Electronic Supporting Information

Reactions of the Transient Species $Cr(CO)_5$(cyclohexane) with C_4H_nE (n = 4, 8; E = O, NH, S) Studied by Time-Resolved Infrared Absorption Spectroscopy

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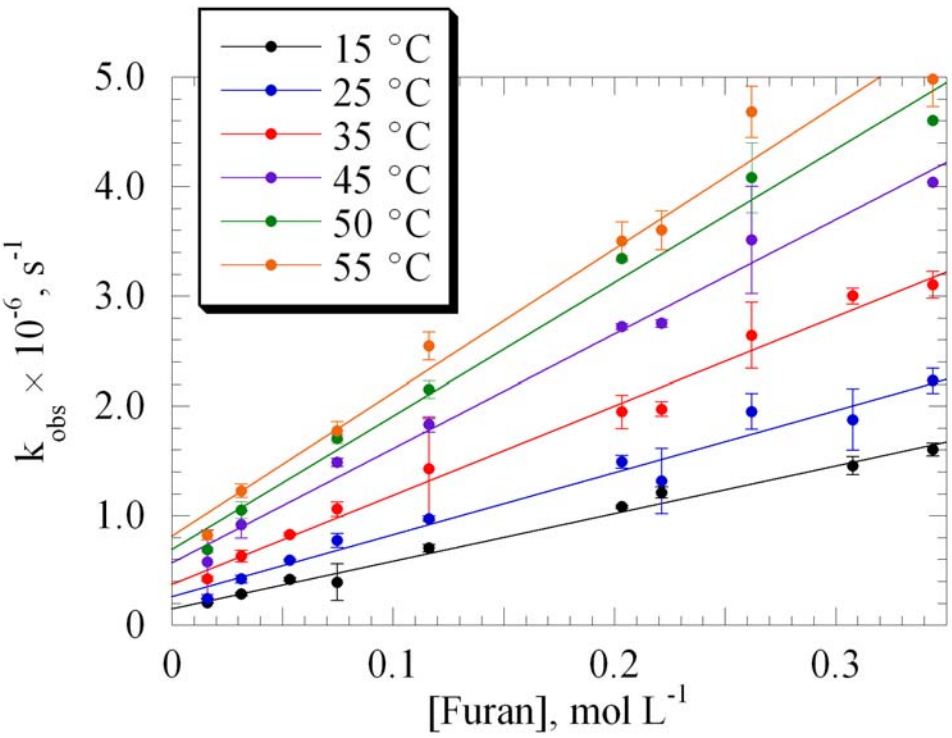

Fig. S-1 k_{obs} as a function of [L] for reaction of $Cr(CO)_5(CyH)$ with furan over the temperature range 15 EC - 55EC. The solid lines represent least-squares linear fits to the data. 1σ error bars are shown.

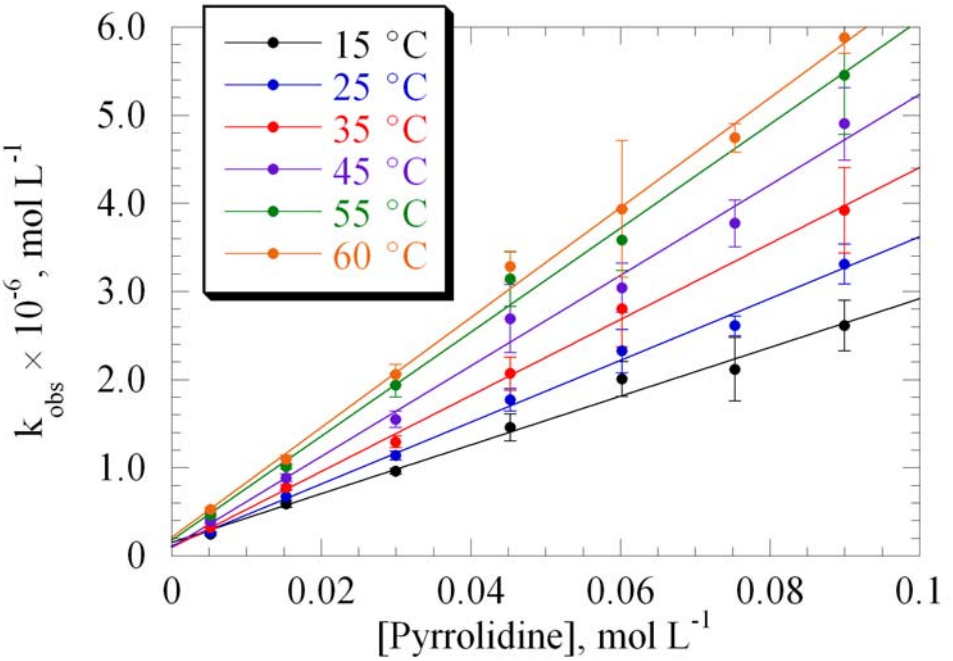

Fig. S-2 k_{obs} as a function of [L] for reaction of $Cr(CO)_5(CyH)$ with pyrrolidine over the temperature range 15 EC - 60 EC. The solid lines are least-squares linear fits to the data. 1σ error bars are shown.

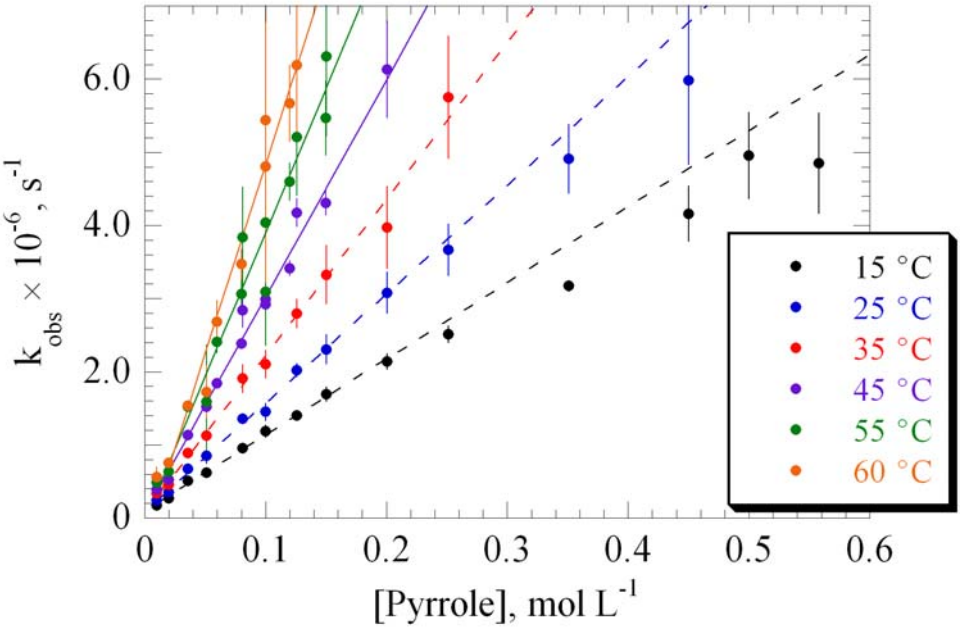

Fig. S-3 k_{obs} as a function of the nominal concentration of [L] for reaction of $Cr(CO)_5(CyH)$ with pyrrole, measured over the temperature range 15 EC - 60 EC. The dashed lines indicate least-squares linear fits to the data at 15 EC - 35 EC for $[Pyr]_{nom} < 0.25$ mol L^{-1} (see the text). The solid lines represent least-squares linear fits to the entire data sets at higher temperatures. 1σ error bars are shown.

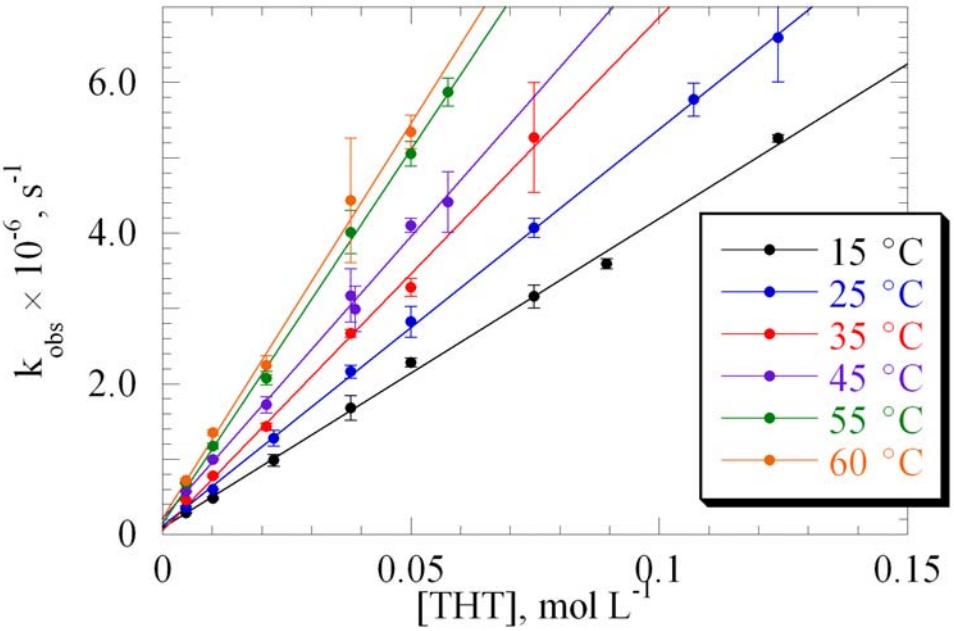

Fig. S-4 k_{obs} as a function of [L] for the reaction of $Cr(CO)_5(CyH)$ with tetrahydrothiophene over the temperature range 15 EC - 60 EC. The solid lines represent least-squares linear fits to data. 1σ error bars are shown.

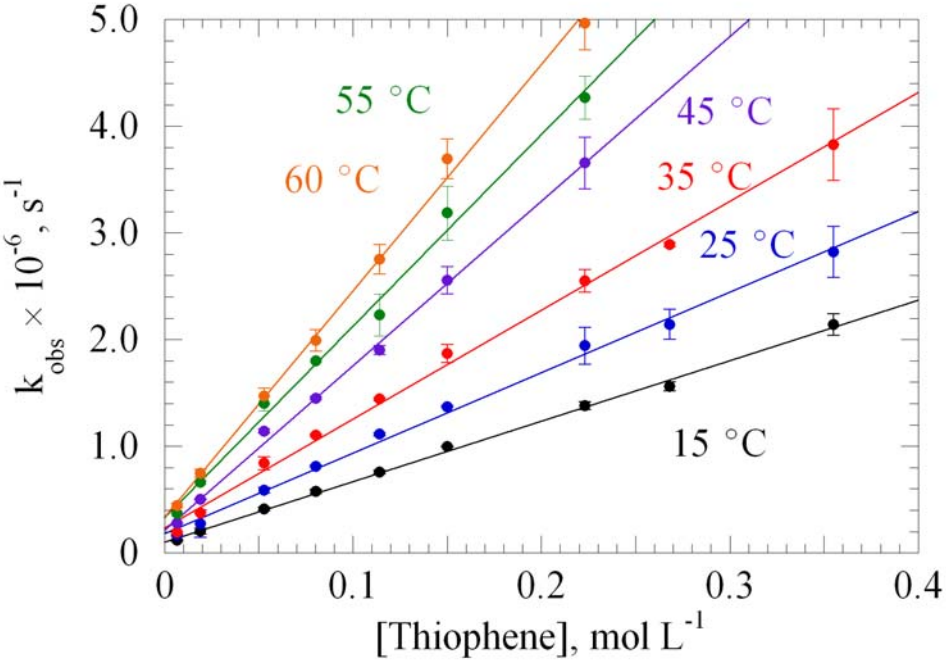

Fig. S-5 k_{obs} as a function of [L] for the reaction of $Cr(CO)_5(CyH)$ with thiophene over the temperature range 15 EC - 60 EC. The solid lines represent least-squares linear fits to data. 1σ error bars are shown.

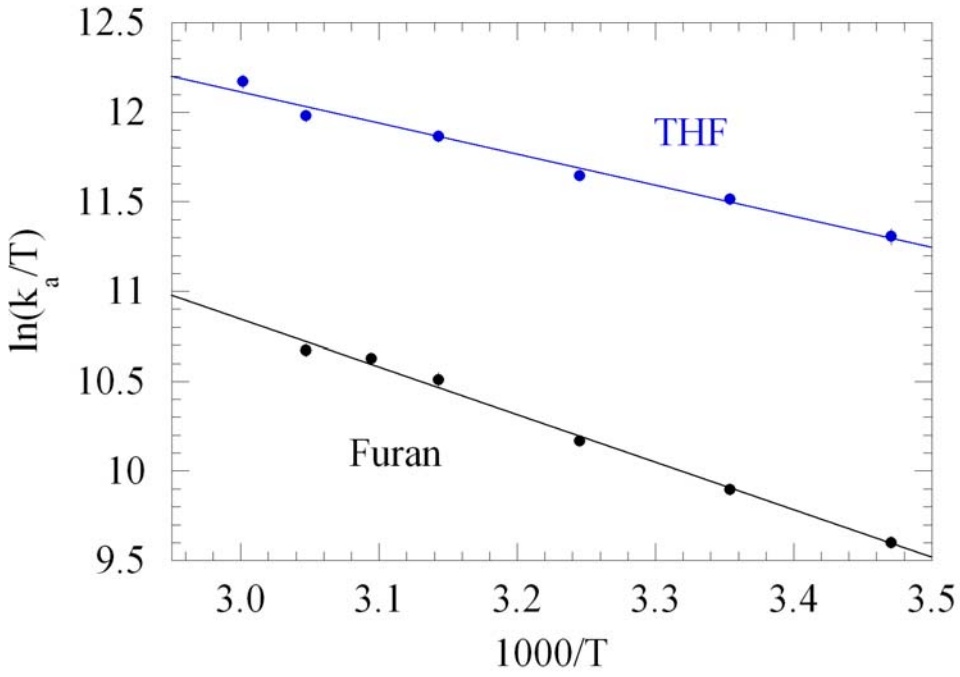

Fig. S-6 Eyring plot for the reaction of $Cr(CO)_5(CyH)$ with THF (blue) and furan (black). The solid lines represent least-squares fits to the data, yielding the activation parameters given in Table 3 of the text.

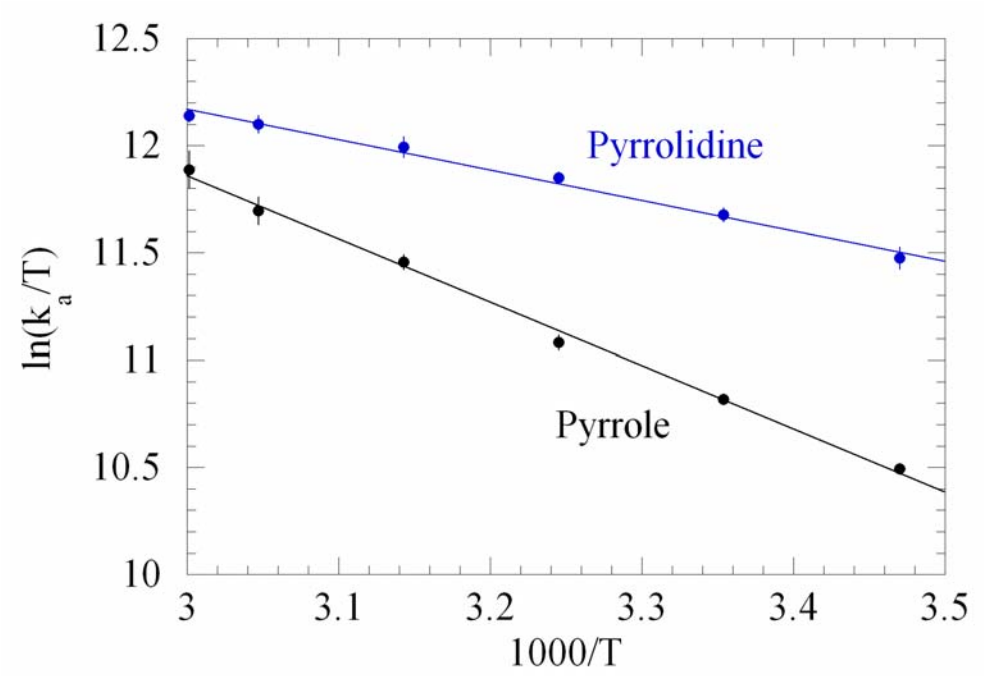

Fig. S-7 Eyring plot for the reaction of $Cr(CO)_5(CyH)$ with pyrrolidine (blue) and pyrrole (black). The solid lines represent least-squares fits to the data, yielding the activation parameters given in Table 3 of the text.

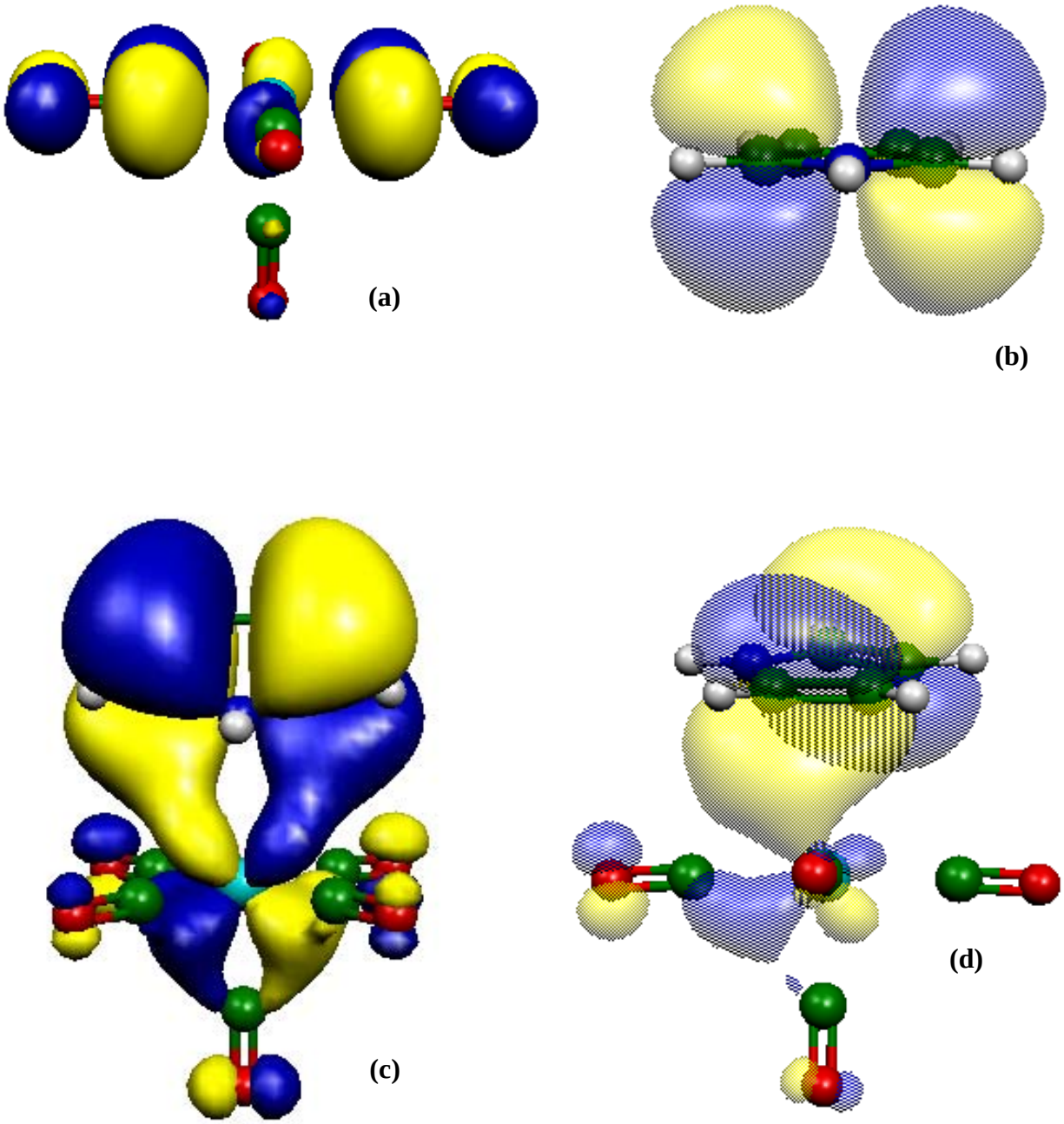

Fig. S-8 MO structures as calculated by DFT. All MOs shown in this figure were calculated by using the B3LYP functional, the Stuttgart 1997 ECP basis set for Cr, and the 6-311++G(2d,2p) basis set for the other atoms. **(a)** Unoccupied MO (LUMO+2) of $Cr(CO)_5$; **(b)** HOMO of pyrrole; **(c)** MO (HOMO-3) of $Cr(CO)_5(\eta^1$-pyrrole) showing the metal-ligand interaction; **(d)** MO (HOMO-3) of $Cr(CO)_5(\eta^2$-pyrrole) showing the metal-ligand interaction.

Table S-1 Pseudo-first order rate constants k_{obs} ($\times 10^{-6}$, s^{-1}) for reaction of $Cr(CO)_5(CyH)$ with THF (1σ uncertainties in parentheses)

[THF], mol L^{-1}	15 EC	25 EC	35 EC	45 EC	55 EC	60 EC
0.0050	0.221 (0.021)	0.284 (0.025)	0.363 (0.006)	0.446 (0.008)	0.563 (0.013)	0.593 (0.051)
0.0110	**0.404 (0.011)**	**0.516 (0.010)**	**0.718 (0.07)**	**0.831 (0.030)**	**1.06 (0.03)**	**1.11 (0.02)**
0.0201	0.746 (0.032)	0.811 (0.015)	1.13 (0.04)	1.52 (0.029)	1.74 (0.11)	1.90 (0.07)
0.0212	**0.738 (0.016)**	**0.920 (0.094)**	**1.14 (0.03)**	**1.37 (0.041)**	**1.61 (0.04)**	**1.73 (0.10)**
0.0407	1.00 (0.01)	1.20 (0.03)	1.89 (0.11)	2.34 (0.075)	2.61 (0.22)	2.80 (0.21)
0.0518	**1.36 (0.04)**	**1.73 (0.09)**	**2.15 (0.17)**	**2.66 (0.22)**	**3.31 (0.18)**	**3.56 (0.22)**
0.0691	1.99 (0.23)	2.32 (0.25)	2.70 (0.26)	3.53 (0.32)	3.98 (0.54)	5.08 (0.32)
0.0789	**1.87 (0.09)**	**2.54 (0.12)**	**3.20 (0.23)**	**3.83 (0.39)**	**4.81 (0.54)**	**5.35 (0.37)**
0.0916	2.28 (0.11)	2.78 (0.05)	3.55 (0.16)	4.35 (0.61)	5.13 (0.58)	
0.102	**2.59 (0.22)**	**3.30 (0.18)**	**3.86 (0.14)**	**5.17 (0.22)**		

Table S-2 Pseudo-first order rate constants k_{obs} ($\times 10^{-6}$, s^{-1}) for reaction of $Cr(CO)_5(CyH)$ with furan (1σ uncertainties in parentheses)

[Furan], mol L^{-1}	15 EC	25 EC	35 EC	45 EC	50 EC	55 EC
0.0162	0.200 (0.004)	0.242 (0.006)	0.421 (0.019)	0.573 (0.03)	0.686 (0.021)	0.821 (0.022)
0.0316	**0.281 (0.014)**	**0.420 (0.034)**	**0.628 (0.054)**	**0.915 (0.12)**	**1.05 (0.08)**	**1.23 (0.11)**
0.0534	0.414 (0.016)	0.590 (0.011)	0.828 (0.011)			
0.0749	**0.390 (0.017)**	**0.773 (0.062)**	**1.06 (0.06)**	**1.48 (0.04)**	**1.70 (0.04)**	**1.77 (0.10)**
0.116	0.700 (0.036)	0.971 (0.025)	1.43 (0.46)	1.83 (0.07)	2.15 (0.08)	2.54 (0.15)
0.203	**1.08 (0.01)**	**1.49 (0.06)**	**1.95 (0.15)**	**2.72 (0.03)**	**3.34 (0.03)**	**3.50 (0.30)**
0.221	1.21 (0.05)	1.32 (0.30)	1.97 (0.07)	2.75 (0.03)		3.60 (0.70)
0.262		**1.95 (0.16)**	**2.64 (0.30)**	**3.51 (0.49)**	**4.08 (0.32)**	**4.68 (0.30)**
0.308	1.45 (0.08)	1.87 (0.28)	3.00 (0.07)			
0.344	**1.60 (0.06)**	**2.22 (0.11)**	**3.10 (0.12)**	**4.69 (0.32)**	**5.12 (0.60)**	**5.49 (0.59)**

Table S-3 Pseudo-first order rate constants k_{obs} ($\times 10^{-6}$, s^{-1}) for reaction of $Cr(CO)_5(CyH)$ with pyrrolidine (1σ uncertainties in parentheses)

[L], mol L^{-1}	15 EC	25 EC	35 EC	45 EC	55 EC	60 EC
0.0052	0.240 (0.012)	0.264 (0.006)	0.323 (0.008)	0.391 (0.027)	0.461 (0.018)	0.528 (0.020)
0.0153	**0.587 (0.039)**	**0.670 (0.076)**	**0.773 (0.031)**	**0.885 (0.043)**	**1.01 (0.03)**	**1.09 (0.05)**
0.0300	0.958 (0.030)	1.14 (0.05)	1.29 (0.07)	1.55 (0.091)	1.94 (0.13)	2.06 (0.12)
0.0453	**1.46 (0.15)**	**1.77 (0.13)**	**2.07 (0.19)**	**2.69 (0.39)**	**3.14 (0.31)**	**3.28 (0.17)**
0.0603	2.01 (0.20)	2.32 (0.25)	2.80 (0.43)	3.04 (0.28)	3.58 (0.35)	3.94 (0.78)
0.0753	**2.12 (0.36)**	**2.61 (0.11)**		**3.77 (0.26)**		**4.74 (0.16)**
0.0900	2.61 (0.29)	3.31 (0.23)	3.93 (0.48)	4.90 (0.41)	5.46 (0.67)	5.88 (0.18)

Table S-4 Pseudo-first order rate constants k_{obs} ($\times 10^{-6}$, s^{-1}) for reaction of $Cr(CO)_5(CyH)$ with pyrrole (1σ uncertainties in parentheses)

[Pyrrole], mol L^{-1}	15 EC	25 EC	35 EC	45 EC	55 EC	60 EC
0.0100	0.176 (0.008)	0.242 (0.034)	0.336 (0.048)	0.386 (0.037)	0.487 (0.17)	0.559 (0.13)
0.0200	**0.273 (0.012)**	**0.350 (0.012)**	**0.455 (0.015)**	**0.522 (0.046)**	**0.634 (0.038)**	**0.751 (0.73)**
0.0356	0.511 (0.009)	0.670 (0.017)	0.885 (0.017)	1.14 (0.022)	1.52 (0.07)	1.54 (0.021)
0.0514	**0.621 (0.018)**	**0.847 (0.10)**	**1.13 (0.15)**	**1.52 (0.078)**	**2.41 (0.15)**	**1.72 (0.35)**
0.0601				1.84 (0.036)	3.06 (0.24)	2.68 (0.29)
0.0801				**2.39 (0.058)**	**3.84 (0.68)**	**3.47 (0.21)**
0.0812	0.956 (0.026)	1.355 (0.053)	1.91 (0.19)	2.84 (0.23)	4.04 (0.24)	
0.100				**2.92 (0.10)**		**4.80 (0.24)**
0.100	1.19 (0.08)	1.45 (0.11)	2.10 (0.19)	2.99 (0.53)	4.60 (0.25)	5.44 (2.20)
0.120				**3.41 (0.10)**	**5.21 (0.80)**	**5.67 (0.52)**
0.126	1.40 (0.04)	2.02 (0.09)	2.79 (0.19)	4.17 (0.19)	5.47 (0.51)	6.19 (0.99)
0.150				**4.31 (0.17)**	**6.31 (1.09)**	
0.151	1.69 (0.10)	2.31 (0.20)	3.32 (0.40)			
0.201	**2.14 (0.11)**	**3.08 (0.28)**	**3.97 (0.56)**	**6.13 (0.66)**		
0.252	2.51 (0.11)	3.67 (0.35)	5.75 (0.83)			
0.351	**3.17 (0.07)**	**4.91 (0.47)**				
0.450	4.16 (0.38)	5.98 (1.15)				
0.500	**4.95 (0.59)**					
0.558	4.85 (0.68)					
0.750	**6.04 (0.04)**					

Table S-5 Pseudo-first order rate constants k_{obs} ($\times 10^{-6}$, s^{-1}) for reaction of $Cr(CO)_5(CyH)$ with tetrahydrothiophene (1σ uncertainties in parentheses)

[THT], mol L^{-1}	15 EC	25 EC	35 EC	45 EC	55 EC	60 EC
0.00480	0.287 (0.007)	0.350 (0.020)	0.452 (0.006)	0.567 (0.006)	0.678 (0.007)	0.716 (0.014)
0.0102	**0.481 (0.015)**	**0.597 (0.003)**	**0.777 (0.015)**	**0.994 (0.013)**	**1.17 (0.04)**	**1.35 (0.04)**
0.0210			1.43 (0.045)	1.72 (0.11)	2.07 (0.09)	2.24 (0.13)
0.0224	**0.981 (0.078)**	**1.28 (0.11)**				
0.0380	1.67 (0.17)	2.16 (0.09)	2.67 (0.05)	3.17 (0.35)	4.01 (0.29)	4.43 (0.83)
0.0388				**2.99 (0.30)**		
0.0500	2.28 (0.06)	2.82 (0.20)	3.28 (0.12)	4.10 (0.09)	5.05 (0.16)	5.34 (0.22)
0.0574				**4.41 (0.40)**	**5.87 (0.19)**	
0.0749	3.16 (0.15)	4.07 (0.13)	5.27 (0.73)			
0.0895	**3.59 (0.07)**					
0.107		5.77 (0.22)				
0.124	**5.26 (0.05)**	**6.59 (0.59)**				

Table S-6 Pseudo-first order rate constants k_{obs} ($\times 10^{-6}$, s^{-1}) for reaction of $Cr(CO)_5(CyH)$ with thiophene (1σ uncertainties in parentheses)

[Thiophene], mol L^{-1}	15 EC	25 EC	35 EC	45 EC	55 EC	60 EC
0.0068	0.117 (0.008)	0.165 (0.008)	0.192 (0.001)	0.275 (0.005)	0.368 (0.020)	0.443 (0.018)
0.0190	**0.205 (0.026)**	**0.273 (0.013)**	**0.372 (0.001)**	**0.503 (0.005)**	**0.661 (0.015)**	**0.746 (0.020)**
0.0529	0.410 (0.015)	0.585 (0.028)	0.839 (0.063)	1.14 (0.02)	1.40 (0.07)	1.47 (0.06)
0.0804	**0.573 (0.019)**	**0.811 (0.007)**	**1.10 (0.01)**	**1.45 (0.01)**	**1.80 (0.01)**	**1.99 (0.01)**
0.114	0.754 (0.016)	1.11 (0.01)	1.44 (0.01)	1.90 (0.04)	2.23 (0.20)	2.75 (0.10)
0.150	**0.996 (0.006)**	**1.37 (0.10)**	**1.87 (0.08)**	**2.55 (0.13)**	**3.19 (0.25)**	**3.69 (0.24)**
0.223	1.38 (0.036)	1.94 (0.17)	2.55 (0.11)	3.65 (0.24)	4.27 (0.20)	4.96 (0.50)
0.268	**1.56 (0.042)**	**2.14 (0.14)**	**2.89 (0.02)**			
0.355	2.14 (0.10)	2.82 (0.24)	3.83 (0.33)			