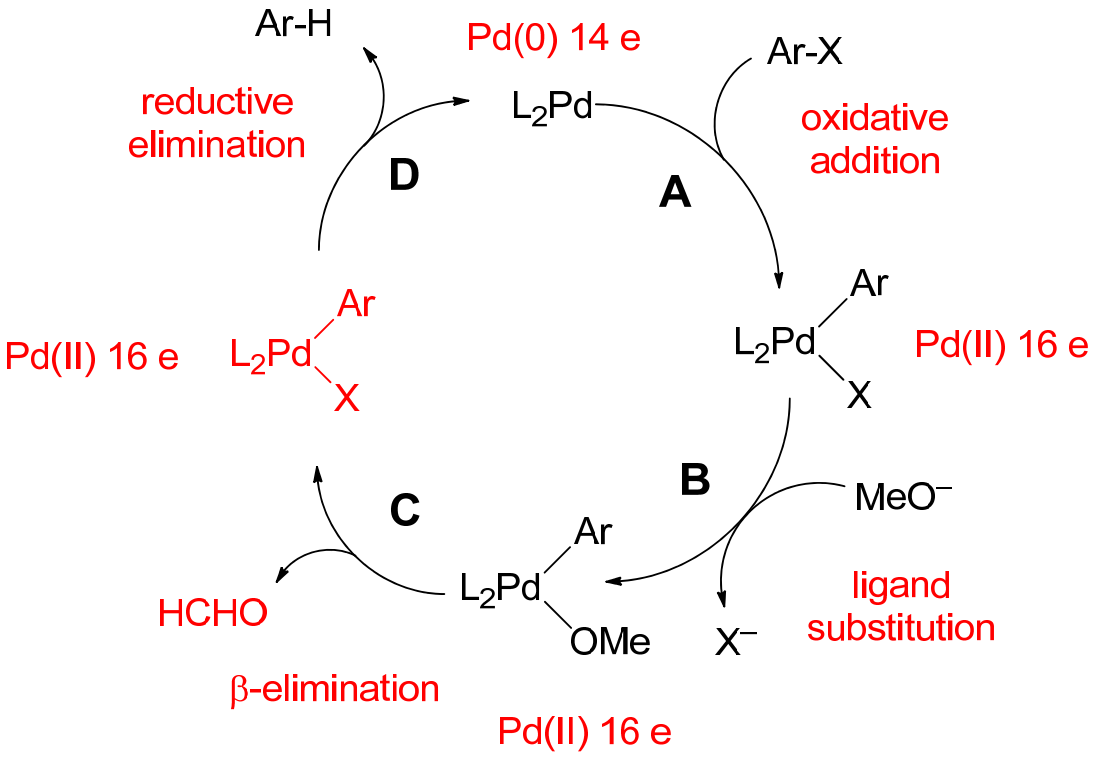
423/523 Organometallic Chemistry
Mid-term, 8:30 am Friday 16th November 2012
50 minutes, 50 marks.

NAME: ____

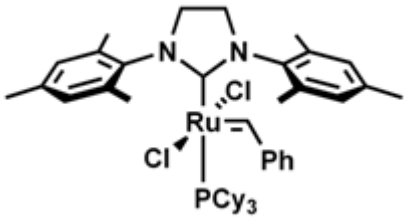
1 IA	2 IIA		3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIII	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1 **H** 1.0079																		2 **He** 4.0026
3 **Li** 6.941	4 **Be** 9.0122		Atomic number **Symbol** Atomic weight										5 **B** 10.811	6 **C** 12.011	7 **N** 14.007	8 **O** 15.999	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]		

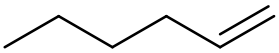
1. Examine the scheme below (L = phosphine). Fill in the boxes with the appropriate structures and give electron counts and oxidation states for all palladium complexes. Write down the overall reaction, and name reactions **A**, **B**, **C** and **D**.

[10 marks]

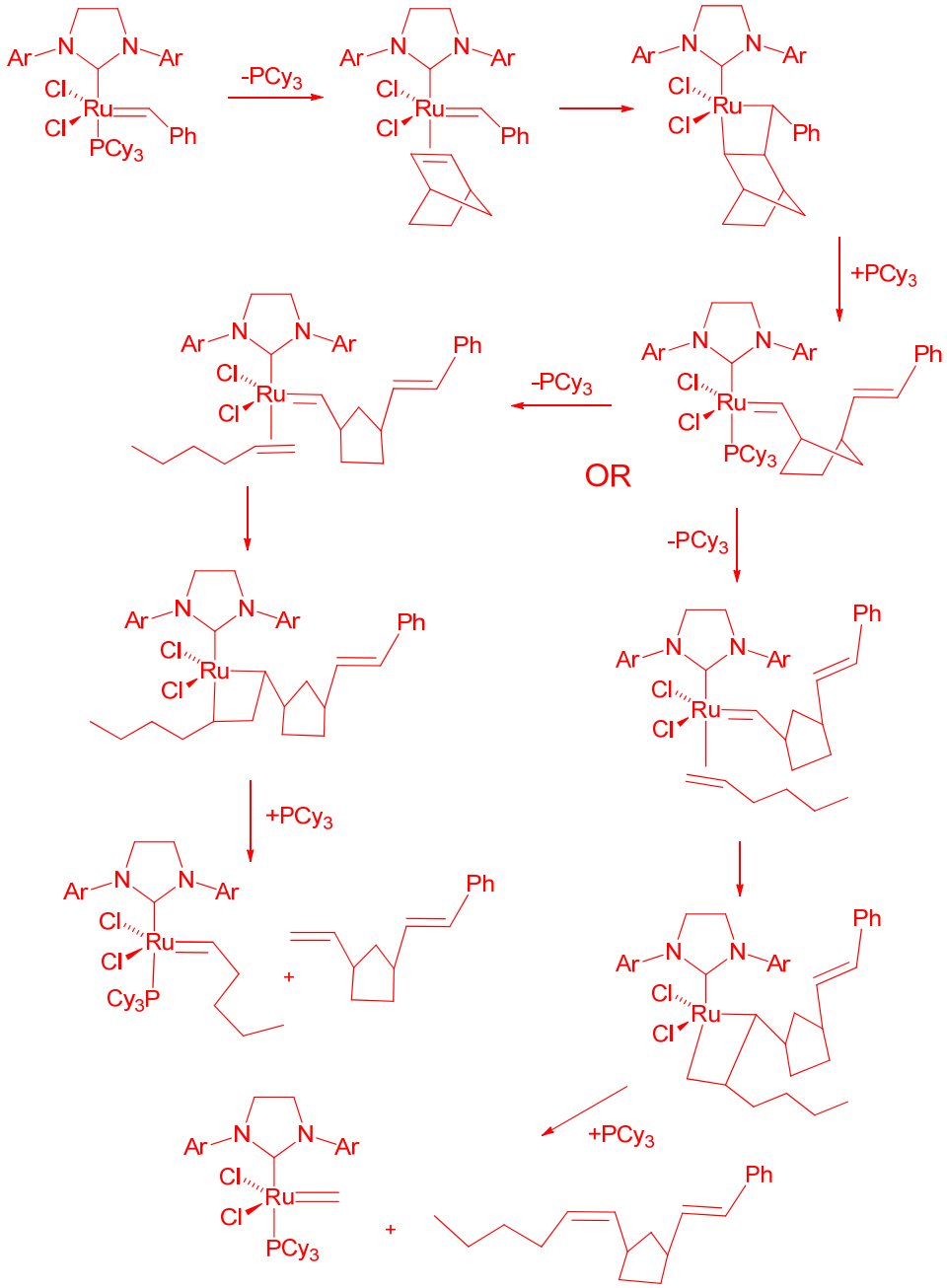


2. Draw the product(s) of the reaction between Grubbs' second generation catalyst and one equivalent of norbornene. Your scheme should indicate the mechanism and include an intermediate. What happens if you then add one equivalent of 1-hexene? Draw the product(s).



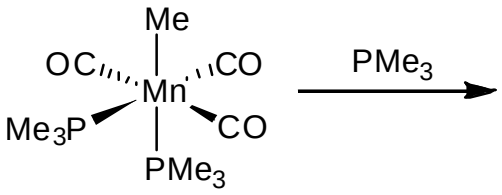
plus  then 

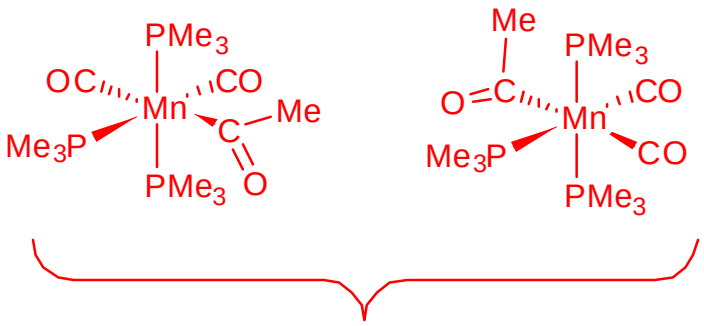
[14 marks]



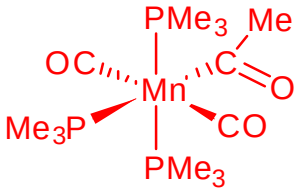
3. Predict the products of the addition of PMe_3 to the complex shown below, showing the structure of each and the expected relative distributions. Note: the products include all the atoms of the original complex and of the PMe_3. Choose ONE of the products, and describe in as much detail as you can its ν(CO) IR spectrum and its ^{31}P NMR spectrum (proton decoupled).

[8 marks]





enantiomers (67%)



33%

IR: 2 terminal CO stretches at ~2000 cm^{-1}
1 C=O at around 1700 cm^{-1}

IR: 1 terminal CO stretch at ~2000 cm^{-1}
1 C=O at around 1700 cm^{-1}

^{31}P NMR: 2P doublet ($^2J_{P\text{-}P}$), 1P triplet ($^2J_{P\text{-}P}$). Signals will be at higher ppm value compared to free phosphine.

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

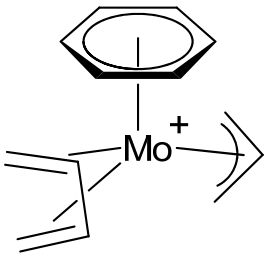
[10 marks]

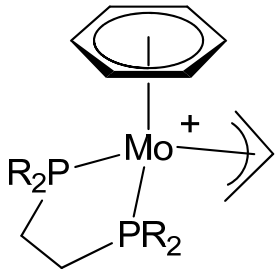
Straight from notes, i.e.

	Homogeneous	**Heterogeneous**
Form	Soluble metal complexes, usually mononuclear	Metals, usually supported, or metal oxides
Active site	well-defined, discrete molecules	poorly defined
Phase	Liquid	Gas/solid
Temperature	**Low** (<250°C)	High (250 – 500°C)
Activity	Moderate	**High**
Selectivity	**High**	Low
Diffusion	**Facile**	Can be very important
Heat transfer	**Facile**	Can be problematic
Product separation	Generally problematic	**Facile**
Catalyst recycle	Expensive	**Simple**
Catalyst modification	**Easy**	Difficult
Reaction mechanisms	**Reasonably well understood**	Poorly understood

5. Use the Davies-Green-Mingos rules to predict the products of the reactions between the following complexes and RS^-. Briefly explain why the nucleophile chooses that particular site of attack.

[8 marks]





1. even before odd
2. open before closed

1. even before odd