**Table S-1.** Kinetic data for exchange of $PPh_3$-$d_{15}$ into $CpRe(PPh_3)_2H_2$.

Exchange of $PPh_3$-$d_{15}$ into $CpRe(PPh_3)_2H_2$ by $^{31}P$ NMR by photolysis

| |
|---|
| $[CpReP_2H_2]$= 0.00514 |
| $[PPh_3$-$d_{15}]$= 0.244 |

| time(sec) | time(min) | $[PPh_3$-$d_{15}]/[PPh_3]$ | $[PPh_3]$ | $\ln(1-[PPh_3]/2C_0)$ |
|---|---|---|---|---|
| 2700 | 45 | 603 | 0.000405 | -0.040157844 |
| 4500 | 75 | 348 | 0.000701 | -0.070642657 |
| 7200 | 120 | 216 | 0.00113 | -0.116405904 |
| 10800 | 180 | 152 | 0.001605 | -0.16978527 |
| 14400 | 240 | 119 | 0.00205 | -0.2224653 |
| 19800 | 330 | 87 | 0.002805 | -0.318582323 |

| statistics: | |
|---|---|
| -0.0009615 | 0.0023085 |
| 1.643E-05 | 0.0031525 |
| 0.9988337 | 0.0039427 |
| 3425.5339 | 4 |
| 0.0532508 | 6.218E-05 |

| |
|---|
| $k_{obs}$= 1.603E-05 $s^{-1}$ |
| 95% limit= 3.103E-07 |
| $k_2$= 6.568E-05 $M^{-1}s^{-1}$ |
| k(HD)/k($PPh_3$)= 36.752959 |

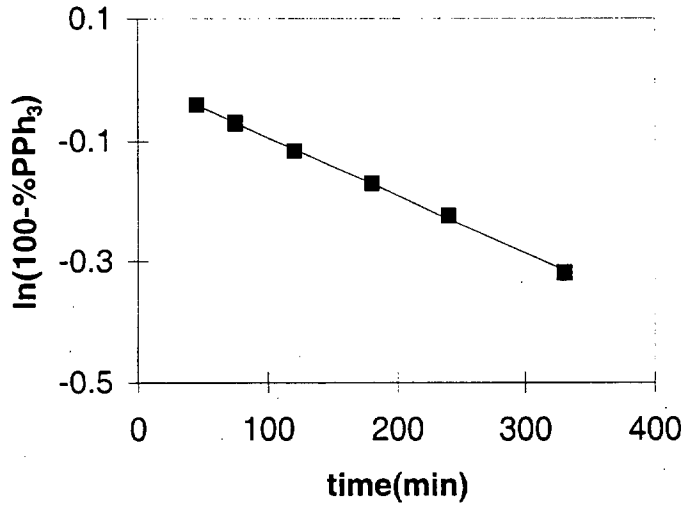


**Table S-2**. Kinetic data for H/D exchange between pentane and $C_6D_6$ catalyzed by $CpRe(PPh_3)_2H_2$.

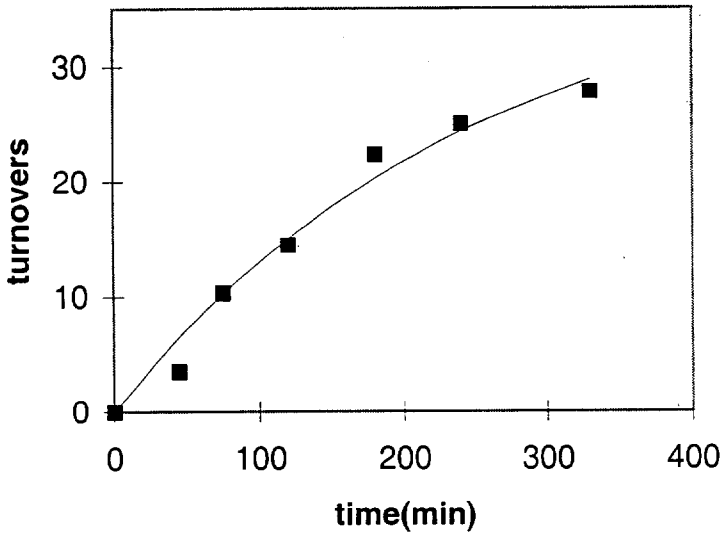
Photochemical H/D exchange between pentane and $C_6D_6$ by $CpRe(PPh_3)_2H_2$.
[pentane]=0.88M
$[CpReP_2H_2]$=0.00514

| time(sec) | time(min) | turnovers | calc | error^2 |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 |
| 2700 | 45 | 3.5 | 6.500766 | 9.004595 |
| 4500 | 75 | 10.3 | 10.228 | 0.005184 |
| 7200 | 120 | 14.5 | 15.04353 | 0.295424 |
| 10800 | 180 | 22.4 | 20.25324 | 4.608574 |
| 14400 | 240 | 25 | 24.3511 | 0.42107 |
| 19800 | 330 | 27.8 | 28.91808 | 1.250102 |
| | | | | 15.58495 |

| | |
|---|---|
| k= | 0.004001 |
| $C_{inf}$= | 39.45423 |
| $k_{obs}$= | 6.67E-05 $s^{-1}$ |

(above fit using solver)

| linest statistics (5 points): | |
|---|---|
| 0.002124 | -0.56573 |
| 0.000153 | 0.960128 |
| 0.984606 | 1.273874 |
| 191.8859 | 3 |
| 311.3837 | 4.868263 |




| | |
|---|---|
| $k_{obs}$= | 0.002124 $s^{-1}$ |
| 95%error= | 0.000184 |
| $k_2$= | 0.002414 $M^{-1}s^{-1}$ |

**Table S-3**. Kinetic data for H/D exchange between propane and $C_6D_6$ catalyzed by $CpRe(PPh_3)_2H_2$.

*Effect of [propane] on H/D exchange with $C_6D_6$ by 0.0128 M $CpRe(PPh_3)_2H_2$ (365 nm).*

| time(min) | 1.28 M | 2.56 M | 3.84 M | simulated data | | | errors | | |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 10 | | | | 1.163336 | 2.312984 | 3.151113 | | | |
| 20 | | | | 2.27538 | 4.515533 | 6.157827 | | | |
| 30 | | | | 3.338392 | 6.612919 | 9.026758 | | | |
| 40 | 0 | 6 | 11 | 4.354535 | 8.610163 | 11.76422 | 18.96198 | 6.812952 | 0.584032 |
| 60 | | | | 6.254388 | 12.32312 | 16.86856 | | | |
| 80 | | | | 7.990402 | 15.68999 | 21.51581 | | | |
| 100 | | | | 9.576705 | 18.74302 | 25.7469 | | | |
| 120 | 11 | 20 | 28 | 11.02621 | 21.51148 | 29.59909 | 0.000687 | 2.28456 | 2.557089 |
| 150 | | | | 12.96949 | 25.18791 | 34.74034 | | | |
| 180 | | | | 14.66689 | 28.36248 | 39.20669 | | | |
| 210 | | | | 16.14953 | 31.1037 | 43.08673 | | | |
| 240 | 19 | 36 | 48 | 17.44457 | 33.47073 | 46.45744 | 2.419347 | 6.397227 | 2.379483 |
| 300 | | | | 19.56382 | 37.27953 | 51.92951 | | | |
| 360 | | | | 21.18071 | 40.11944 | 56.05923 | | | |
| 420 | | | | 22.41433 | 42.23693 | 59.17588 | | | |
| 480 | 24 | 44 | 62 | 23.35552 | 43.81578 | 61.52798 | 0.415351 | 0.033938 | 0.222799 |
| 580 | | | | 24.45506 | 45.60628 | 64.23738 | | | |
| 680 | | | | 25.15551 | 46.70403 | 65.93231 | | | |
| 780 | | | | 25.60172 | 47.37705 | 66.99262 | | | |
| 880 | 25 | 47 | 67 | 25.88597 | 47.78968 | 67.65593 | 0.784942 | 0.623591 | 0.43024 |
| 1000 | | | | 26.09446 | 48.08003 | 68.13296 | | | |
| | | | | | | | 22.5823 | 16.15227 | 6.173644 |

| | | | | |
|---|---|---|---|---|
| $C_{inf}$= | 26.38486 | 48.44354 | 68.76416 | |
| k= | 0.004509 | 0.004892 | 0.004691 | $min^{-1}$ |

(fit using solver)

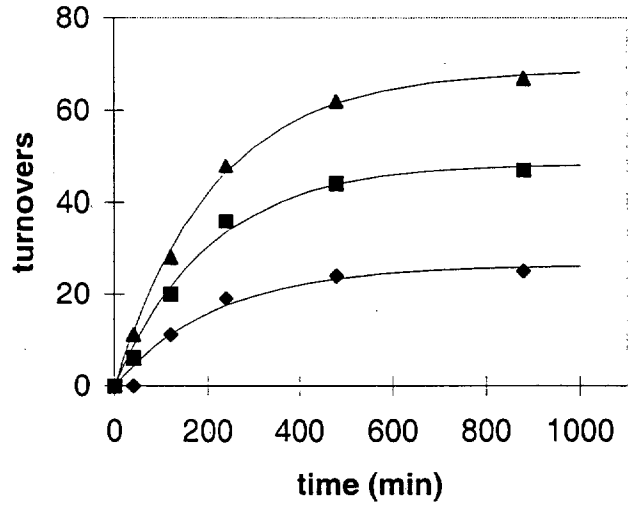
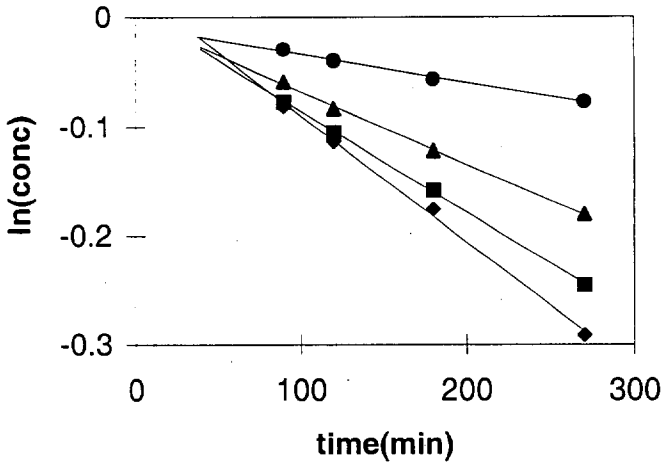


**Table S-4**. Kinetic data for exchange of $PMe_3$ into $CpRe(PPh_3)_2H_2$.

Effect of $[PMe_3]$ on photosubstitution of $CpRe(PPh_3)_2H_2$

| | $[Re]_0$= | 0.00514 | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $[PMe_3]$= | .574 M | .109 M | .027 M | .0053 M | .574 M | .109 M | .027 M | .0053 M |
| time(sec) | time(min) | conc | conc | conc | conc | ln(conc) | ln(conc) | ln(conc) | ln(conc) |
| 0 | 0 | 0.00514 | 0.00514 | 0.00514 | 0.00514 | 0 | 0 | 0 | 0 |
| 5400 | 90 | 0.00474 | 0.00476 | 0.00485 | 0.00499 | -0.08102 | -0.07681 | -0.05807 | -0.02962 |
| 7200 | 120 | 0.00459 | 0.00463 | 0.00473 | 0.00494 | -0.11317 | -0.1045 | -0.08313 | -0.03969 |
| 10800 | 180 | 0.00431 | 0.00439 | 0.00455 | 0.00486 | -0.17612 | -0.15772 | -0.12193 | -0.05601 |
| 16200 | 270 | 0.00384 | 0.00402 | 0.00429 | 0.00476 | -0.29158 | -0.24577 | -0.18077 | -0.07681 |
| | | | with zeroes | | k= | 1.80E-05 | 1.52E-05 | 1.12E-05 | 4.74E-06 |
| | | | | | 95% error= | 1.63E-06 | 5.19E-07 | 3.20E-07 | 4.70E-07 |
| | | | without zeroes | | k= | 1.95E-05 | 1.56E-05 | 1.12E-05 | 4.32E-06 |
| | | | | | 95% error= | 1.53E-06 | 5.47E-07 | 6.73E-07 | 4.62E-07 |

without zeroes:




with zeroes:

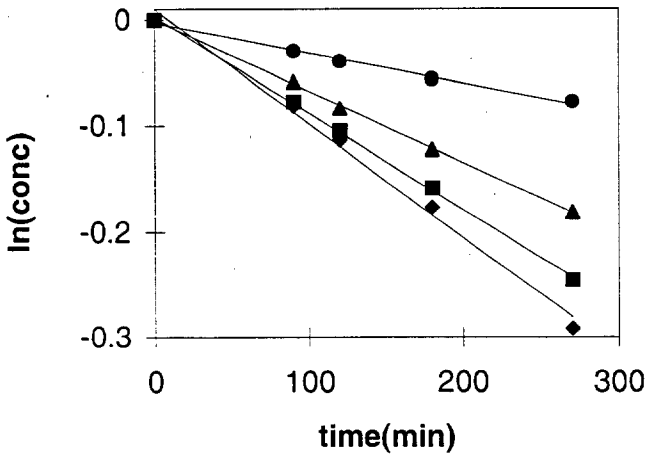
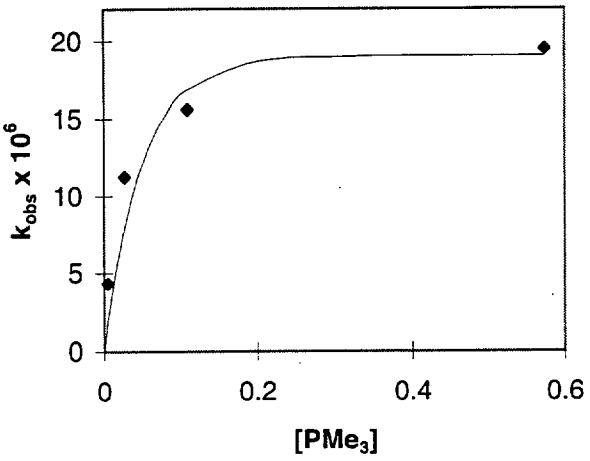


**Table S-5.** Plots of saturation kinetics for exchange of $PMe_3$ into $CpRe(PPh_3)_2H_2$.

$k_{obs}$ vs $[PMe_3]$ for substitution in $CpRe(PPh_3)_2H_2$.

| $[PMe_3]$ | $k_{obs}x10^6$ | $k_{calc}$ | $1/[PMe_3]$ | $1/k_{obs}$ | error |
|---|---|---|---|---|---|
| 1E-08 | 1E-08 | 3.8E-06 | 1E+08 | 1E+08 | 1E-11 |
| 0.002 | | 0.745001 | | | |
| 0.0045 | | 1.635307 | | | |
| 0.0053 | 4.318828 | 1.910932 | 188.68 | 0.232 | 5.798 |
| 0.01 | | 3.444116 | | | |
| 0.015 | | 4.924454 | | | |
| 0.021 | | 6.51611 | | | |
| 0.027 | 11.21078 | 7.927783 | 37.037 | 0.089 | 10.778 |
| 0.04 | | 10.46275 | | | |
| 0.06 | | 13.27731 | | | |
| 0.08 | | 15.16397 | | | |
| 0.109 | 15.61649 | 16.85221 | 9.1743 | 0.064 | 1.527 |
| 0.2 | | 18.652 | | | |
| 0.32 | | 18.96843 | | | |
| 0.45 | | 18.99766 | | | |
| 0.574 | 19.47859 | 18.9998 | 1.7422 | 0.051 | 0.2292 |
| | $C_{inf}$= | 19 | | | 18.332 |
| | k= | 20 | Solver values | | |




Double Reciprocal plot:

| [PMe3] | kobs |
|---|---|
| 0.0053 | 4.32E-06 |
| 0.027 | 1.12E-05 |
| 0.109 | 1.56E-05 |
| 0.574 | 1.95E-05 |

| 1/[PMe3] | 1/k |
|---|---|
| 188.68 | 2E+05 |
| 37.037 | 89200 |
| 9.1743 | 64035 |
| 1.7422 | 51338 |

| | | | 95% error |
|---|---|---|---|
| $k_{-1}/k_1k_2$= | slope= | 948.32 | 42.17 |
| $1/k_1$= | intercept= | 52928.47 | 4059 |

| | | |
|---|---|---|
| $k_1$= | 1.89E-05 | 1.4E-06 |
| $k_{-1}/k_2$= | 0.017917 | 0.0008 |