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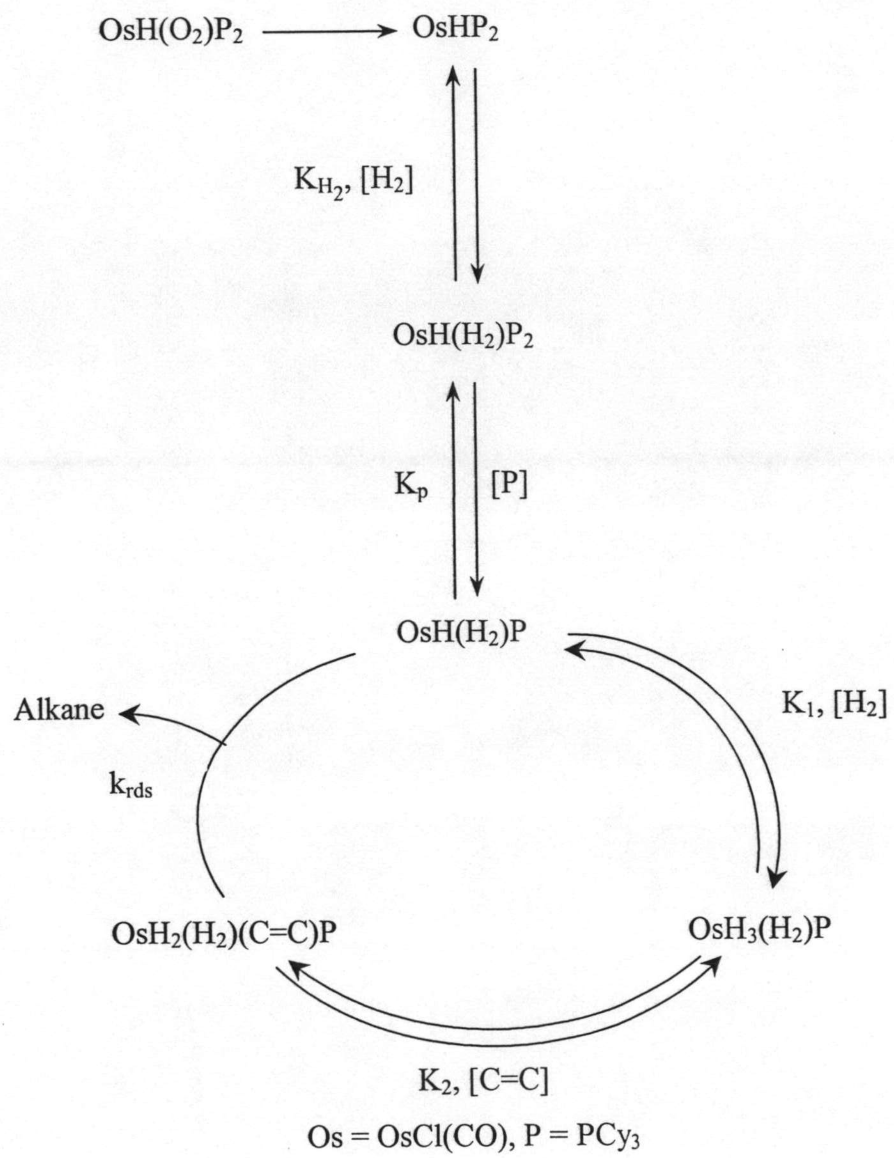
APPENDIX A

Preparation of $OsHCl(CO)(O_2)(PCy_3)_2$

Osmium(III) chloride trihydrate (1 g) is dissolved in 100 mL of 2-methoxyethanot in a 500 mL round bottomed flask with gas inlet tube, reflux condenser, and gas exit bubbler. The 5 g of tricyclohexylphosphine is added and the flask purged with nitrogen. The solution is refluxed for about 4-5 hours, and then cooled down to room temperature. The solution is left for overnight. The crystalline product is collected by transfer solvent under nitrogen atmosphere. The crystalline product is washed with methanol for 3 times. The 50 mL of hexane is added to dissolve the crystalline product. The oxygen gas is passed through the solution until the white crystalline is collected. The white crystalline product is washed with cold hexane for 2 times and dried in vacuum.

APPENDIX B

a) Derivation of the expression from the proposed mechanism for cis-1,4-poly(isoprene) hydrogenation by $OsHCl(CO)(O_2)(PCy_3)_2$.



Using the steady state assumption for reaction intermediates, the following equilibria define as the concentrations of each may be related to the rate-determining step according to:

$$K_2 = \frac{[OsH_2(H_2)(C{=}C)P]}{[OsH_3(H_2)P]\,[C{=}C]} \qquad [OsH_3(H_2)P] = \frac{1}{K_2\,[C{=}C]}\,[OsH_2(H_2)(C{=}C)P] \tag{B1}$$

$$K_1 = \frac{[OsH_3(H_2)P]}{[OsH(H_2)P]\,[H_2]} \qquad [OsH(H_2)P] = \frac{1}{K_1K_2[C{=}C][H_2]}\,[OsH_2(H_2)(C{=}C)P] \tag{B2}$$

$$K_p = \frac{[OsH(H_2)P]\,[P]}{[OsH(H_2)P_2]} \qquad [OsH(H_2)P_2] = \frac{[P]}{K_p\,K_1K_2[C{=}C][H_2]}\,[OsH_2(H_2)(C{=}C)P] \tag{B3}$$

$$K_{H_2} = \frac{[OsH(H_2)P_2]}{[OsHP_2]\,[H_2]} \qquad [OsHP_2] = \frac{[P]}{K_{H_2}\,K_p\,K_1K_2[C{=}C][H_2]^2}\,[OsH_2(H_2)(C{=}C)P] \tag{B4}$$

A material balance on the osmium charged to the system yields;

$$[Os]_T = [OsH_2(H_2)(C{=}C)P] + [OsH_3(H_2)P] + [OsH(H_2)P] + [OsH(H_2)P_2] + [OsHP_2] \tag{B5}$$

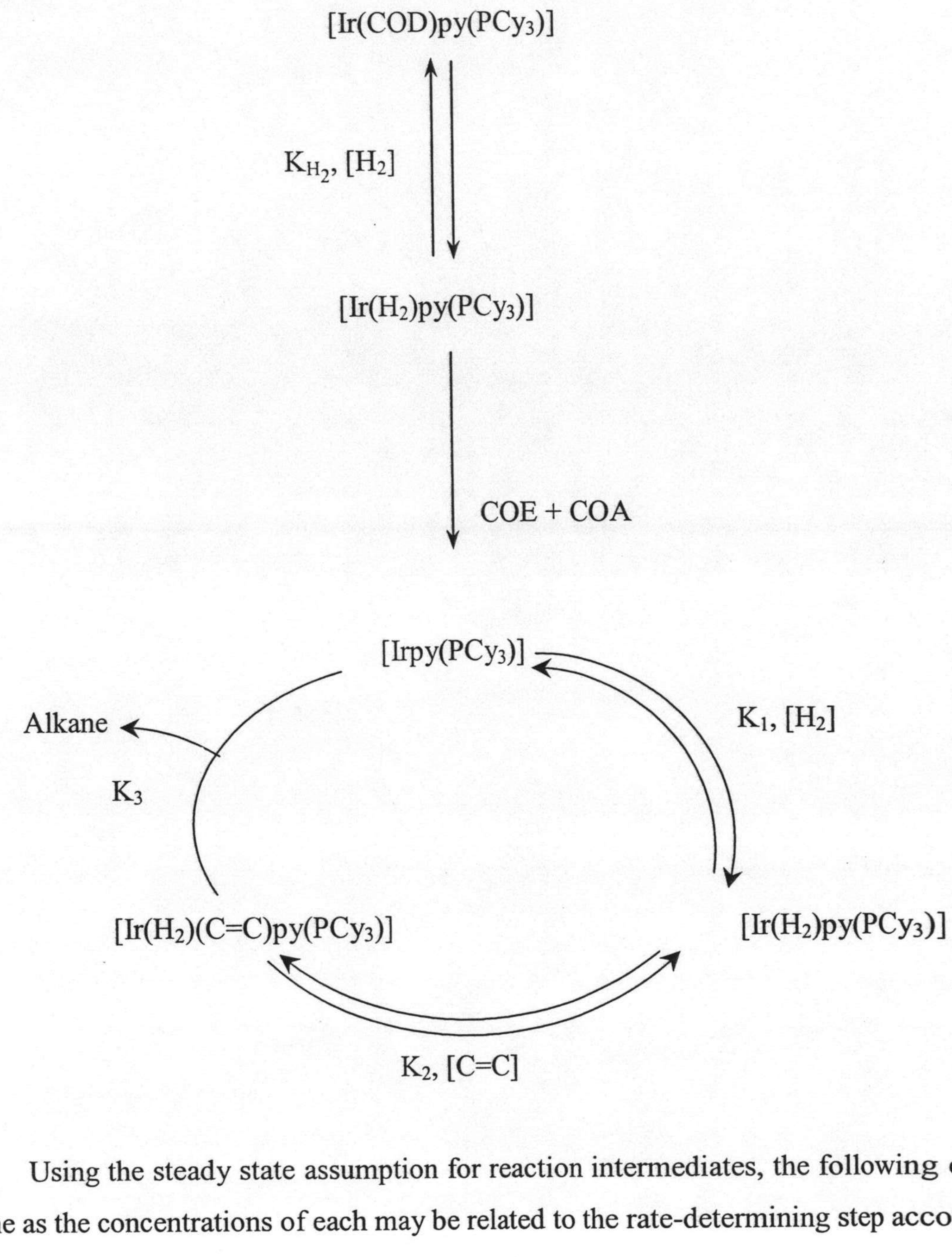
Which, using equations B1-B4 is transformed to;

$$[Os]_T = [OsH_2(H_2)(C{=}C)P] * \left(1 + \frac{1}{K_2\,[C{=}C]} + \frac{1}{K_1K_2[C{=}C][H_2]} + \frac{[P]}{K_p\,K_1K_2[C{=}C][H_2]} + \frac{[P]}{K_{H_2}\,K_p\,K_1K_2[C{=}C][H_2]^2}\right) \tag{B6}$$

Rearranging B6 yields;

$$[OsH_2(H_2)(C{=}C)P] = \frac{[Os]_T\,K_{H_2}K_pK_1K_2[C{=}C][H_2]^2}{[P] + K_{H_2}[P][H_2] + K_{H_2}K_p[H_2] + K_{H_2}K_pK_1[H_2]^2(1+K_2[C{=}C])} \tag{B7}$$

b) Derivation of the expression from the proposed mechanism for cis-1,4-poly(isoprene) hydrogenation by [Ir(COD)py(PCy$_3$)]PF$_6$.



Using the steady state assumption for reaction intermediates, the following equilibria define as the concentrations of each may be related to the rate-determining step according to:

$$K_2 = \frac{[Ir(H_2)py(C{=}C)P]}{[Ir(H_2)pyP]\,[C{=}C]} \qquad [Ir(H_2)pyP] = \frac{1}{K_2\,[C{=}C]}\,[Ir(H_2)py(C{=}C)P] \qquad (B8)$$

$$K_1 = \frac{[Ir(H_2)pyP]}{[IrpyP]\,[H_2]} \qquad [IrpyP] = \frac{1}{K_1K_2[C{=}C][H_2]}\,[Ir(H_2)py(C{=}C)P] \qquad (B9)$$

A material balance on the osmium charged to the system yields;

$$[Ir]_T = [Ir(H_2)py(C{=}C)P] + [Ir(H_2)pyP] + [IrpyP] \qquad (B10)$$

Which, using equations B8-B9 is transformed to;

$$[Ir]_T = [Ir(H_2)py(C{=}C)P] *(1+\frac{1}{K_2\,[C{=}C]} + \frac{1}{K_1K_2[C{=}C][H_2]}) \qquad (B11)$$

Rearranging B11 yields;

$$[Ir(H_2)py(C{=}C)P] = \frac{[Ir]_T\,K_1\,K_2\,[C{=}C]\,[H_2]}{1 + K_1[H_2] + K_1K_2[C{=}C][H_2]} \qquad (B12)$$

VITA

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