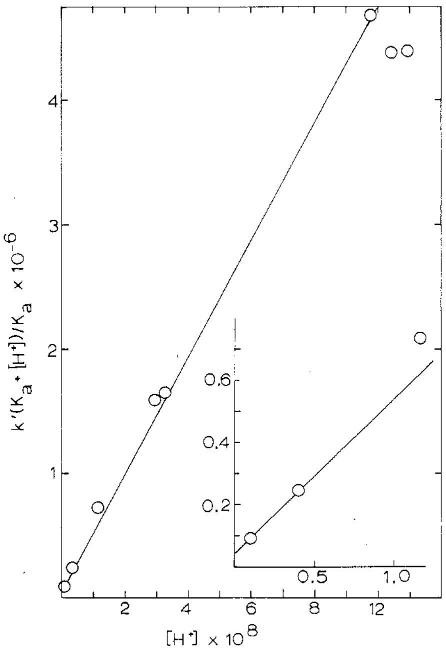

Figure 2. Plot of $[k'(K_a + [H^+])/K_a] \times 10^{-6}$ as a function of $[H^+] \times 10^8$ for the reduction of hemin by dithionite where $k' = k_{obsd}/(1.4 \times 10^{-9})^{1/2}[S_2O_4^{2-}]^{1/2}$ and pK_a is 5.89. The inset shows in more detail the region near the origin.

conditions of these experiments. The results were consistent with the simultaneous binding of 2 mol of pyridine/mol of hemin. The concentration of hemin required for the reaction to reach 50% completion was 0.01 M, yielding an equilibrium constant of 1.0×10^4 M^{-2} for the reaction

$$H^+ + 2py + H_2O\text{-}Hm\text{-}OH \rightleftarrows py\text{-}Hm\text{-}py$$

The spectrum of the product after reduction of the bis(pyridine) complex was identical with that reported for the bis(pyridine) complex of heme.[11] The observed rate constant was determined as a function of $[S_2O_4^{2-}]$ in 0.05 M pyridine as is shown in Figure 1. (Our titration results show that the complex is completely formed under these conditions.) As in the case of the reduction of hemin, the observed rate constant is proportional to $[S_2O_4^{2-}]^{1/2}$ with a similar mechanism. From the slope of the line the rate constant for reduction by SO_2^- was equal to $(8.5 \pm 0.7) \times 10^7$ M^{-1} s^{-1}. The rate constant was measured as a function of pyridine concentration and did not vary over a fourfold range (0.05–0.20 M).

Discussion

The rate constants for the reduction of the bis(pyridine), aquo, and hydroxide complexes of hemin by SO_2^- are 8.5×10^7, 6.0×10^6, and 5×10^3 M^{-1} s^{-1}, respectively. The reduction of the bis(pyridine) complex occurs via an outer-sphere mechanism since the observed rate constant would be inversely proportional to the pyridine concentration if the pyridine molecule were displaced by SO_2^- as would be the case in an inner-sphere mechanism. In the case of the aquo and hydroxide complexes, it is more difficult to determine whether the reaction occurs via an inner- or outer-sphere mechanism. In the case of the reduction of the water-soluble cobalt(III) porphyrin, the mechanism was determined to be outer-sphere since the rate of substitution was much slower than the rate of reduction.[3] Such is not the case here. The rate of reaction of a water-soluble iron(III) porphyrin with imidazole has been measured and rate constants on the order of 10^7 M^{-1} s^{-1} have been obtained for the reaction of both the aquo and hydroxide species.[12] Based on these data it is difficult to unambiguously assign either an inner- or outer-sphere mechanism. However, if the rate of substitution were rate limiting as might be expected in an inner-sphere mechanism, then one would expect little difference in the rates of reduction of the aquo and hydroxide species since the rates of substitution are expected to be the same. However, the rates are markedly different and this difference is consistent with that previously observed for reduction reactions involving outer-sphere mechanisms; e.g. the reduction of a water-soluble cobalt(III) porphyrin by SO_2^-[3] and the reduction of metmyoglobin by the *trans*-1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetraacetate complex of iron(III).[13]

The bis(pyridine) complex of hemin is reduced more rapidly than the aquo complex. This is consistent with the observation that pyridine stabilizes the iron(II) oxidation state relative to the iron(III) state because of the stability associated with the fully filled t_{2g} orbitals in the low-spin d^6 electronic configuration.[11] In the case of the water-soluble cobalt(III) porphyrin, the aquo complex was reduced more rapidly than the bis(pyridine) complex. In this case, the low-spin d^6 configuration is associated with Co(III); hence, in this case, the Co(III) oxidation state is stabilized relative to Co(II) by coordination with pyridine.

The results obtained in this study can be compared with those observed in the reduction of heme proteins by dithionite. The following rate constants have been observed for the reduction by SO_2^-: metmyoglobin,[8] 2.7×10^6 M^{-1} s^{-1}; ferricytochrome *c*,[6,14] 3.8×10^7 M^{-1} s^{-1} (there is some disagreement with respect to the mechanism here); and cyanoferricytochrome *c*,[15] 7×10^5 M^{-1} s^{-1}. Thus our value for the reduction of the aquo complex by SO_2^- is very similar to rate constants observed for heme proteins.

Acknowledgment. This work was supported by National Science Foundation Grant GB 37097.

Registry No. py-Hm-py, 15723-81-6; H_2O-Hm-OH_2^+, 26025-40-1; H_2O-Hm-OH, 37098-83-2; $S_2O_4^{2-}$, 14844-07-6.

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Organonitrogen Derivatives of Metal Carbonyls. 12. Reactions of Cyclopentadienylmetal Tricarbonyl Chlorides of Molybdenum and Tungsten with Pyrazole and Imidazole[1]

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Received March 9, 1977 AIC70187S

Recently we reported reactions of $C_5H_5M(CO)_3Cl$ (M = Mo and W) with the ketoximes[3] RR'C=NOH and acetone

Table I. Properties of the New Compounds Prepared in This Work

Compd[a]	Color	Mp, °C		Anal.				Mol wt	Conductance	Infrared spectrum		
				% C	% H	% N	% Cl			ν(CO), cm^{-1}	I_a/I_s	2θ, deg
$[CpMo(CO)_2(PzH)_2]Cl$	Dark red	110–111	Calcd	40.1	3.3	14.4	9.1		26.3	1976, 1873	1.0	90
			Found	40.3	3.3	14.5	9.2					
$[CpMo(CO)_2(PzH)_2][PF_6]$	Red	147–149 dec	Calcd	31.3	2.6	11.2			29.6	2001, 1883	1.0	90
			Found	31.5	2.7	11.2						
$CpMo(CO)_2(PzH)Cl$	Purple	117–118 dec	Calcd	37.4	2.8	8.7	11.1	321	2.9	1970, 1865	1.1	93
			Found	37.6	2.9	8.7	10.7	344				
$[CpW(CO)_2(PzH)_2]Cl$	Dark red	140–141 dec	Calcd	32.7	2.7	11.8	7.4		26.8	1947, 1839	0.9	87
			Found	32.9	2.8	11.7	7.4					
$CpW(CO)_2(PzH)Cl$	Dark red	121–123 dec	Calcd	29.4	2.2	6.9	8.7	409	6.4	1954, 1840[b]	1.7	105
			Found	29.8	2.3	6.6	8.5	394				
$[CpMo(CO)_2(ImH)_2]Cl$	Red	175–176 dec	Calcd	40.1	3.3	14.4	9.1		27.3	1951, 1856[c]	1.0	90
			Found	39.9	3.4	14.6	9.2					
$[CpMo(CO)_2(ImH)_2][PF_6]$	Red	129–130	Calcd	31.3	2.6	11.2			27.5	1981, 1875	1.0	90
			Found	33.2	2.3	11.1						
$CpMo(CO)_2(ImH)Cl$	Dark red	152–154 dec	Calcd	37.4	2.8	8.7	11.1		2.2	1965, 1851[b]	1.3	98
			Found	38.3	3.0	8.6	10.9					
$[CpW(CO)_2(ImH)_2]Cl$	Red	206 dec	Calcd	32.7	2.7	11.8	7.5		28.0	1931, 1830[c]	1.1	93
			Found	32.5	2.8	11.7	7.4					
$CpW(CO)_2(ImH)Cl$	Dark red	145–147 dec	Calcd	29.4	2.2	6.9	8.7		8.7	1941, 1822[b]	1.1	93
			Found	29.6	2.3	6.7	8.6					
$CpMo(CO)_2(py)Cl$	Red-black	98–99 dec	Calcd	43.4	3.0	4.2	10.7			1965, 1867	1.0	90
			Found	43.7	3.1	4.2	10.6					
$CpMo(CO)_2(C_6H_4N_3H)Cl$	Purple	170 dec	Calcd	41.9	2.7	11.3	9.5			1972, 1878	0.65	78
			Found	41.9	2.7	11.4	9.6					

[a] Key: Cp = cyclopentadienyl, PzH = pyrazole, ImH = imidazole, py = pyridine, $C_6H_4N_3H$ = benzotriazole. [b] These infrared spectra were obtained in acetonitrile rather than dichloromethane solutions. [c] These infrared spectra were obtained in KBr pellets rather than dichloromethane solutions.

phenylhydrazone[1] in pyridine solution to result in deprotonation to give the complexes $RR'CNOM(CO)_2C_5H_5$ and $[(CH_3)_2CNNC_6H_5]M(CO)_2C_5H_5$ (M = Mo and W), respectively. These results suggested that other reactions of $C_5H_5M(CO)_3Cl$ in pyridine with organic compounds containing potentially acidic hydrogen could lead to novel complexes. We therefore investigated reactions of $C_5H_5M(CO)_3Cl$ with pyrazole (PzH), in pyridine solution in an attempt to prepare transition metal analogues of the pyrazaboles[4] of the general type $[C_5H_5M(CO)_2Pz]_2$ in which a $C_5H_5M(CO)_2$ (M = Mo and W) unit replaces an RB unit. However, such reactions of pyrazole did not lead to deprotonation but instead to the formation of the previously unreported complexes $C_5H_5M(CO)_2(PzH)Cl$ and $[C_5H_5M(CO)_2(PzH)_2]^+Cl^-$. This paper describes these new pyrazole complexes in detail as well as related complexes of imidazole and pyridine.

Experimental Section

Microanalyses (Table I) were performed by the Atlantic Microanalytical Laboratory, Atlanta, Ga. Molecular weights (Table I) were determined in benzene solution using a Mechrolab Model 301 vapor pressure osmometer located in the laboratory of Professor G. E. Boyd at the University of Georgia. Molar conductances (Table I) were measured at room temperature in dimethyl sulfoxide solution using a Model 31 conductivity bridge manufactured by the Yellow Springs Manufacturing Co., Yellow Springs, Ohio. The dimethyl sulfoxide used for these conductivity measurements was dried overnight over sodium hydroxide and distilled over fresh sodium hydroxide at 40 °C (0.6 mm). Melting and decomposition points (Table I) were taken in capillaries and are uncorrected.

Infrared spectra in the ν(CO) region (Table I) were recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Each spectrum was calibrated against the 1601-cm^{-1} band of polystyrene film. When permitted by solubility, dichloromethane solutions were used for recording the ν(CO) frequencies. However, the ν(CO) frequencies of the complexes $C_5H_5Mo(CO)_2(PzH)Cl$ and $C_5H_5M(CO)_2(ImH)Cl$ (M = Mo and W) were obtained in acetonitrile solution. The ν(CO) frequencies of the sparingly soluble complexes $[C_5H_5M(CO)_2(ImH)_2]Cl$ were obtained in potassium bromide pellets. The relative intensities of the asymmetric and symmetric ν(CO) frequencies (I_a/I_s in Table I) were estimated by assuming a triangular band shape which makes their areas proportional to $W_{1/2}H$ where $W_{1/2}$ is the width at half-height and H is the band height. Although this method is relatively crude, meaningful I_a/I_s values sufficiently accurate to differentiate between lateral and diagonal isomers[5–7] can be obtained readily by this method from routine spectra on the Model 621 infrared spectrometer.

Proton NMR spectra (Table II) were recorded on a Varian T-60 spectrometer at 60 MHz. Carbon-13 NMR spectra (Table II) were recorded on a Jeolco PFT-100 spectrometer operating at 25.0349 MHz, with proton noise decoupling and a deuterium lock using a 6-s repetition rate. Unless otherwise indicated both the proton and carbon-13 NMR were run in $(CD_3)_2SO$ solutions using tetramethylsilane as an internal standard. In the carbon-13 NMR spectra chromium(III) acetylacetonate was added in ~0.15% concentration as a shiftless relaxation reagent[8] to facilitate observation of the metal carbonyl resonances.

The cyclopentadienylmetal tricarbonyl chlorides, $C_5H_5M(CO)_3Cl$ (M = Mo and W), were prepared on a 0.1 mol scale by an adaptation described elsewhere[3] of the standard published method.[9] The heterocycles pyridine (py), pyrazole (PzH), imidazole (ImH), and benzotriazole were standard commercial products. The pyrazole was purified by vacuum sublimation. The pyridine was dried over solid potassium hydroxide and then freshly distilled over barium oxide. Solvents were saturated with nitrogen before use in organometallic experiments. In addition all organometallic reactions were run in a dry nitrogen atmosphere.

Reactions of $C_5H_5M(CO)_3Cl$ (M = Mo and W) with the Nitrogen Heterocycles (Table III). The indicated amounts of $C_5H_5M(CO)_3Cl$ and the nitrogen heterocycle were heated in the indicated solvent for the indicated period of time (see Table III). The indicated products were isolated as described in Table III.

Conversion of $[C_5H_5Mo(CO)_2L_2]Cl$ to $[C_5H_5Mo(CO)_2L_2][PF_6]$ (L = PzH or ImH). A methanol solution containing at least a twofold excess of NH_4PF_6 was treated with the $[C_5H_5Mo(CO)_2L_2]Cl$ derivative. The methanol was then removed at ~25 °C (25 mm). Excess NH_4PF_6 was washed away from the residue with small portions of water. The crude $[C_5H_5Mo(CO)_2(PzH)_2][PF_6]$ was recrystallized from a ternary mixture of acetone/dichloromethane/hexane. The crude $[C_5H_5Mo(CO)_2(ImH)_2][PF_6]$ was recrystallized from water.

Conversion of $[C_5H_5Mo(CO)_2(PzH)_2]Cl$ to $C_5H_5Mo(CO)_2(PzH)Cl$. A solution of 3.34 g (8.7 mmol) of $[C_5H_5Mo(CO)_2(PzH)_2]Cl$ in 200 mL of dry acetone was stirred for 5 h at room temperature. Removal of acetone at 25 °C (25 mm) using a rotary evaporator gave nearly a quantitative yield of crude $C_5H_5Mo(CO)_2(PzH)Cl$, which was purified by crystallization from a mixture of dichloromethane and hexane.

Table II. NMR Spectra of the New Compounds Prepared in This Work

	Proton NMR spectrum,[b] τ				Carbon-13 NMR spectrum, δ			
Compd[a]	Solvent	Heterocycle protons[c]	NH	C_5H_5	Solvent	CO	Heterocycle carbons[c]	C_5H_5
$[CpMo(CO)_2(PzH)_2]Cl$	$(CD_3)_2SO$	1.95 d (3), 2.75 d (3), 3.52 t (3)	−3.95 br	3.98 s	$CDCl_3$[d]	249.9	147.5, 133.3, 108.1	96.3
$[CpMo(CO)_2(PzH)_2][PF_6]$	$(CD_3)_2SO$	2.17 d (2), 2.77, 3.56	−3.21 br	4.13 s	$(CD_3)_2SO$	253.2	146.4, 134.3, 107.7	96.9
$CpMo(CO)_2(PzH)Cl$	$CDCl_3$	2.22 [2], 3.48 m	−2.58 br	4.43 s	$(CD_3)_2SO$	262.7, 254.1	147.6, 131.4, 108.3	96.4
$[CpW(CO)_2(PzH)_2]Cl$	$(CD_3)_2SO$	1.94 d (2), 2.59 d (2), 3.53 t (2)	−3.94 br	3.75 s	$(CD_3)_2SO$	248.4	147.0, 134.6, 107.7	95.3
$CpW(CO)_2(PzH)Cl$	$(CD_3)_2SO$	~2.2 [2], 3.51 m	−2.73 br	4.28 s	$(CD_3)_2SO$	259.0, 252.2	146.6, 133.6, 107.4	95.2
$[CpMo(CO)_2(ImH)_2]Cl$	$(CD_3)_2SO$	2.04, 2.64, 3.29	~−3.3 vbr	4.02 s	$(CD_3)_2SO$	257.3	141.2, 131.7, 118.4	96.8
$[CpMo(CO)_2(ImH)_2][PF_6]$	$(CD_3)_2SO$	1.80, 2.33, 2.96	*e*	3.70 s	$(CD_3)_2SO$	257.0	141.4, 131.9, 118.6	96.8
$CpMo(CO)_2(ImH)Cl$	$(CD_3)_2SO$	1.81, 2.66, 2.70	~−2.9 vbr	4.32 s	$(CD_3)_2SO$	259.0, 252.9	140.0, 131.9, 117.6	96.7
$[CpW(CO)_2(ImH)_2]Cl$	$(CD_3)_2SO$	2.02, 2.74, 3.26	*e*	3.87 s	$(CD_3)_2SO$	252.6	142.8, 132.6, 118.8	95.4
$CpW(CO)_2(ImH)Cl$	$(CD_3)_2SO$	1.70, 2.62, 2.68	~−3.1 vbr	4.12 s	$(CD_3)_2SO$	261.0, 254.9	140.8, 132.5, 117.8	95.3
$CpMo(CO)_2(py)Cl$	$(CD_3)_2SO$	1.37 dd (7, 2), 1.61 d (4), 2.20 d (7), ~2.6 m		4.23 s	$(CD_3)_2SO$	265.2, 254.1	155.6 [2], 138.3 [1], 124.9 [2]	97.4
$CpMo(CO)_2(C_6H_4N_3H)Cl$	$(CD_3)_2SO$	2.15 br, 2.35 br	−1.15 vbr	4.15 s				

[a] Key: Cp = cyclopentadienyl, PzH = pyrazole, ImH = imidazole, py = pyridine, $C_6H_4N_3H$ = benzotriazole. [b] Key: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, vbr = very broad, coupling constants in Hz are given in parentheses ( ). [c] Relative intensities other than unity are indicated in brackets [ ]. [d] Because of the instability of $[CpMo(CO)_2(PzH)_2]Cl$ toward pyrazole dissociation (see text) the carbon-13 NMR spectrum of $[CpMo(CO)_2(PzH)_2]Cl$ also always contained the resonances from $CpMo(CO)_2(PzH)Cl$. [e] These NH proton resonances were too weak and broad to be observed unequivocally.

Results and Discussion

The reactions of $C_5H_5M(CO)_3Cl$ (M = Mo and W) with pyrazole give products either of the types $[C_5H_5M(CO)_2(PzH)_2]Cl$ or $C_5H_5M(CO)_2(PzH)Cl$ depending upon the reaction conditions. Use of pyridine as a solvent for the reactions between $C_5H_5M(CO)_3Cl$ and pyrazole does not result in deprotonation of the pyrazole to pyrazolyl derivatives and gives the same products as similar reactions in hydrocarbon solvents.

The two species $[C_5H_5M(CO)_2(PzH)_2]Cl$ and $C_5H_5M(CO)_2(PzH)Cl$ appear to be readily interconverted by the following process involving nucleophilic attack by chloride on the $[C_5H_5M(CO)_2(PzH)_2]^+$ cation

$$[C_5H_5M(CO)_2(PzH)_2]Cl \rightleftharpoons C_5H_5M(CO)_2(PzH)Cl + PzH \qquad (1)$$

Thus solutions of $[C_5H_5M(CO)_2(PzH)_2]Cl$ in organic solvents liberate pyrazole with formation of $C_5H_5M(CO)_2(PzH)Cl$ over a period of minutes in the case of the molybdenum derivative and over a period of hours in the case of the tungsten derivative as indicated by their proton NMR spectra. The molybdenum derivative $[C_5H_5Mo(CO)_2(PzH)_2]Cl$ is so unstable in solution with respect to formation of $C_5H_5Mo(CO)_2(PzH)Cl$ and pyrazole that all attempts to obtain carbon-13 NMR spectra of $[C_5H_5Mo(CO)_2(PzH)_2]_2Cl$ resulted in spectra of mixtures of $[C_5H_5Mo(CO)_2(PzH)_2]Cl$, $C_5H_5Mo(CO)_2(PzH)Cl$, and pyrazole. In contrast to $[C_5H_5Mo(CO)_2(PzH)_2]Cl$ the corresponding hexafluorophosphate salt $[C_5H_5Mo(CO)_2(PzH)_2][PF_6]$ is indefinitely stable at room temperature owing to the negligible nucleophilicity of the PF_6^- anion.

Other reactions of the metal–pyrazole derivatives confirm the ease of reaction 1 in either direction. Thus the formation of $[C_5H_5M(CO)_2(PzH)_2]Cl$ or $C_5H_5M(CO)_2(PzH)Cl$ from $C_5H_5M(CO)_3Cl$ and pyrazole appears to be determined solely by the pyrazole:$C_5H_5M(CO)_3Cl$ ratio. Pyrazole:$C_5H_5M(CO)_3Cl$ ratios of 1 lead exclusively to the corresponding $C_5H_5M(CO)_2(PzH)Cl$ derivative whereas use of excess pyrazole (e.g., pyrazole:$C_5H_5M(CO)_3Cl$ ratios of 4) leads exclusively to the corresponding $[C_5H_5M(CO)_2(PzH)_2]Cl$ derivatives. Furthermore, $C_5H_5W(CO)_3Cl$ reacts with $[C_5H_5W(CO)_2(PzH)_2]Cl$ to give $C_5H_5W(CO)_2(PzH)Cl$ in the mutual solvent pyridine according to the equation (M = W)

$$C_5H_5M(CO)_3Cl + [C_5H_5M(CO)_2(PzH)_2]Cl \rightarrow 2C_5H_5M(CO)_2(PzH)Cl + CO \qquad (2)$$

Mechanistically, this process can involve dissociation of pyrazole from $[C_5H_5M(CO)_2(PzH)_2]Cl$ by eq 1 followed by the separately demonstrated reaction of this pyrazole with $C_5H_5M(CO)_3Cl$ to give $C_5H_5M(CO)_2(PzH)Cl$.

The reactions of $C_5H_5M(CO)_3Cl$ (M = Mo and W) with imidazole also give both $[C_5H_5M(CO)_2(ImH)_2]Cl$ and $C_5H_5M(CO)_2(ImH)Cl$ derivatives depending upon the mole ratios of imidazole to $C_5H_5M(CO)_3Cl$. However, there are several important differences between the imidazole and pyrazole complexes. The imidazole complexes are much less soluble in solvents of limited polarity than the corresponding pyrazole complexes. Furthermore, the complexes $[C_5H_5M(CO)_2(ImH)_2]Cl$ are stable in solution at room temperature toward dissociation of imidazole to form $C_5H_5M(CO)_2(ImH)Cl$ in accord with the much higher basicity of imidazole ($pK_a \approx 7.03$) than of pyrazole ($pK_a \approx 2.53$).[10] Also the reactions of $C_5H_5M(CO)_3Cl$ with imidazole even in a 1:1 mole ratio in hot hydrocarbon solvents give $[C_5H_5M(CO)_2(ImH)_2]Cl$ in accord with the insolubility of this latter complex in hot hydrocarbons. Formation of $C_5H_5M(CO)_2(ImH)Cl$ from $C_5H_5M(CO)_3Cl$ and imidazole in a 1:1 mole ratio requires pyridine as a solvent in which $[C_5H_5M(CO)_2(ImH)_2]Cl$ is soluble.

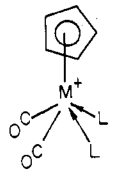
The physical and spectroscopic properties of the new py-

Table III. Some Reactions of $C_5H_5M(CO)_3Cl$ (M = Mo and W) with Nitrogen Heterocycles

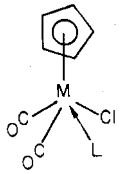
$CpM(CO)_3Cl$ (g, mmol)[a]	Heterocycle[a] (g, mmol)	Solvent[b] (mL)	Temp, °C	Time, h	Product (g, mmol)[a]
$CpMo(CO)_3Cl$ (2.8, 10)	PzH (2.8, 41.2)	Hex (180)	70	2	$[CpMo(CO)_2(PzH)_2]Cl$ (3.6, 9.4)[c]
$CpMo(CO)_3Cl$ (1.4, 5)	PzH (0.34, 5)	Hex (70)	68	2	$CpMo(CO)_2(PzH)Cl$ (1.6, 4.9)[c]
$CpMo(CO)_3Cl$ (1.4, 5)	PzH (1.4, 20)	Benz (70)	80	2	$[CpMo(CO)_2(PzH)_2]Cl$ (1.6, 4.1)[d,e]
$CpMo(CO)_3Cl$ (1.4, 5)	PzH (1.4, 20)	MCH (70)	100	3	Dec
$CpMo(CO)_3Cl$ (1.0, 3.6)	PzH (1.7, 25)	py (80)	65	2.5	$[CpMo(CO)_2(PzH)_2]Cl$ (1.4, 3.6)[f,g]
$CpMo(CO)_3Cl$ (2.8, 10)	PzH (0.68, 10)	py (150)	65	1	$CpMo(CO)_2(PzH)Cl$ (2.8, 10)[f,h]
$CpMo(CO)_3Cl$ (2.8, 10)	ImH (2.7, 40)	Hex (200)	70	3	$[CpMo(CO)_2(ImH)_2]Cl$ (3.1, 8)[c,i]
$CpMo(CO)_3Cl$ (1.4, 5)	ImH (0.34, 5)	Tol (10) and Hex (60)	80	2	1:1 mixture of $[CpMo(CO)_2(ImH)_2]Cl$ and $CpMo(CO)_2(ImH)Cl$ (by NMR)[c]
$CpMo(CO)_3Cl$ (2.5, 8.9)	ImH (1.9, 30)	py (250)	75	4	$[CpMo(CO)_2(ImH)_2]Cl$ (2.4, 6.2)[f,j,k]
$CpMo(CO)_3Cl$ (2.8, 10)	ImH (0.68, 10)	py (150)	65	2	$CpMo(CO)_2(ImH)Cl$ (1.7, 5.3)[f,l]
$CpMo(CO)_3Cl$ (1.4, 5)	$C_6H_4N_3H$ (1.0, 5)	Hex (70)	70	2	$CpMo(CO)_2(C_6H_4N_3H)Cl$ (1.8, 4.9)[c,l]
$CpMo(CO)_3Cl$ (1.4, 5)	py (1.5, 20)	Hex (50)	70	2	$CpMo(CO)_2(py)Cl$ (1.6, 5)[c]
$CpW(CO)_3Cl$ (1.8, 5)	PzH (1.5, 20)	Tol (70)	110	6	$[CpW(CO)_2(PzH)_2]Cl$ (1.96, 4.1)[d,m]
$CpW(CO)_3Cl$ (1.8, 5)	PzH (0.34, 5)	MCH (70)	100	3	$CpW(CO)_2(PzH)Cl$ (1.93, 4.7)[c]
$CpW(CO)_3Cl$ (3.7, 10)	PzH (2.7, 40)	py (200)	116	4	$[CpW(CO)_2(PzH)_2]Cl$ (2.9, 6.1)[f,n]
$CpW(CO)_3Cl$ (3.7, 10)	PzH (0.68, 10)	py (200)	116	1	$CpW(CO)_2(PzH)Cl$ (2.8, 7.5)[f,o]
$CpW(CO)_3Cl$ (1.85, 5)	$[CpW(CO)_2(PzH)_2]Cl$ (2.4, 6)	py (200)	116	4	$CpW(CO)_2(PzH)Cl$ (4.1, 10)[f,m,g]
$CpW(CO)_3Cl$ (1.85, 5)	ImH (1.36, 20)	Tol (70)	110	4	$[CpW(CO)_2(ImH)_2]Cl$ (2.2, 4.6)[c,i]
$CpW(CO)_3Cl$ (1.85, 5)	ImH (0.34, 5)	Tol (70)	110	3	$[CpW(CO)_2(ImH)_2]Cl$ (1.7, 3.6)[c]
$CpW(CO)_3Cl$ (3.7, 10)	ImH (2.8, 40)	py (200)	116	1	$[CpW(CO)_2(ImH)_2Cl$ (3.6, 7.5)[c,n]
$CpW(CO)_3Cl$ (1.85, 5)	ImH (0.34, 5)	py (200)	116	1	$CpW(CO)_2(ImH)Cl$ (1.3, 3.2)[c,p]
$CpW(CO)_3Cl$ (0.37, 1)	$[CpW(CO)_2(ImH)_2]Cl$ (0.48, 1)	py (70)	116	1	$CpW(CO)_2(ImH)Cl$ (0.36, 0.88)[f,n]

[a] Key: Cp = cyclopentadienyl, PzH = pyrazole, ImH = imidazole, py = pyridine, $C_6H_4N_3H$ = benzotriazole. [b] Key: Hex = hexane, Benz = benzene, MCH = methylcyclohexane, Tol = toluene. [c] The product was isolated by filtering the reaction mixture. Any excess heterocycle was washed out of the product with hexane and/or diethyl ether. [d] The reaction mixture was filtered through Celite. Solvent was removed from the filtrate under vacuum at room temperature. [e] The product was crystallized from a mixture of dichloromethane and hexane. [f] Solvent was removed from the reaction mixture under vacuum at room temperature. [g] The crude product was chromatographed on a Florisil column in dichloromethane solution. [h] The product was purified by low-temperature crystallizations from mixtures of dichloromethane, diethyl ether, and hexane. [i] Excess imidazole was washed from the crude product with dichloromethane. [j] The crude product was crystallized from water. [k] The crude product was crystallized from a mixture of methanol and diethyl ether. [l] The produce was crystallized from a mixture of methanol, dichloromethane, and hexane. [m] The crude product was crystallized from a mixture of dichloromethane and methanol. [n] Pyrazole or imidazole was removed from the crude product by sublimation at ~50 °C (0.05 mm) and washing with diethyl ether. The product was crystallized from a mixture of methanol and diethyl ether. [o] The crude product was chromatographed on a silica gel column prepared in dichloromethane. The product was eluted with diethyl ether. [p] The crude product was crystallized from a mixture of methanol, dichloromethane, and diethyl ether.

razole and imidazole complexes are in accord with their formulations. In dimethyl sulfoxide solutions the complexes $[C_5H_5M(CO)_2L_2]Cl$ (M = Mo and W, L = PzH and ImH) have conductances (26–28 Ω^{-1} cm^2/mol) similar to those of the corresponding hexafluorophosphates $[C_5H_5Mo(CO)_2L_2][PF_6]$ (28–30 Ω^{-1} cm^2/mol) and higher by factors 3–12 relative to the corresponding nonionic derivatives $C_5H_5M(CO)_2LCl$. The infrared spectra of all of the $C_5H_5M(CO)_2$ derivatives exhibit the expected two ν(CO) frequencies. The relative intensities of these two ν(CO) frequencies (I_a/I_s) are around unity indicating OC–M–CO angles around 90°. These complexes therefore are predominantly the lateral (cis) isomers I and II (M = Mo and W, L = PzH and ImH) rather than the corresponding diagonal (trans) isomers. The formation of lateral $C_5H_5M(CO)_2XY$ derivatives rather than diagonal $C_5H_5M(CO)_2XY$ derivatives in substitution reactions of $C_5H_5M(CO)_3X$ with relatively poor π-acceptor ligands is a logical extension of the familiar trans effect[11] to $C_5H_5MA_4$ systems. The carbon-13 NMR spectra of the $[C_5H_5M(CO)_2L_2]^+$ and $C_5H_5M(CO)_2LCl$ derivatives indicate that the two carbonyl groups are equivalent and nonequivalent, respectively, in accord with structures I and II, respectively. The proton NMR spectra of the imidazole and pyrazole complexes (Table II) exhibit broad resonances around τ ~−3 arising from the N–H hydrogen.



I



II

Previous workers[12,13] have had difficulty in obtaining pure $C_5H_5Mo(CO)_2(NC_5H_5)Cl$ from $C_5H_5Mo(CO)_3Cl$ and pyridine. Our success in obtaining not only the imidazole and pyrazole complexes described in this paper but also ketoximato complexes[3] from reactions of $C_5H_5M(CO)_3Cl$ with appropriate compounds in pyridine solution suggests that cyclopentadienylmolybdenum carbonyl complexes of pyridine might have rather limited stability. However, we have now found that reaction of pyridine with $C_5H_5Mo(CO)_3Cl$ in a 4:1 mole ratio in boiling hexane gives a quantitative yield of red-black $C_5H_5Mo(CO)_2(NC_5H_5)Cl$, shown to be the lateral isomer II (M = Mo, L = pyridine) by the infrared I_a/I_s ν(CO) ratio of unity. No evidence for the formation of a $[C_5H_5Mo(CO)_2(NC_5H_5)_2]Cl$ derivative of type I was obtained even though an excess of pyridine was used in this reaction. Reaction of $C_5H_5Mo(CO)_3Cl$ with benzotriazole also gives the purple complex $C_5H_5Mo(CO)_2(C_6H_4N_3H)Cl$ suggested by the infrared I_a/I_s ν(CO) ratio of 0.65 to be the lateral isomer II (M = Mo, L = benzotriazole).

Summary

The reactions of $C_5H_5M(CO)_3Cl$ (M = Mo and W) with pyrazole (PzH) and imidazole (ImH) give either the ionic $[C_5H_5M(CO)_2L_2]^+Cl^-$ or the nonionic $C_5H_5M(CO)_2LCl$ (M = Mo and W, L = PzH and ImH) depending upon the conditions, mainly the mole ratios of reactants. The pyrazole complexes $[C_5H_5M(CO)_2(PzH)_2]Cl$ dissociate readily in solution at room temperature to give $C_5H_5M(CO)_2(PzH)Cl$ and free pyrazole whereas the corresponding imidazole

complexes are stable at room temperature toward such dissociation.

Acknowledgment. We are indebted to the Air Force Office of Scientific Research for partial support of this work under Grant AFOSR-75-2689.

Registry No. $[CpMo(CO)_2(PzH)_2]Cl$, 64129-84-6; $[CpMo(CO)_2(PzH)_2][PF_6]$, 64057-34-7; $CpMo(CO)_2(PzH)Cl$, 64057-32-5; $[CpMo(CO)_2(ImH)_2]Cl$, 64090-75-1; $[CpMo(CO)_2(ImH)_2][PF_6]$, 64057-31-4; $CpMo(CO)_2(ImH)Cl$, 64057-29-0; $CpMo(CO)_2(C_6H_4N_3H)Cl$, 64091-66-3; $CpMo(CO)_2(py)Cl$, 64057-28-9; $[CpW(CO)_2(PzH)_2]Cl$, 64057-27-8; $CpW(CO)_2(PzH)Cl$, 64057-26-7; $[CpW(CO)_2(ImH)_2]Cl$, 64057-25-6; $CpW(CO)_2(ImH)Cl$, 64057-37-0; $CpMo(CO)_3Cl$, 12128-23-3; $CpW(CO)_3Cl$, 12128-24-4; ^{13}C, 14762-74-4.

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Kinetics of the Oxidation of $Cu(phen)_2^+$ and $Cu(bpy)_2^+$ by Aminopolycarboxylatocobalt(III) Complexes

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Received May 26, 1977 AIC70385J

Considerable progress has been made recently toward understanding the mechanisms by which blue (or type 1) copper proteins donate and accept electrons.[1] We have reported that the electron-transfer reactivity of reduced (Cu(I)) stellacyanin with the ethylenediaminetetraacetatocobaltate(III) ion ($Co(EDTA)^-$) differs markedly from that observed when the tris(1,10-phenanthroline)cobalt(III) ion ($Co(phen)_3^{3+}$) is the oxidant.[2] Observed rate constants for the oxidation of cuprous stellacyanin (St(I)) by $Co(EDTA)^-$ approach a saturation limit with increasing $[Co(EDTA)^-]$ at pH 7, consistent with a mechanism involving rapid preequilibrium oxidant–protein complex formation followed by rate-limiting intramolecular Cu(I) to Co(III) electron transfer

$$\mathrm{Co(EDTA)^- + St(I)} \overset{Q_p}{\rightleftarrows} \mathrm{Co(EDTA)^-\text{–}St(I)} \xrightarrow{k_2} \mathrm{Co(EDTA)^{2-}\text{–}St(II)}$$

(Q_p = 149 M^{-1}, k_2 = 0.169 s^{-1}; 25.1 °C, pH 7.0, μ 0.5 M (phosphate)).[2] Activation parameters based on k_2 ($\Delta H^{\ddagger} = 1.8$ kcal/mol, $\Delta S^{\ddagger} = -56$ cal/(mol deg)) suggest that electron transfer within the oxidant–protein complex is substantially nonadiabatic. By contrast, second-order kinetics were found for the oxidation of reduced stellacyanin by $Co(phen)_3^{3+}$ ($k = 1.8 \times 10^5$ M^{-1} s^{-1}; 25 °C, pH 7.0, μ 0.5 M (phosphate)).[3] Activation parameters for the $Co(phen)_3^{3+}$–St(I) reaction ($\Delta H^{\ddagger} = 6.1$ kcal/mol, $\Delta S^{\ddagger} = -14$ cal/(mol deg)) and comparisons of apparent St(I)–St(II) self-exchange electron-transfer rate constants obtained by applying relative Marcus theory to rate data for the cross reactions with $Fe(EDTA)^{2-}$ and $Co(phen)_3^{3+}$ indicate that oxidation of the protein Cu(I) center by $Co(phen)_3^{3+}$ occurs by an adiabatic outer-sphere mechanism.[3]

The unusual redox reactivity of $Co(EDTA)^-$ with reduced stellacyanin has been attributed to the formation of an oxidant–protein precursor complex in which overlap between the donor redox orbital of the distorted tetrahedral type 1 Cu(I) center and the e_g acceptor orbital of the oxidant is poor; it is thus concluded that nonadiabicity is not a requisite feature of the outer-sphere oxidation of Cu(I) by $Co(EDTA)^-$.[2] In order to provide further support for this conclusion we report here rate data for the oxidation of the bis(1,10-phenanthroline)copper(I) ($Cu(phen)_2^+$) and bis(2,2′-bipyridine)copper(I) ($Cu(bpy)_2^+$) ions by three aminopolycarboxylatocobalt(III) complexes: $Co(EDTA)^-$, $Co(CyDTA)^-$, $Co(PDTA)^-$ (CyDTA = *trans*-1,2,-diaminocyclohexanetetraacetate, PDTA = propylenediaminetetraacetate).

Experimental Section

Reagent grade chemicals and triply distilled water were used for all experiments. Nitrogen gas passed through two chromous scrubbing towers was used to deoxygenate kinetics solutions. Sodium acetate buffers were used to maintain the ionic strength at 0.5 M and the pH at 6.0 in all experiments.

$Na[Co(EDTA)]\cdot 4H_2O$,[4] $K[Co(PDTA)]\cdot H_2O$,[5] and $K[Co(CyDTA)]\cdot 3H_2O$[6] were prepared by literature methods. The purity of these salts was established through microanalyses for C, H, and N and through comparisons of UV–visible spectra with those in the literature.[7] Solutions of the sodium salts of all oxidants were used in kinetic studies; to exchange K^+ for Na^+, solutions of K[Co(PDTA)] and K[Co(CyDTA)] were passed through a column containing Chelex 100 cation-exchange resin in the sodium form. The concentrations of oxidant solutions were evaluated spectrophotometrically using literature extinction coefficients.[7]

Solutions of $Cu(phen)_2^+$ and $Cu(bpy)_2^+$ were prepared by mixing a tenfold excess of ligand with cupric acetate and reducing anaerobically with the equivalent amount of ascorbic acid. Formation constants for $Cu(phen)_2^+$ and $Cu(bpy)_2^+$[8] ensure that these are the only Cu(I) species present in appreciable concentration under the experimental conditions. This conclusion was reinforced by demonstrating that observed rate constants do not vary as the ratio $[\mathrm{ligand}]_{tot}/[\mathrm{Cu(I)}]_{tot}$ is varied from 2.1 to 50. To avoid contaminating $Cu(phen)_2^+$ and $Cu(bpy)_2^+$ solutions with iron, all transfers were made using Teflon needles.

The kinetics of oxidation of $Cu(phen)_2^+$ and $Cu(bpy)_2^+$ by aminopolycarboxylatocobalt(III) complexes was monitored by following the absorbance decrease at 435 nm (Cu(I) to ligand charge-transfer absorption) using a Durrum D-110 stopped flow spectrophotometer. Pseudo-first-order conditions were employed, maintaining the concentration of the cuprous complex at ca.10–25 μM and varying the oxidant concentration from 2.5×10^{-4} to 2.5×10^{-2} M (10–1000-fold excess). Absorbance–time data were collected as photographs of traces on a Tektronix 564 B oscilloscope or as output from a Hewlett-Packard Model 7004 B X-Y recorder. Three separate runs were usually performed for each pair of solutions mixed in the stopped-flow apparatus.

Absorption spectra were recorded using a Cary 17 spectrophotometer, and pH measurements were made with an Ionalyzer Model 801 instrument.

Results and Discussion

First-order plots of ln ($A_t - A_\infty$) vs. time derived from absorbance–time data for the oxidation of $Cu(phen)_2^+$ and $Cu(bpy)_2^+$ by $Co(EDTA)^-$, $Co(PDTA)^-$, and $Co(CyDTA)^-$ were found to be linear for greater than 90% completion of the reactions. Observed rate constants (k_{obsd}) were derived from the linear least-squares slopes of these plots. Data obtained for $Co(EDTA)^-$ as the oxidant are given in Table I.[9] For all of the redox reactions considered, plots of k_{obsd} (25 °C) vs. [oxidant] were found to be linear with small positive intercepts (0.04–0.23 s^{-1}) over the 50–100-fold concentration ranges covered. We conclude that electron transfer from Cu(I) to Co(III) obeys the rate law

$$-d[\mathrm{Cu(I)}]/dt = k[\mathrm{Cu(I)}][\mathrm{Co(III)}]$$