

in the later case increase from 2158 cm^{-1} in the free molecule to 2195 cm^{-1} in the complex.¹⁴

To our knowledge the structure of $(\text{CO})_5\text{Cr}(\text{CNCH}_3)$ has not been determined. The CNC angle in pentacarbonyl(isocyanide)chromium complexes with known structure is between 168.5 (4) $^\circ$ in $(\text{CO})_5\text{CrCNCN}$ ¹⁵ and 176.0 (3) $^\circ$ in $(\text{CO})_5\text{CrNC-CNCo}(\text{CO})_3$,¹⁶ and the C=N bonds (1.160 (5) and 1.167 (5) Å) are not lengthened. Small CNC angles down to 133.1 (8) $^\circ$ have been observed in $\text{Fe}(\text{CN}-t\text{-Bu})_5$,¹⁷ but there are no competing strong π acceptors present in this complex.

The strong difference between CH_3NC and CF_3NC in ligand behavior can be rationalized by the difference in the energies of the π^* LUMO. The energy of the π^* orbital is considerably lower in CF_3NC (0.125 au ¹⁸) than in CH_3NC (0.215 au ⁸), and lowering of this orbital increases the π acceptor ability of the ligand.

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Registry No. $(\text{CF}_3\text{NC})\text{Cr}(\text{CO})_5$, 88902-50-5.

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Effect of Nitrogenous Bases on the Electrochemical Oxidation of a Bis(phosphine)-Bridged Tetrakis(isocyanide)rhodium(I) Dimer

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In recent years there have been several reports of studies involving bis(phosphine)-bridged tetrakis(isocyanide)rhodium(I) dimers.¹⁻⁴ We have previously reported that the electrochemical behavior of binuclear Rh(I) complexes of the type $[\text{Rh}_2(\text{dpm})_2(\text{RNC})_4][\text{PF}_6]_2$ (dpm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$) is strongly solvent dependent.¹ In the noncoordinating solvent CH_2Cl_2 , a quasi-reversible one-electron transfer is observed at +0.60 V (vs. SCE). An irreversible electron transfer corresponding to the removal of a second electron is observed near the solvent limit. In CH_3CN , the second one-electron oxidation occurs at less positive potentials and is more readily observed. It was concluded that the removal of a second electron from the $[\text{Rh}_2(\text{dpm})_2(\text{RNC})_4][\text{PF}_6]_2$ complexes in the coordinating solvent CH_3CN leads to a binuclear Rh(II) species that is stabilized by the coordination of solvent molecules. The dimeric cation was formulated as $[\text{Rh}_2(\text{dpm})_2(\text{RNC})_4(\text{CH}_3\text{CN})_2]^{4+}$.

The ability of CH_3CN to facilitate the removal of a second electron from the binuclear Rh(I) complex suggested that there might be a correlation between the peak potential for the removal of the second electron and the basicity of the ligands coordinating in the transannular positions of the dimeric cation shown in Figure 1. To test this hypothesis we have investigated the electrochemical behavior, via cyclic voltammetry, of $[\text{Rh}_2(\text{dpm})_2(n\text{-C}_4\text{H}_9\text{NC})_4][\text{PF}_6]_2$ in the presence of pyridine and several substituted pyridines with different σ donor abilities. During our investigation of the tetrakis(isocyanide)rhodium(I) dimers a report

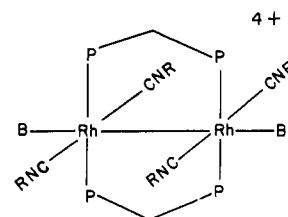


Figure 1. Proposed structure of the rhodium(II) diadduct $[\text{Rh}_2(\text{RNC})_4(\text{dpm})_2(\text{B})_2][\text{PF}_6]_4$. The phenyl groups have been omitted from the bis(phosphine) ligands.

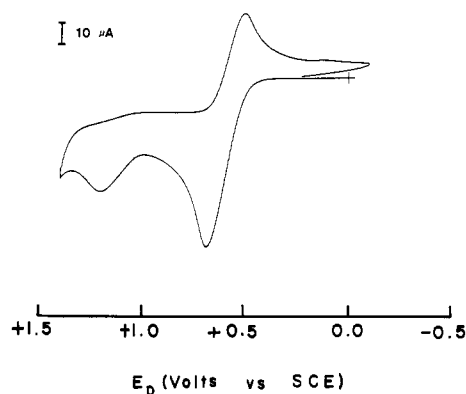


Figure 2. Cyclic voltammogram of $[\text{Rh}_2(n\text{-C}_4\text{H}_9\text{NC})_4(\text{dpm})_2][\text{PF}_6]_2$ in CH_2Cl_2 and 0.1 M TBAH (sweep rate 100 mV s^{-1}).

of a similar study involving tetrakis(carboxylato)rhodium(II) dimers appeared.⁵

Experimental Section

Materials. The $[\text{Rh}_2(\text{dpm})_2(n\text{-C}_4\text{H}_9\text{NC})_4][\text{PF}_6]_2$ was prepared according to literature procedures.^{2,3} Pyridine was stored over KOH and distilled from BaO immediately before use. All substituted pyridines (Aldrich) were reagent grade and were used as received. The dichloromethane (Fisher) was the spectroanalyzed grade and was used without further purification. The tetrabutylammonium hexafluorophosphate (TBAH) was prepared from $(n\text{-C}_4\text{H}_9)_4\text{NI}$ and KPF_6 in water and was recrystallized five times from acetone-water and dried under vacuum.

Instrumentation. All cyclic voltammetric experiments were performed at 25 $^\circ\text{C}$ with a function generator of the design of Woodward and co-workers⁶ and a Princeton Applied Research Model 364 polarographic analyzer. The experiments were conducted with a Pt-inlay (Beckman) working electrode, a Pt-grid counter electrode, and a saturated calomel reference electrode (SCE). All voltammograms were recorded on a Houston Instruments Omnigraphic 2000 X-Y recorder.

Results and Discussion

The cyclic voltammogram of a 1.0 mM solution of $[\text{Rh}_2(n\text{-C}_4\text{H}_9\text{NC})_4(\text{dpm})_2][\text{PF}_6]_2$ in CH_2Cl_2 and 0.1 M TBAH is shown in Figure 2. The quasi-reversible couple at +0.60 V has been previously shown¹ to result from a one-electron transfer. The oxidation process occurring at +1.3 V is the irreversible transfer of a second electron. In the presence of a coordinating species, the second oxidation peak moves to less positive potentials, indicating that the oxidation process occurs more readily in the presence of a Lewis base. This shift in oxidation potential is indicative of stabilization of the Rh(II) dimer through coordination of the Lewis base. The Lewis bases used in this study are substituted pyridines.

Figure 3 shows the oxidation peaks for $[\text{Rh}_2(n\text{-C}_4\text{H}_9\text{NC})_4(\text{dpm})_2][\text{PF}_6]_2$ in the presence of the weak base 3-cyanopyridine and the stronger base 3,4-dimethylpyridine. There are two general trends evident from the voltammograms, with each trend being a function of the basicity of the substituted pyridine. The first is the decrease in the cathodic peak current for the quasi-reversible couple as the base strength increases. This behavior is consistent

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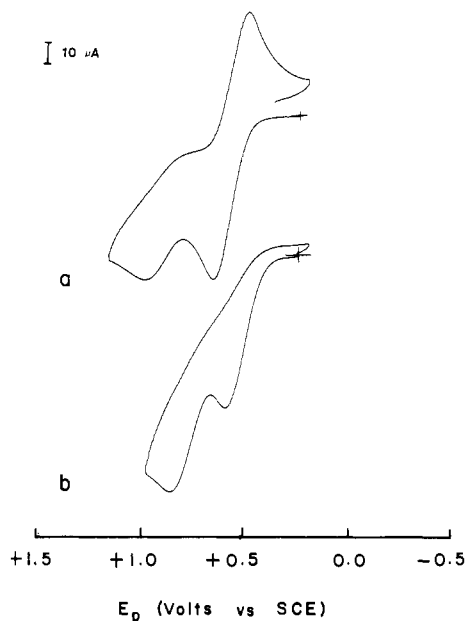
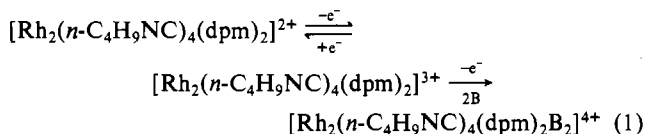


Figure 3. Cyclic voltammogram of $[\text{Rh}_2(n\text{-C}_4\text{H}_9\text{NC})_4(\text{dpm})][\text{PF}_6]_2$ (sweep rate 100 mV s^{-1}): (a) twofold excess of 3-cyanopyridine; (b) twofold excess of 3,4-dimethylpyridine in CH_2Cl_2 and 0.1 M TBAH.

with an increase in the rate of coordination and electron transfer during the second oxidation process as the base strength increases. This is supported by the fact that in the case of those strong bases for which it is possible to at least partially isolate the first oxidation peak, the cathodic component of the quasi-reversible couple is still present.

The second trend that is evident from the voltammograms is the shift in the potential of the second oxidation peak to less positive values as the basicity of the pyridine increases. Interestingly, the oxidation process occurring at $E_p = +0.67 \text{ V}$ is apparently only slightly affected by the presence of the base since shifts in the peak potential are very small on going from a solution with no base present through a series of solutions containing the various bases. These small shifts (<10%) suggest that the pyridine ligands do not strongly coordinate to the dimer during the first oxidation process.

The shift in the second oxidation peak upon addition of the bases is indicative of the stabilization of the binuclear Rh(II) species by transannular addition of the bases. The ratio of nitrogenous base to Rh(I) dimer was 4:1 in all cases. This ratio favors complete coordination of the Rh(II) dimer by the base. The overall oxidation process is described by eq 1.



The difference in peak potential for the second oxidation process prior to the addition of base and after the addition of base is denoted as ΔE_{p2} and is found to increase as the base strength increases. The σ donor ability of the substituted pyridine is measured by its pK_b values obtained from reported pK_a values.^{7,8} The ΔE_{p2} and pK_b values are given in Table I. The plot in Figure 4 displays a linear relationship between ΔE_{p2} and pK_b .

The effect of the nitrogenous bases on E_p for the second oxidation process for $[\text{Rh}_2(n\text{-C}_4\text{H}_9\text{NC})_4(\text{dpm})][\text{PF}_6]_2$ can be explained by considering how coordination of the base perturbs the

Table I. Potential Shifts for Oxidation of $[\text{Rh}_2(n\text{-C}_4\text{H}_9\text{NC})_4(\text{dpm})_2][\text{PF}_6]_2$ in CH_2Cl_2 Containing Substituted Pyridines

base	pK_b^a	ΔE_{p2}^b , mV
4-(dimethylamino)pyridine	4.29	0.565
3,4-dimethylpyridine	7.39	0.476
4-ethylpyridine	7.98	0.460
pyridine	8.77	0.400
4-benzoylpyridine	10.65	0.316
4-cyanopyridine	12.12	0.292
3-cyanopyridine	12.55	0.271

^a Value determined from pK_a values given for 4-ethylpyridine and 3,4-dimethylpyridine in ref 7. All other values were determined from pK_a values given in ref 8. ^b ΔE_{p2} represents the shift in the peak potential of the second oxidation process after base is added.

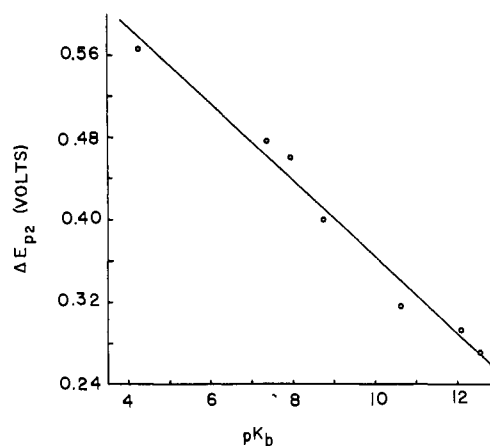


Figure 4. Plot of the shift in peak potential of the second oxidation process, ΔE_{p2} , vs. pK_b of the added base.

HOMO of the one-electron oxidation product. The bonding in tetrakis(isocyanide) bis(phosphine)-bridged Rh(I) dimers has been described.⁹ The HOMO for the Rh(I) dimer is the σ^* orbital resulting from the overlap of the $4d_{z^2}$ orbitals on the two rhodium atoms. In formation of the dinuclear Rh(II) complex, the two electrons are removed from the σ^* orbital. The ease with which the second electron is removed and the subsequent stabilization of the Rh(II) dimer depend on the relative energies of the metal d_{z^2} orbital and the ligand donor orbital. As the σ donor strength of the axial nitrogenous base increases, the energy separation between the metal d_{z^2} and the axial ligand σ orbitals is decreased. This improved match in orbital energy with an increase in base strength shifts the $\sigma^*(4d_{z^2})$ orbital to higher energy, thus facilitating the removal of electrons from this orbital and leading to greater stabilization of the Rh(II) diadduct. This explains the relationship between ΔE_{p2} and pK_b we have shown in Figure 4.

Though the correlation between the peak potential for the second oxidation process for Rh(I) dimers of the type discussed here and the σ donor strength of the pyridines can be explained from consideration of electronic factors alone, steric factors could play a role in this relationship. The *n*-butyl isocyanide ligand and the substituted pyridines used in this study were selected so as to minimize and normalize the steric interactions; therefore, electronic factors should dominate for the system studied here.

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Registry No. TBAH, 3109-63-5; $[\text{Rh}_2(n\text{-C}_4\text{H}_9\text{NC})_4(\text{dpm})_2][\text{PF}_6]_2$, 95250-84-3; 4-(dimethylamino)pyridine, 1122-58-3; 3,4-dimethylpyridine, 583-58-4; 4-ethylpyridine, 536-75-4; pyridine, 110-86-1; 4-benzoylpyridine, 14548-46-0; 4-cyanopyridine, 100-48-1; 3-cyanopyridine, 100-54-9.

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