423/523 Organometallic Chemistry
Mid-term, 10:00 am Thursday 22nd October 2009

NAME: ______________ ______________________

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

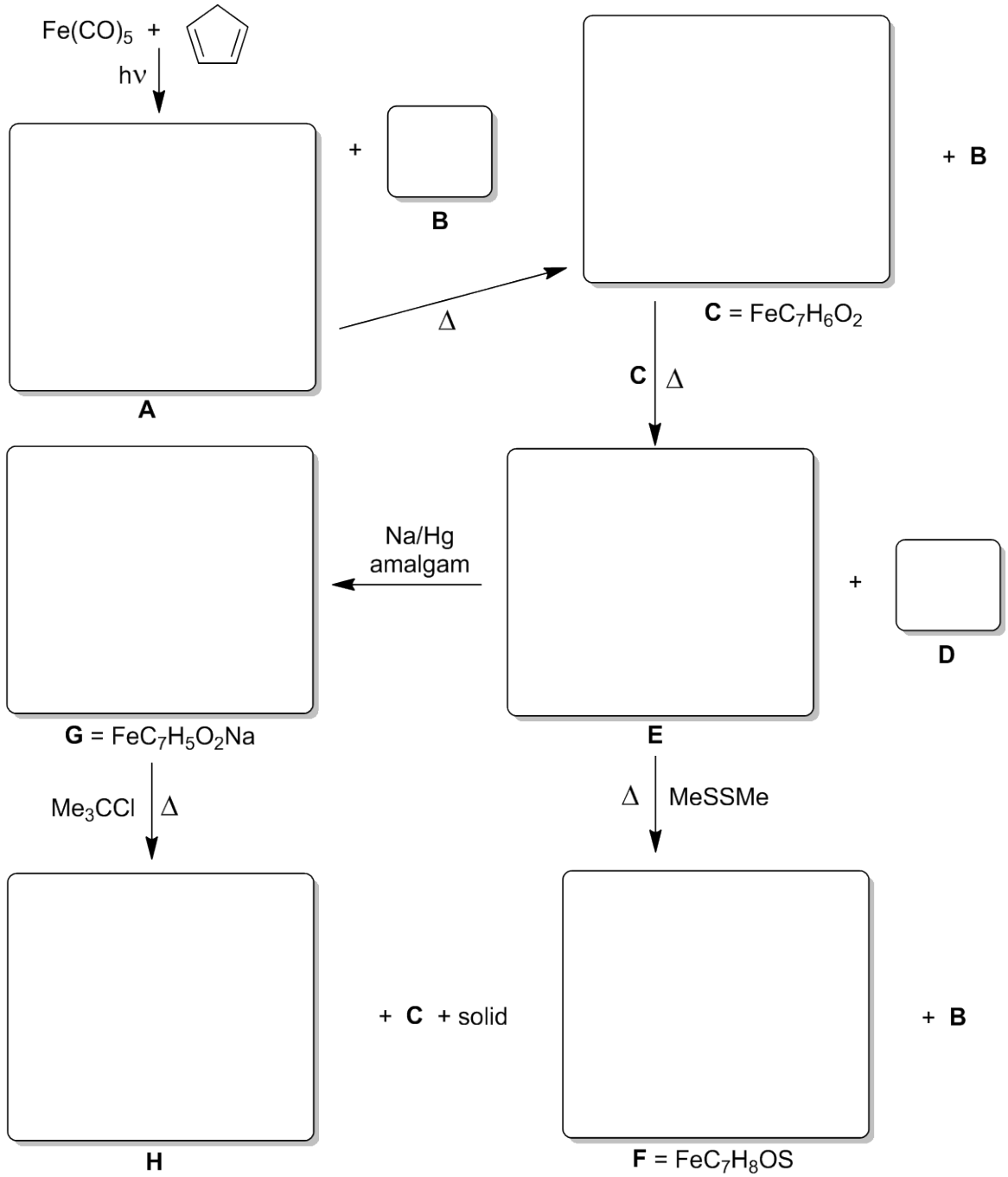
1 IA	2 IIA		3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIII	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1 H 1.0079																		2 He 4.0026
3 Li 6.941	4 Be 9.0122												5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305												13 Al 26.982	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]							

Key: Atomic number / **Symbol** / Atomic weight

†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. Irradiating $Fe(CO)_5$ with UV light in the presence of cyclopentadiene results in the formation of **A** and colourless gas **B**. **A** has four different ^1H NMR environments in a 2:2:1:1 ratio. Heating **A** further results in the release of more **B** to make **C**, having the formula $FeC_7H_6O_2$. Molecule **C** reacts rapidly with itself at room temperature to eliminate colourless gas **D**, forming solid **E**. Compound **E** has two strong IR bands, one near 1850 cm^{-1}, the other near 2000 cm^{-1}. Heating **E** with MeSSMe gives a product **F** that has an elemental analysis consistent with FeC_7H_8OS and with a single strong IR band near 2000 cm^{-1}. Treatment of **E** with Na metal generates solid **G** of empirical formula $FeC_7H_5O_2Na$. Reaction of **G** with Me_3CCl in a non-polar solvent produces **C**, **H** and a white precipitate. Draw structures for **A** to **H** in the appropriate boxes below.

[14 marks]



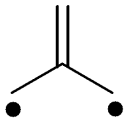
2. Draw the two singly occupied molecular orbitals of the cycloheptatrienyl anion, $[C_7H_7]^-$. Sketch alongside each of these singly occupied MOs the metal orbitals with the correct symmetry for a bonding interaction. Assume the *z*-axis runs through the metal centre and the centre of the ring of carbon atoms.

[6 marks]

4. *N*-heterocyclic carbenes are very poor π-acceptors, and are less tunable both sterically and electronically than phosphines. Explain the reasons for these observations.

[8 marks]

5. Trimethylenemethane (below) is a planar diradical and very unstable in the free state. However, it is stable as a ligand for transition metals, and all four carbon atoms bind to the metal. Draw possible resonance forms for this ligand binding to a metal, and suggest how it might be distorted from planarity on binding. How many electrons does it donate to the metal? In an $M(CO)_3(\eta^4$-trimethylenemethane) complex, what is the oxidation state of M?



[7 marks]

6. Cobaltocene, Cp_2Co, is stable at room temperature, but the rhodium analogue dimerizes to give the compound $Rh_2C_{20}H_{20}$. Draw two possible structures for the product; both should obey the 18 electron rule.

[7 marks]