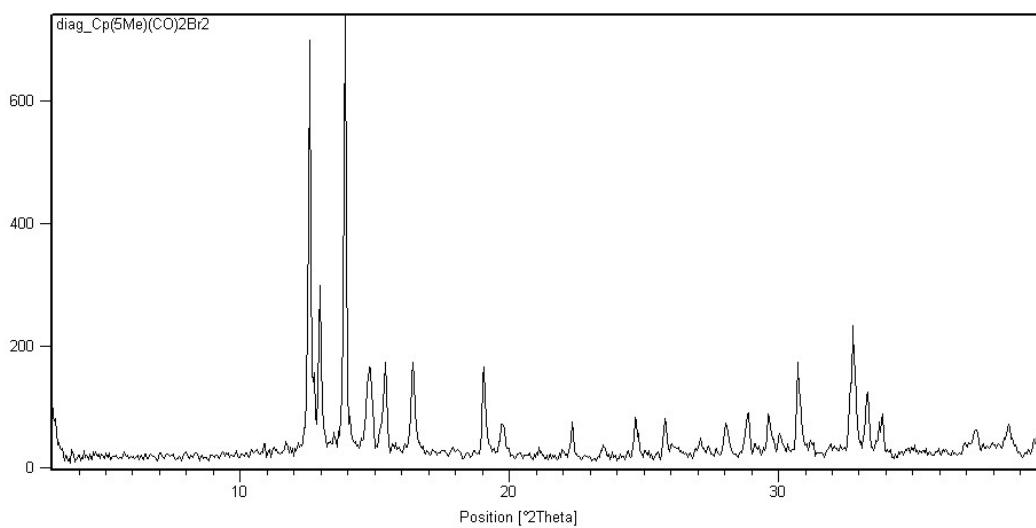
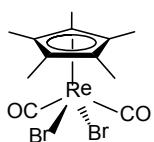


Figure S22. PXRD pattern of *diag*-Cp^{*}Re(CO)₂Br₂

lat-Cp^{*}Re(CO)₂Br₂

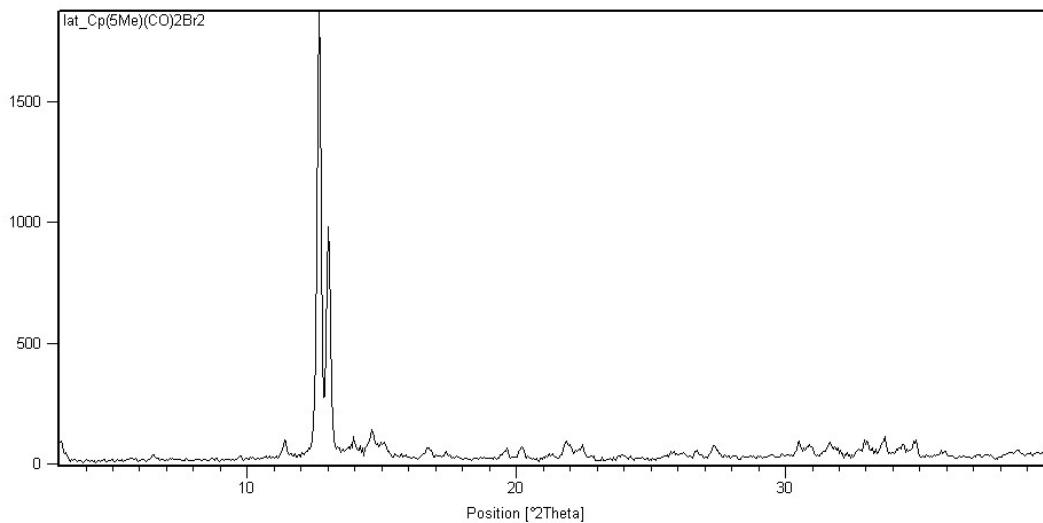
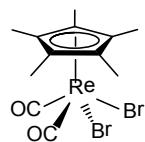


Figure S23. PXRD pattern of *lat*-Cp^{*}Re(CO)₂Br₂

lat-Cp^{*}Re(CO)₂I₂

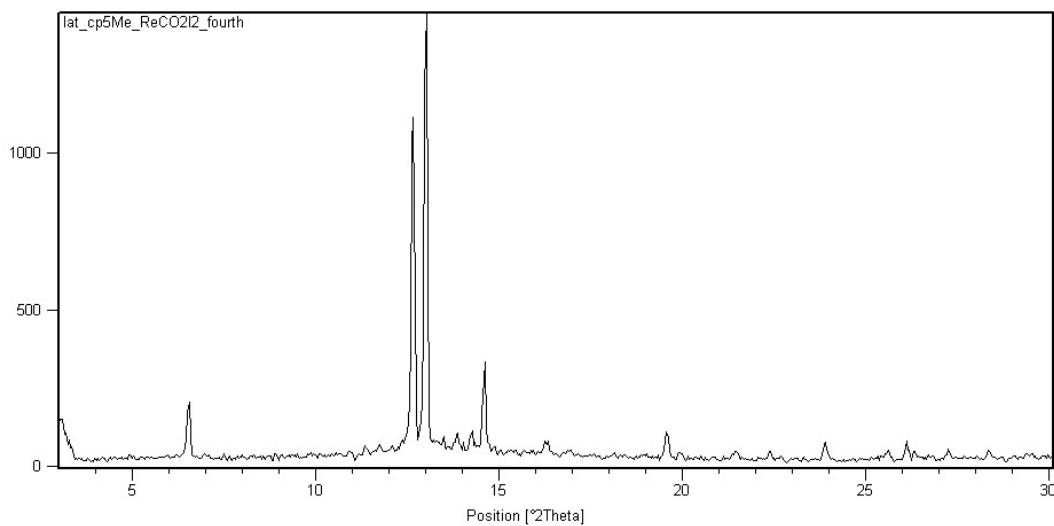
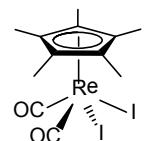


Figure S24. PXRD pattern of *lat*-Cp^{*}Re(CO)₂I₂

7. Comparison between experimental and simulated PXRD patterns

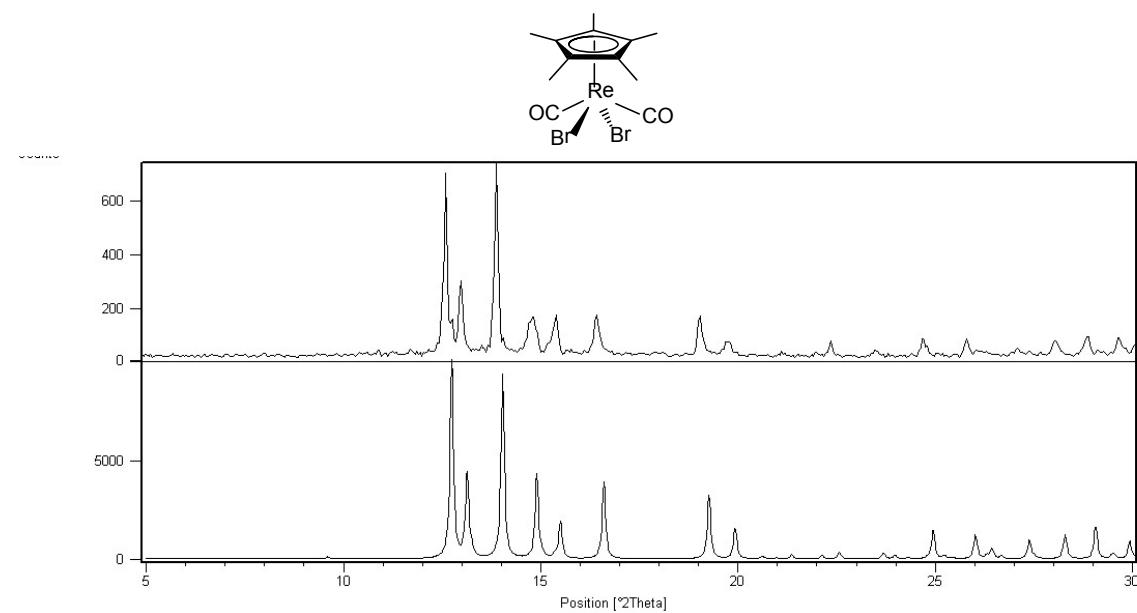


Figure S25. (Top) Experimental PXRD, (bottom) simulated* PXRD of *diag*-Cp*Re(CO)₂Br₂
(*F. W. B. Einstein, A. H. Klahn-Oliva, D. Sutton and K. G. Tyres, *Organometallics*, **1986**, *5*, 53)

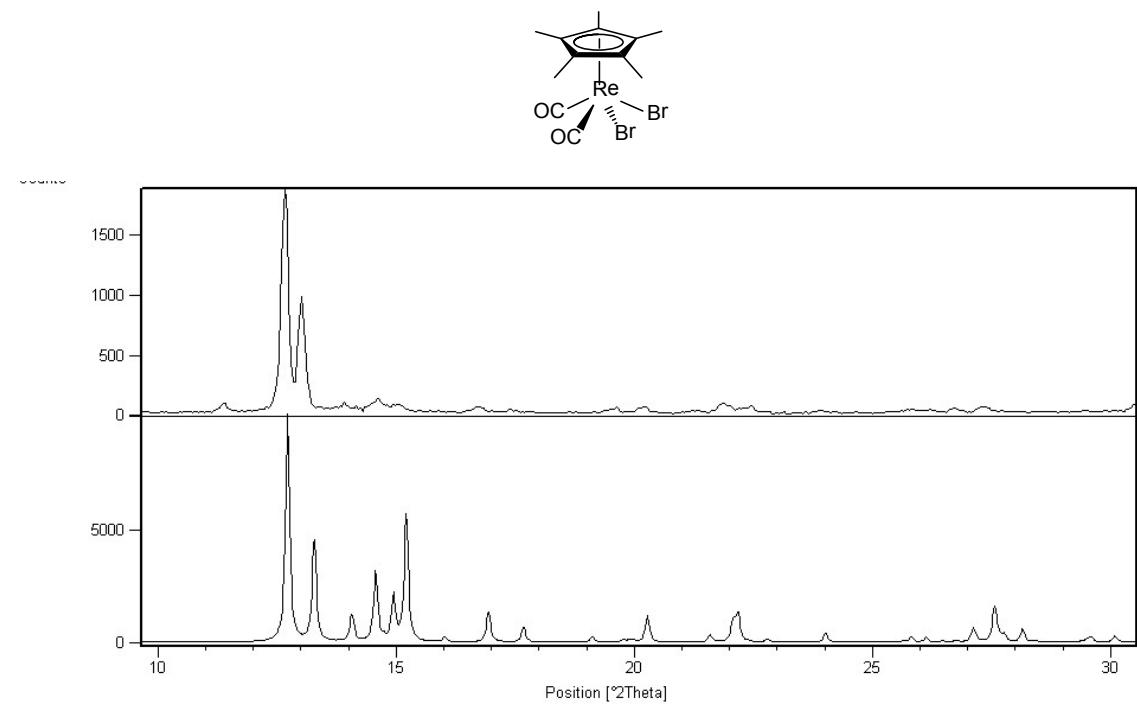


Figure S26. (Top) Experimental PXRD, (bottom) simulated* PXRD of *lat*-Cp*Re(CO)₂Br₂
(*F. Zobi, B. Spingler and R. Alberto, *Eur. J. Inorg. Chem.*, **2008**, 4205.)

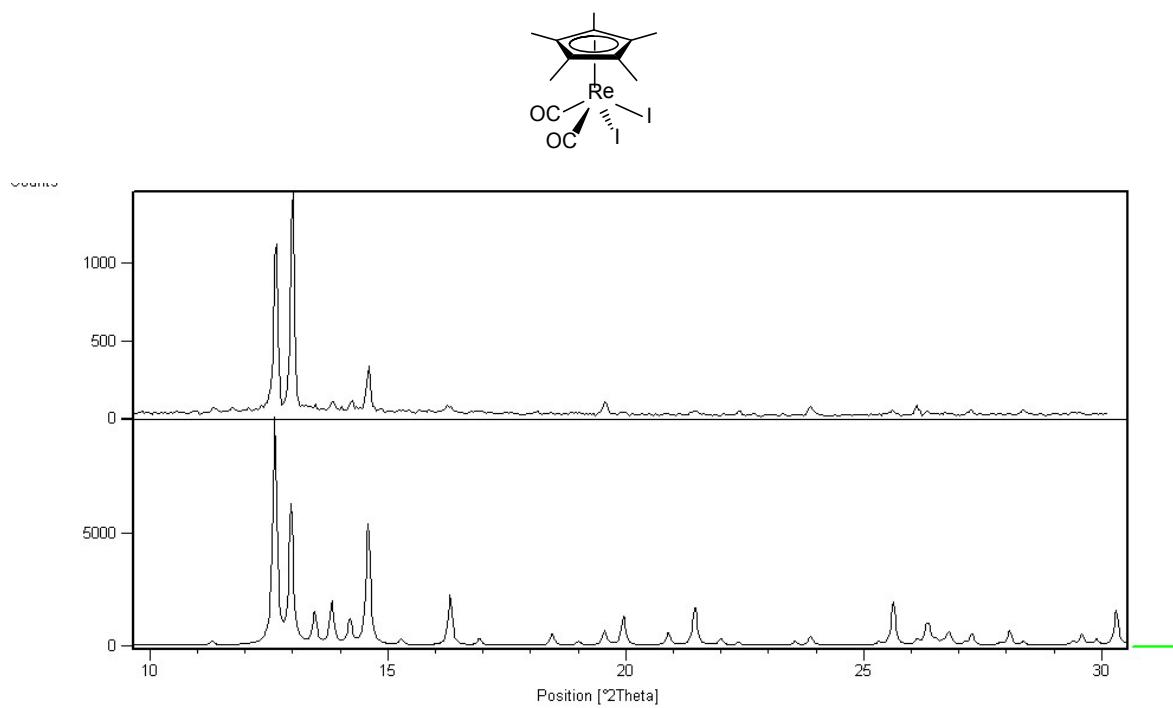


Figure S27. (Top) Experimental PXRD, (bottom) simulated* PXRD of *lat*-Cp*Re(CO)₂I₂
(*F. W. B. Einstein, A. H. Klahn-Oliva, D. Sutton and K. G. Tyres, *Organometallics*, **1986**, *5*, 53)

8. Comparison of FTIR-ATR spectra for 1, *lat*-2, *diag*-2 and milled reaction mixture

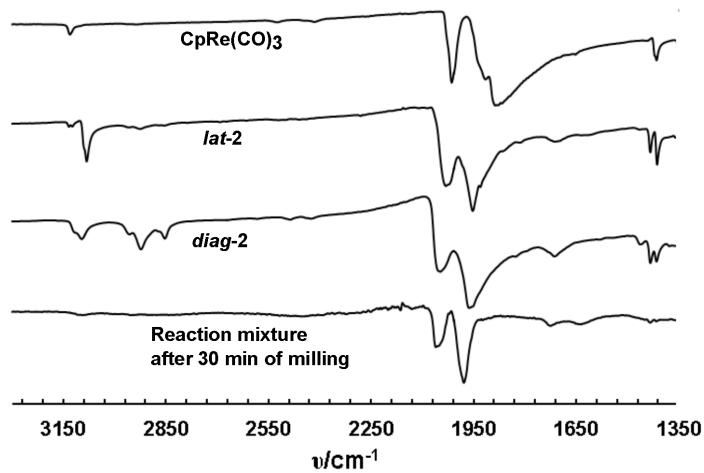


Figure S28. From top-to-bottom: an overlay of the FTIR spectra of CpRe(CO)₃, *lat*-CpRe(CO)₂Br₂, *diag*-CpRe(CO)₂Br₂ and the reaction mixture after 30 minutes of milling.