Derivation of Equation (2)

Assume that pyrrole (Pyr) exists in an equilibrium with its dimer (P_2):

$$K_{eq} = \frac{[P_2]}{[Pyr]^2} \tag{S1}$$

We can rewrite this equilibrium in terms of the nominal pyrrole concentration (i.e. the amount of pyrrole originally added to the solution), $[Pyr]_{nom}$:

$$K_{eq} = \frac{[P_2]}{\{[Pyr]_{nom} - 2[P_2]\}^2} \tag{S2}$$

Eq (S2) equation rearranges to

$$4K_{eq}[P_2]^2 - (4[Pyr]_{nom}K_{eq} + 1)[P_2] + [Pyr]_{nom}^2 K_{eq} = 0 \tag{S3}$$

Solving for $[P_2]$ (the root that gives $[P_2] < [Pyr]_{nom}$) gives the expression shown in eq (S4):

$$[P_2] = \frac{(4[Pyr]_{nom}K_{eq} + 1) - \sqrt{(4[Pyr]_{nom}K_{eq} + 1)^2 - 16[Pyr]_{nom}^2 K_{eq}^2}}{8K_{eq}} \tag{S4}$$

The expression under the radical is of the form $(x + 1)^2 - x^2 = 2x + 1$, and thus reduces to $8[Pyr]_{nom}K_{eq} + 1$. We can use this expression for $[P_2]$ to derive an expression for k_{obs} in terms of $[Pyr]_{nom}$ and K_{eq}, eq (2):

$$k_{obs} = k_a[Pyr] = k_a\{[Pyr]_{nom} - 2[P_2]\}$$

$$= k_a\left\{[Pyr]_{nom} - 2\left[\frac{\left(4[Pyr]_{nom}K_{eq} + 1\right) - \sqrt{8[Pyr]_{nom}K_{eq} + 1}}{8K_{eq}}\right]\right\}$$

$$= k_a\left\{[Pyr]_{nom} - [Pyr]_{nom} - \frac{1 - \sqrt{8[Pyr]_{nom}K_{eq} + 1}}{4K_{eq}}\right\}$$

$$= k_a\left[\frac{\left(\sqrt{8[Pyr]_{nom}K_{eq} + 1}\right) - 1}{4K_{eq}}\right] \tag{2}$$

Table S1. Pseudo-First Order Rate Constants (k_{obs}) for the Reaction of $W(CO)_5(CyH)$ with L = Pyrrolidine[a]

[L],	k_{obs}, 10^{-5} s^{-1}				
mol L^{-1}	20 °C	30 °C	40 °C	50 °C	60 °C
0.0051	1.26 (0.03)	1.64 (0.02)	1.73 (0.03)	1.99 (0.04)	2.22 (0.05)
0.0190	**4.32 (0.03)**	**4.99 (0.11)**	**5.69 (0.06)**	**6.44 (0.09)**	**7.39 (0.11)**
0.0397	8.45 (0.12)	10.44 (0.14)	11.37 (0.50)	12.90 (0.38)	14.08 (0.38)
0.0690	**14.90 (0.31)**	**18.28 (0.33)**	**20.38 (0.48)**	**21.86 (0.78)**	**25.59 (1.27)**
0.0954	18.84 (0.17)	21.66 (0.19)	24.79 (0.29)	27.65 (0.23)	30.87 (0.33)
0.108	**21.47 (0.10)**	**23.40 (0.12)**	**25.52 (0.14)**	**30.35 (0.15)**	**33.63 (0.19)**
0.132	25.62 (0.21)	28.65 (0.32)	32.51 (0.30)	37.23 (0.77)	41.31 (0.77)
0.143	**27.32 (1.27)**	**33.83 (1.62)**	**37.62 (2.37)**	**43.22 (2.21)**	**47.20 (2.64)**

[a] 1σ uncertainties to the fits are given in parentheses.

Table S2. Pseudo-First Order Rate Constants (k_{obs}) for the Reaction of $W(CO)_5(CyH)$ with L = Pyrrole[a]

$[Pyr]_{nom}$,[b]	k_{obs}, 10^{-5} s^{-1}				
mol L^{-1}	20 °C	30 °C	40 °C	50 °C	60 °C
0.045	2.94 (0.01)	2.62 (0.01)	4.84 (0.02)	4.40 (0.01)	7.50 (0.03)
0.100	**4.20 (0.03)**	**5.57 (0.05)**	**7.52 (0.05)**	**9.38 (0.07)**	**11.10 (0.11)**
0.198	7.62 (0.04)	9.89 (0.04)	13.20 (0.11)	17.30 (0.17)	20.60 (0.28)
0.213	**7.62 (0.05)**	**9.52 (0.08)**	**12.36 (0.13)**	**16.36 (0.28)**	**20.34 (0.21)**
0.322	10.90 (0.03)	14.50 (0.10)	20.80 (0.19)	23.40 (0.20)	32.80 (0.50)
0.432	**14.00 (0.15)**	**19.40 (0.19)**	**26.30 (0.37)**	**34.1 (0.49)**	**42.60 (0.85)**
0.598	17.90 (0.10)	24.50 (0.30)	32.80 (0.44)	37.80 (0.55)	55.00 (0.98)
0.610	**15.03 (0.15)**	**20.43 (0.19)**	**32.7 (0.33)**	**37.26 (0.57)**	—
0.650	15.94 (0.59)	22.54 (0.68)	30.02 (1.01)	—	—
0.980	**21.06 (0.85)**	**29.81 (0.88)**	**45.28 (1.07)**	—	—
1.031	20.50 (0.40)	—	—	—	—
1.540	**28.25 (1.04)**	**42.17 (1.50)**	**59.21 (4.91)**	—	—

[a] 1σ uncertainties to the fits in parentheses. [b] Nominal concentration of pyrrole added to the solution; see text for discussion of the relationship of $[Pyr]_{nom}$ to the true concentration of pyrrole monomers.