423/523 Organometallic Chemistry
Mid-term, 12:30 pm Friday 20th November 2009
50 minutes, 50 marks.

NAME: _____

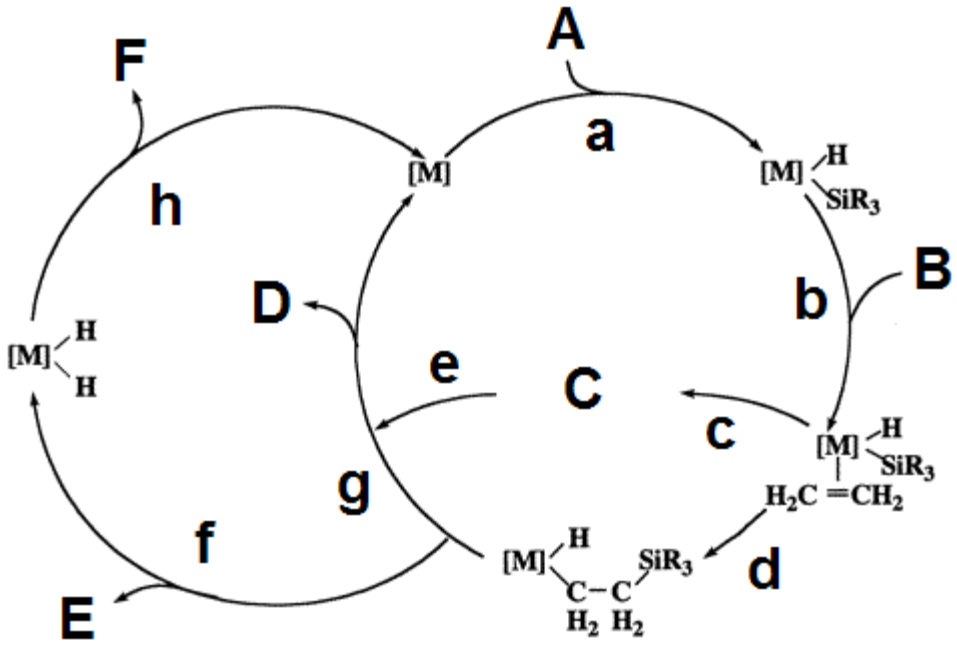
You may use this cover page if you run out of space in the answer booklet.

1 IA	2 IIA		3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIII	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1 **H** 1.0079																		2 **He** 4.0026
3 **Li** 6.941	4 **Be** 9.0122		Atomic number **Symbol** Atomic weight										5 **B** 10.811	6 **C** 12.011	7 **N** 14.007	8 **O** 15.999	9 **F** 18.998	10 **Ne** 20.180
11 **Na** 22.990	12 **Mg** 24.305												13 **Al** 26.982	14 **Si** 28.086	15 **P** 30.974	16 **S** 32.065	17 **Cl** 35.453	18 **Ar** 39.948
19 **K** 39.098	20 **Ca** 40.078		21 **Sc** 44.956	22 **Ti** 47.867	23 **V** 50.942	24 **Cr** 51.996	25 **Mn** 54.938	26 **Fe** 55.845	27 **Co** 58.933	28 **Ni** 58.693	29 **Cu** 63.546	30 **Zn** 65.39	31 **Ga** 69.723	32 **Ge** 72.61	33 **As** 74.922	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.80
37 **Rb** 85.468	38 **Sr** 87.62		39 **Y** 88.906	40 **Zr** 91.224	41 **Nb** 92.906	42 **Mo** 95.94	43 **Tc** [98]	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 118.71	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.29
55 **Cs** 132.91	56 **Ba** 137.33	57-70 †	71 **Lu** 174.97	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.84	75 **Re** 186.21	76 **Os** 190.23	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.98	84 **Po** [209]	85 **At** [210]	86 **Rn** [222]
87 **Fr** [223]	88 **Ra** [226]	89-102 ‡	103 **Lr** [262]	104 **Rf** [261]	105 **Db** [262]	106 **Sg** [266]	107 **Bh** [264]	108 **Hs** [269]	109 **Mt** [268]	110 **Ds** [281]	111 **Rg** [272]							

†lanthanides	57 **La** 138.91	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** [145]	62 **Sm** 150.36	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04
‡actinides	89 **Ac** [227]	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** [237]	94 **Pu** [244]	95 **Am** [243]	96 **Cm** [247]	97 **Bk** [251]	98 **Cf** [251]	99 **Es** [252]	100 **Fm** [257]	101 **Md** [258]	102 **No** [259]

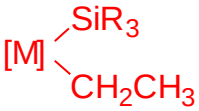
1. Examine the scheme below. Draw structures for **A**, **B**, **C**, **D**, **E** and **F**. Describe steps **a**, **b**, **c**, **d**, **e**, **f**, **g** and **h**, including transition states for steps **a** and **f**. Given that [M] is IrL_2X, give oxidation states and electron counts for all metal complexes. What do you think is the desired product? Why? What other product(s) might you expect from the reaction?

[16 marks]

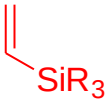


A $HSiR_3$

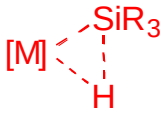
B

C 

D $EtSiR_3$

E 

F H_2

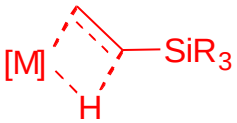
a concerted oxidative addition of Si-H 

b alkene association

c 1,2-insertion of alkene into M-H bond

d 1,2-insertion of alkene into M-Si bond

e reductive elimination of Si-C

f beta elimination of vinyl silane 

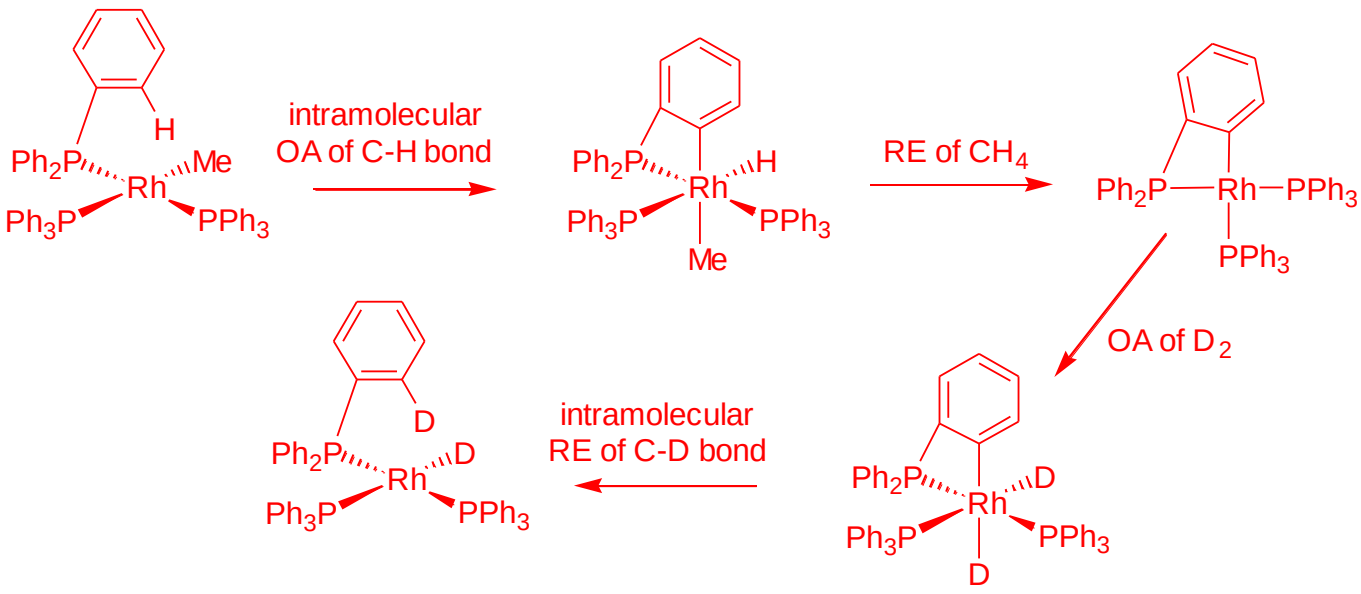
g reductive elimination of C-H

h reductive elimination of H-H

All metal complexes are +3 except for [M] which is +1
[M] is 14 then proceeding: 16, 18, 16, 16, 16
$EtSiR_3$; it is the atom-economical product
$R_3SiCH{=}CHSiR_3$, $R_3SiCH_2CH_2SiR_3$

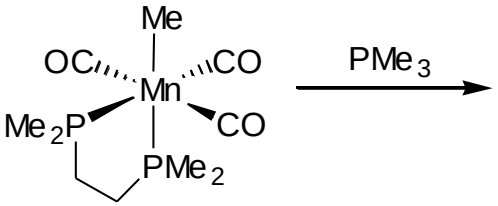
2. The complex $Rh(Me)(PPh_3)_3$ reacts with D_2 to produce $Rh(D)(PPh_3)_2(PPh_2\{C_6H_4D\})$ and CH_4. Give reactions that explain this product distribution.

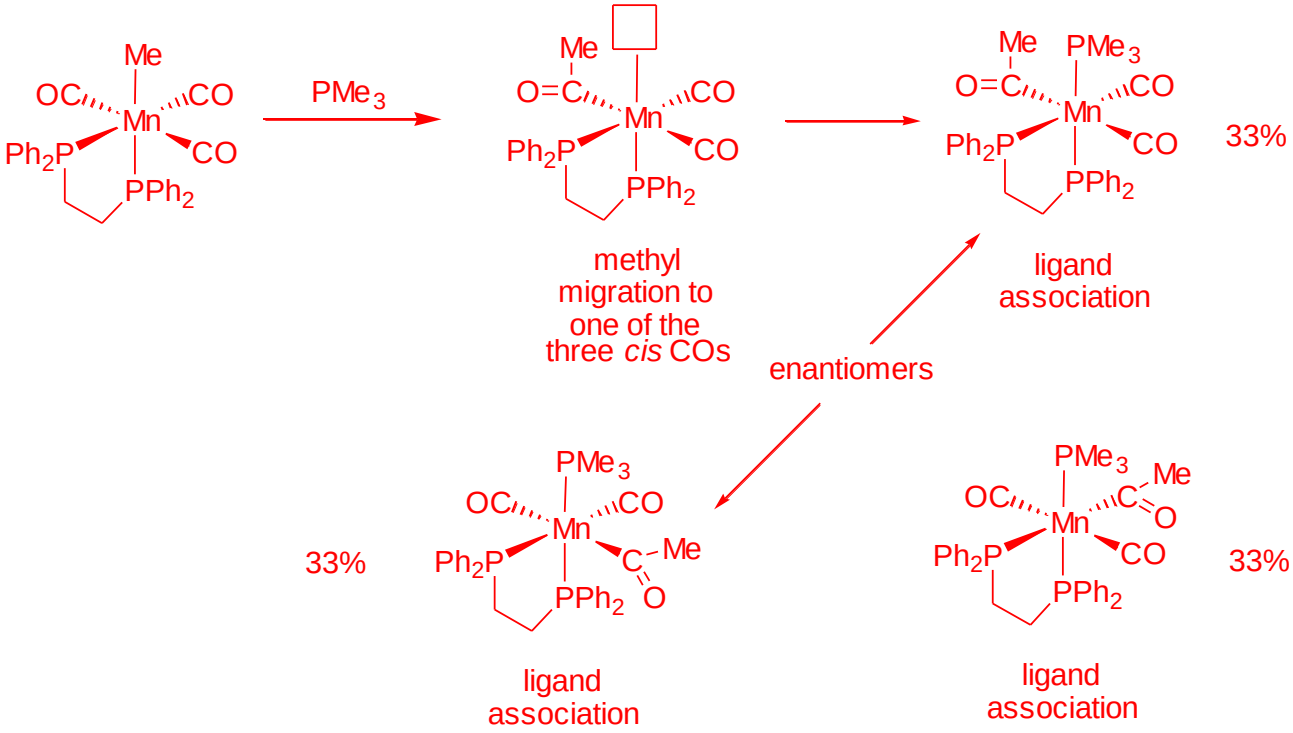
[8 marks]



3. Predict the products of the following reaction, showing the structure of each and the expected relative distributions. Choose ONE of the products, and describe in as much detail as you can its ν(CO) IR spectrum and its ^{31}P NMR spectrum (proton decoupled).

[8 marks]





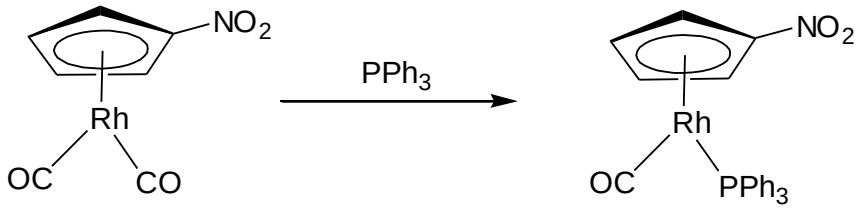
All products exhibit 2 CO stretches around 2000 cm^{-1} and one around 1700 cm^{-1}. All ^{31}P NMR should be 3 doublets of doublets.

4. Explain the difference between homogeneous and heterogeneous catalysts and detail the advantages/disadvantages of both.

[12 marks]

Straight from notes.

5. Propose a mechanism for the following reaction. Your mechanism must be consistent with the following observations: (a) using excess PPh_3, the rate is first order in rhodium complex; (b) $\Delta S^{\ddagger}$ is negative.



[6 marks]

Associative. Intermediate must be 18e i.e. a ring-slipped cyclopentadienyl: