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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

John Paul Folkers

ENTITLED Substitution Reactions of $Re_8C(CO)_{24}^{2-}$. Synthesis, Characteriza-

tion, and Cyclic Voltammetry of $Re_7C(CO)_{20}(NO)^{2-}$

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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John R. Shapley
Instructor in Charge

APPROVED: *H. C. Hummel*

for HEAD OF DEPARTMENT OF Chemistry

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Substitution Reactions $Re_8C(CO)_{24}{}^{2-}$.

Synthesis, Characterization, and Cyclic Voltammetry of

$Re_7C(CO)_{20}(NO)^{2-}$.

By

John Paul Folkers

Thesis

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I. INTRODUCTION

The organometallic compound $CpRe(CO)_3$ (Cp = C_5H_5) was first synthesized by two different groups in 1958.[1,2] The chemistry of the rhenium center in this compound has since been extensively studied. Most of the reactions have been replacement of a carbon monoxide in hopes of enhancing the catalytic activity of the metal center.[3] A coordinated carbon monoxide has been replaced by NO^+ [4,5], N_2R^+ [6], phosphines[7], and many other ligands.[3,4,7] An additional reaction is the reduction of CO with $NaBH_4$ to form a coordinated methyl group.[8] Electrophilic attack has also been done to replace hydrogens from the cyclopentadienyl ring. A hydrogen can be replaced by lithium by addition of n-butyl lithium. Subsequent addition of dimethylformamide will remove the lithium and replace it with a -CHO group, which can be subsequently oxidized or reduced to make other cyclopentadienyl substituted complexes.[9] However, reactions that remove the cyclopentadienyl ring are hardly ever done on compounds such as $CpRe(CO)_3$ since the aromatic ring is stabilized by being formally a tridentate, six electron donor ligand to the metal as an anion.

Another similar six electron donor to a metal center is the trans face of the monocapped octahedral metal carbide cluster

anion, $[Re_7C(CO)_{21}{}^{3-}]$. Like the cyclopentadienyl group, this face of the cluster is also formally three coordinate and a six electron donor. Consequently, an analogy could be made between the cluster and the organic ligand as six electron donors to a capping metal center. In addition, the anionic cluster, like the cyclopentadienyl ring, can be capped with a variety of organometallic species such as $Pt(CH_3)_3$ and $Rh(cyclooctadiene)$.[10] Another of these organometallic fragments that can cap both the cluster and the cylopentadienyl ring is $Re(CO)_3$ (Figure 1). The resultant cluster anion, $[Re_8C(CO)_{24}{}^{2-}]$, can be easily formed by pyrolysis of $Re_2(CO)_{10}$ with sodium at 210 ^{o}C.[11] By studying the reactivity of the $Re(CO)_3$ moiety capping the hepta-rhenium cluster, an understanding of the similarities between the hepta-rhenium cluster and cyclopentadienyl as electron donators to $Re(CO)_3$ can be attained.

Another reason for studying substitution reactions onto metal clusters is to increase the reactivity of that cluster for possible catalytic uses. It has been shown that the presence of a nitrosyl ligand on a metal cluster will enhance the reactivity of the cluster.[12] This increase in reactivity comes from the ability of small electrophilic moieties to induce the breakage of metal-metal bonds.[13] Consequently, there has been extensive work done on nitrosyl substituted metal clusters.[12-22] Some of these clusters are monosubstituted such as $[Os_{10}C(CO)_{23}(NO)^-]$ [12] and $HRu_6C(CO)_{15}(NO)$ [14], and others have been polysubstituted like $Ru_6C(CO)_{17}(NO)_2$ [19] and $Fe_6(CO)_{11}(NO)_4$ [22]. In
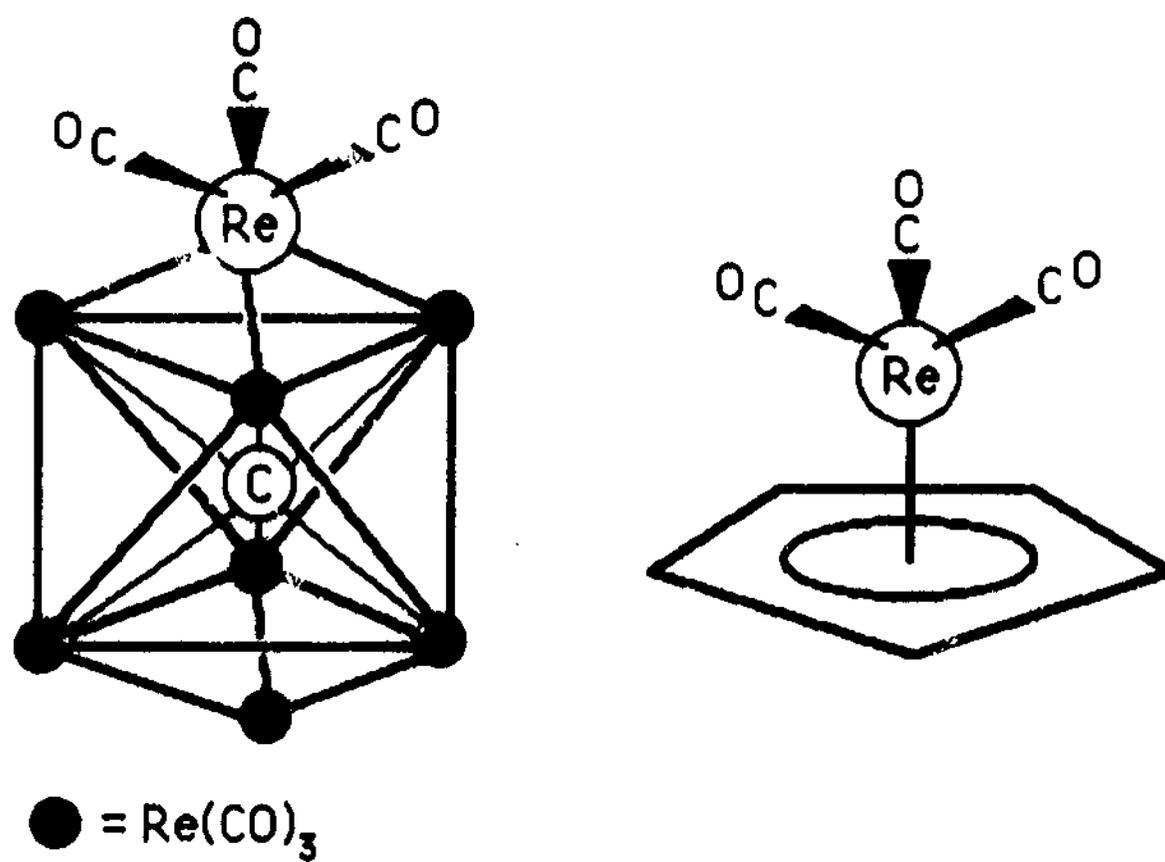
Figure 1. Comparison of Re(CO)₃ capping Re₇C(CO)₂₁³⁻ and C₅H₅⁻.

some disubstituted nitrosyl clusters, the nitrosyl ligands may be removed as nitrous oxide.[19] This type of environmentally important catalytic reaction that changes nitric oxide to the less noxious nitrous oxide has also been shown for monometallic compounds, such as $RhCl_3 \cdot xH_2O$ in the presence of nitric oxide and carbon monoxide.[23]

Metal clusters compounds have also found a wide variety of applications in other fields of catalysis. The clusters can be used as homogeneous catalysts and also as precursors for oxide-supported heterogeneous catalysts.[24] In addition, theoretical studies on different aspects of adsorption have proceeded by placing the adsorbate moiety on a "minimetal" surface represented by two or more metal atoms. By definition, metal clusters have three or more closely grouped metal atoms which have metal-metal bonds. Therefore, metal clusters can act as models for larger metallic surfaces providing much information about the species involved in chemisorption.[25]

This thesis describes the several reactions conducted with $[Re_7C(CO)_{21}{}^{3-}]$ and $[Re_8C(CO)_{24}{}^{2-}]$ Infrared spectrometry, fast-atom bombardment mass spectrometry, and cyclic voltammetry were the methods used to characterize the products. The operation of a cyclic voltammograph was an especially important part of this work, and it will be described in detail.

II. EXPERIMENTAL

All operations were carried out under nitrogen with the use of standard Schlenk techniques. Photochemical reactions were carried out in a quartz vessel with ultraviolet light provided by a medium-pressure mercury lamp. Reaction solvents were dried and distilled immediately prior to use. $[Re_8C(CO)_{24}][A]_2$ and $[Re_7C(CO)_{21}][A]_3$ $(A = N(C_2H_5)_4^+$ and $N(P(C_6H_5)_3)_2^+)$ were prepared by literature methods.[11] Triphenylphosphine was recrystallized from ethanol. $[NO][BF_4]$ (Aldrich) was purified by sublimation ($180^\circ C$, 10^{-3} torr) and stored in a glove box. $[N_2C_6H_5][BF_4]$, $[N_2C_6H_4CH_3][BF_4]$, and $[N_2C_6H_4N(CH_3)_2][BF_4]$ were used without further purification. $[NBu_4][PF_6]$ (Aldrich) was recrystallized from ethyl acetate/hexane and then from acetonitrile/diethylether. $[NBu_4][ClO_4]$ (G. Fredrick Smith Chemical) was used as received. All reactions were followed by infrared spectrometry until the carbonyl stretching peaks of the starting material had disappeared.

Infrared spectra were obtained on a Perkin-Elmer model 1750 Infrared Fourier Transform Spectrometer. The melting point determination was done on a Mel-Temp melting point apparatus by Laboratory Devices. Cyclic voltammetry was performed with a Bioanalytical

Systems CV-1B potentiostat utilizing a normal three-electrode cell with a Bioanalytical Systems platinum working electrode and a Bioanalytical Systems Ag/AgCl (3M Cl⁻) reference electrode at a typical scan rate of 100 mV/sec. The dichloromethane or acetonitrile solutions were 0.10 M in supporting electrolyte ($[NBu_4][PF_6]$ or $[NBu_4][ClO_4]$) and 0.2 mM in compound. Under these conditions the $Cp_2Fe^{0/+}$ couple had a $E_{1/2}$ = 0.462 V and ΔE_p = 74 mV. Fast-atom bombardment (FAB) mass spectra were performed by the Mass Spectrometry Center at the University of Illinois. Elemental analyses were done by the Microanalytical Laboratory of the School of Chemical Sciences at the University of Illinois.

Preparation of $[Re_7C(CO)_{20}(NO)][PPN]_2$. $[Re_7C(CO)_{21}][PPN]_3$ (54.7 mg, 15.54 µmol) and $NOBF_4$ (1.9 mg, 16.3 µmol) were stirred in dichloro- methane (ca. 15 mL) for 2 hours. The solution was then filtered to remove excess $NOBF_4$ and concentrated to 2 mL. Methanol (ca. 15 mL) was carefully layered on top of the solution, and the mixture was allowed to stand at room temperature. After two days, air stable crystals of $[Re_7C(CO)_{20}(NO)][PPN]_2$ (23.4 mg, 7.85 µmol, 50.5%) were obtained by filtration and dried in vacuo. Anal. Calcd. for $C_{93}H_{60}N_3O_{21}P_4Re_7$: C, 37.45; H, 2.03; N, 1.32. Found: C, 38.20; H, 1.96; N, 1.32. IR (dichloromethane) ν_{CO}: 2050(w), 1997(vs), 1986(s), 1911(w) cm⁻¹; ν_{NO}: 1693(w) cm⁻¹; ν_{NO}(KBr): 1697(w) cm⁻¹, ν_{NO} (THF): 1695(w) cm⁻¹, ν_{NO} (acetonitrile): 1690 cm⁻¹.

Reaction of [Re$_6$C(CO)$_{24}$][N(C$_2$H$_5$)$_4$]$_2$ and [NO][BF$_4$]. [Re$_6$C(CO)$_{24}$]
[N(C$_2$H$_5$)$_4$]$_2$ (201 mg, 82.6 µmol) and NOBF$_4$ (14.7 mg, 126 µmol) were
added to dichloromethane (40 mL). Due to the insolubility of the
rhenium cluster in dichloromethane and the extreme moisture
sensitivty of NOBF$_4$, extra NOBF$_4$ (13.3 mg, 114 µmol) had to be added
to the original solution to push the reaction to completion. After 69
hours the reaction was found to be complete by infrared spectrometry.
The solvent was filtered leaving red solid behind which was found to be
unreacted [Re$_6$C(CO)$_{24}$] [N(C$_2$H$_5$)$_4$]$_2$. Concentration of the filtrate left a
brown residue. Attempts to crystallize the residue led to the formation
of crytals of [Re$_7$C(CO)$_{20}$(NO)][N(C$_2$H$_5$)$_4$] by infrared. All spectral data
below was obtained before crystallization was attempted. IR
(dichloromethane) v_{CO}: 2028(s), 2020(vs), 1954(w), 1897(w) cm^{-1}.
FAB-MS (negative ion) m/z (^{187}Re): 2182 (Re$_8$C(CO)$_{23}$(NO)), 1911
(Re$_7$C(CO)$_{20}$(NO)), 1911 - 28x (Re$_7$C(CO)$_{20}$(NO) - x CO)(x = 1 - 9), 1640
(Re$_6$C(CO)$_{17}$(NO)).

Reaction of [Re$_6$C(CO)$_{24}$][PPN]$_2$ and [NO][BF$_4$]. [Re$_6$C(CO)$_{24}$][PPN]$_2$
(54.5 mg, 16.76 µmol) and NOBF$_4$ (1.9mg, 16.3 µmol) were added to
dichloromethane (ca. 10 mL), and the mixture was stirred. Since the
reaction had not run to completion after 4 hrs, an excess of NOBF$_4$ was
added to the solution. After two more hours of reaction, the solution

was filtered away from excess $NOBF_4$ and the solvent was removed. The solid residue was washed with water, isopropanol, and dissolved in tetrahydrofuran in an attempt to remove the contaminant [PPN][BF_4]. Washing and dissolution converted the product to [$Re_7C(CO)_{20}(NO)$][PPN]$_2$. Anal. Calcd. for $C_{60}H_{30}N_2O_{24}P_2Re_8$: C, 26.55; H, 1.11; N, 1.03. Calcd. for $C_{93}H_{60}N_3O_{21}P_4Re_7$: C, 37.45; H, 2.03; N, 1.41. Found: C, 36.92; H, 1.94;, N, 1.24. IR (dichloromethane) v_{CO} (before conversion): 2028(vs), 2022(s), 1955(w), 1913(w) cm^{-1}; v_{NO}:1749(w) cm^{-1}; v_{NO} (THF): 1745(w) cm^{-1}; v_{CO} (after conversion): 1997(vs), 1986(s), 1917(m, br) cm^{-1}.

Attempted reaction of [$Re_8C(CO)_{24}$][N(C_2H_5)$_4$]$_2$ with $NOBF_4$ in CH_3CN. [$Re_8C(CO)_{24}$][N(C_2H_5)$_4$]$_2$ (29.0 mg, 11.9 µmol) and $NOBF_4$ (2.7 mg, 23.1 µmol) were stirred in acetonitrile (15 mL). Because the infrared spectrum of the solution did not change after four hours of stirring, additional $NOBF_4$ (3.0 mg, 25.7 µmol) was addded to the solution. Since no reaction had occurred after 22 hours of stirring, the solvent was removed to recover [$Re_8C(CO)_{24}$][N(C_2H_5)$_4$]$_2$.

Trial reaction of [$Re_8C(CO)_{24}$][N(C_2H_5)$_4$]$_2$ with [$N_2C_6H_5$][BF_4]. Small amounts of [$Re_8C(CO)_{24}$][N(C_2H_5)$_4$]$_2$ and [$N_2C_6H_4N(CH_3)_2$][BF_4] were added to a small vial and dissolved in dichloromethane. The mixture was shaken briefly. After three hours, the strong carbonyl stretching absorptions of the octa-rhenium cluster at 2003 and 2011

cm^{-1} were replaced by two new strong peaks at 2016 and 2028 cm^{-1}.

Attempted reaction of $[Re_8C(CO)_{24}][N(C_2H_5)_4]_2$ with $[N_2C_6H_4$-$N(CH_3)_2][BF_4]$. $[Re_8C(CO)_{24}][N(C_2H_5)_4]_2$ (52.4 mg, 21.5 μmol) and $[N_2C_6H_4N(CH_3)_2][BF_4]$ (5.7 mg, 24.3 μmol) were stirred in dichloromethane (ca. 40 mL). Due to the insolubility of both of the reactants in dichloromethane, the solvent was removed and replaced by acetone (ca. 15 mL). No reaction occurred in the acetone over a one week period. The solvent was then removed and the starting material cluster was recovered.

Reaction of $[Re_8C(CO)_{24}][PPN]_2$ with $[N_2C_6H_4CH_3][BF_4]$. $[Re_8C$-$(CO)_{24}][PPN]_2$ (47.5 mg, 14.6 μmol) and $[N_2C_6H_4CH_3][BF_4]$ (4.9 mg, 23.8 μmol) were stirred together in dichloromethane (20 mL). After 24 hours of reaction, the infrared carbonyl stretching frequencies of the starting material at 2011 and 2004 cm^{-1} had been replaced by peaks at 2029(s), 2025(sh), and 2016(s) cm^{-1}. The solvent was then removed and the residue was washed with water to remove excess $[N_2C_6H_4CH_3][BF_4]$. The residue was then dissolved in acetone (8 mL) and then the solution was layered with ethanol (20 mL). Storage at -15 °C produced a solid that had infrared peaks at 1975, 1993, 2004, and 2011 cm^{-1} suggesting decomposition in solution.

Second Reaction of $[Re_8C(CO)_{24}][PPN]_2$ with $[N_2C_6H_4CH_3][BF_4]$. $[Re_8C(CO)_{24}][PPN]_2$ (37.2 mg, 11.44 μmol) and $[N_2C_6H_4CH_3][BF_4]$ (2.4 mg, 11.7 μmol) were stirred together in dichloromethane (ca. 15 mL) for 24

hours. Because the infrared spectra of the solution showed the reaction to be incomplete, excess $[N_2C_6H_4CH_3][BF_4]$ (7.0 mg, 33.83 µmol) had to be added over the course of a few days to make the reaction go to completion. The reaction did not go through a infrared detectable intermediate. After the reaction was finished, the solvent was removed leaving a brown residue. IR (dichloromethane) v_{CO}: 2052(s), 2037(vs), 1941(vs, br), 1910(s, br) cm^{-1}. FAB-MS (negative ion): m/z (^{187}Re) 2718 ($[Re_8C(CO)_{23}(N_2)][PPN]$ or $[Re_8C(CO)_{24}][N(C_2H_5)_4]_2$), 2447 ($[Re_7C(CO)_{21}]$ [PPN]), 2271 ($Re_8C(CO)_{23}(N_2C_6H_4CH_3)$), 2176 ($[Re_6C(CO)_{18}][PPN]$).

Attempted reaction of $[Re_8C(CO)_{24}][N(C_2H_5)_4]_2$ with $P(C_6H_5)_3$. $[Re_8C(CO)_{24}][N(C_2H_5)_4]_2$ (38.2 mg, 15.7 µmol) was dissolved in tetrahydrofuran (15 mL). This solution was stirred while being irradiated with ultraviolet light for 2.5 hours. Triphenylphosphine (4.3 mg, 16.4 µmol) was then added to the solution. Periodic infrared spectra showed that no reaction had taken place during 19 hours of subsequent irradiation. The solution was heated at reflux for three hours. Afterwards, the infrared spectrum still showed no reaction. Additional irradiation for 17 hours lead to no change in the infrared spectrum between 2100 and 1900 cm^{-1}. However, two large broad peaks appeared at 1727 and 1779 cm^{-1}. $(CH_3)_3NO$ (1.2 mg, 16.0 µmol) was added to the solution. The solution was stirred for a day with no change in the infrared occurring. After irradiation for another 22 hours, the peaks

for the starting material disappeared and a rhenium mirror was formed on the side of the reaction vessel. Attempts to crystallize the product(s) were not successful. IR (THF) v_{CO}: 2025(w), 1904(w), 1779(vs,br), 1727(s,br) cm^{-1}. FAB-MS: no peaks above 800 m/z and no assignable peaks.

Preparation of [PPN][BF$_4$]. [PPN][Cl] (0.516 g, 0.899 mmol) and [Na][BF$_4$] (0.0996 g, 0.907 mmol) were dissolved in 300 mL and 40 mL of water respectively. The precipitate that was formed was filtered off and redissolved in dichloromethane (50 mL). This solution was dried over MgSO$_4$. After the solution was removed from the drying agent, the solvent was removed leaving a white powder of [PPN][BF$_4$] (0.430 g, 0.650 mmol, 72.35%). The white crystals of the solid were formed by dissolving the product in a hot mixture of chlorobenzene and hexane (ca. 5:1) and then cooling to -20 °C. Anal. Calcd. for BC$_{36}$F$_4$H$_{30}$NP$_2$: C, 69.13; H, 4.83; N, 2.24; P, 9.90. Calcd. for BC$_{36}$F$_4$H$_{30}$NP$_2$·CH$_2$Cl$_2$: C, 62.57; H, 4.54; N, 1.97; P, 8.72. Found (before recrystallization): C, 63.04; H, 4.26; N, 1.91; P, 7.67. Found (after recrystallization): C, 69.22; H, 4.87; N, 2.25; P, 9.74. Melting point: 234 °C.

III. RESULTS AND DISCUSSION

(A) Reactions with $Re_6C(CO)_{24}^{2-}$.

(1) Reaction with Triphenylphosphine.

To study the analogy between the cyclopentadienyl ring and the cluster $Re_7C(CO)_{21}^{3-}$ as six electron donors to the $Re(CO)_3$ moiety, reactions that had been previously performed on $(C_5H_5)Re(CO)_3$ were tried on the cluster $Re_8C(CO)_{24}^{2-}$. In one of these reactions, a group of Russian chemists photolyzed a tetrahydrofuran solution of $(C_5H_5)Re(CO)_3$ with ultraviolet light for thirty minutes to remove one carbon monoxide and replace it with a THF molecule. Subsequent addition of better electron donors than THF such as triphenylphosphine, pyridine, or diphenylacetylene formed the respective substituted compounds.[7]

A similar method was tried with $Re_8C(CO)_{24}^{2-}$ to substitute a carbon monoxide with triphenylphosphine. A tetrahydrofuran solution of the cluster was irradiated with ultraviolet light for 2.5 hours. During irradiation, nitrogen was slowly bubbled through the solution to remove any released carbon monoxide from the solution. A slight excess of PPh_3 was then added to the solution. No reaction occurred

upon addition or subsequent irradiation. The solution was then refluxed which also did not change the carbonyl stretching frequencies in the infrared spectrum of the solution. However, two peaks began to grow at 1727 and 1779 cm^{-1}, but these were not followed because they are not in the normal, terminal carbonyl frequency range. Since it was presumed that no reaction had taken place, an excess of trimethylamine N-oxide was then added to the solution. The $(CH_3)_3NO$ can donate an oxygen to a carbon monoxide to form the labile carbon dioxide creating an open coordination site. After the addition of $(CH_3)_3NO$, the solution was irradiated for another twenty two hours which led to the formation of a rhenium mirror on the side of the quartz tube that faced the ultraviolet lamp. The irradiation also led to the complete disappearance of all strong infrared peaks in the 1800 to 2200 cm^{-1} range; the peaks at 1727 and 1779 cm^{-1} were the only strong bands in the 1600 to 2200 cm^{-1} range of the infrared spectrum. Both the positive and the negative fast-atom bombardment mass spectra of a residue of the reaction product gave no peaks over 800 m/z.

Peaks in 1600 to 1800 cm^{-1} range are commonly associated with bridging carbonyls in organometallic compounds or carbonyls in organic compounds. The two peaks in this range from the irradiation reaction, however, could not be assigned to any known rhenium compounds. Due to the lack of terminal carbonyl stretching frequencies in the infrared, the lack of mass spectral peaks above 800 m/z, and formation of rhenium mirror during irradiation, the product or products

formed were probably all from decomposition of the cluster. The decomposition probably occurred because of the excessive amount of time, sixty hours, that the cluster was irradiated. Therefore, the $Re(CO)_3$ moiety capping the hepta-rhenium cluster does not react to form a triphenylphosphine substituted derivative in the same manner as it does on the cyclopentadienyl ring. A bulky compound like PPh_3 may not be able to substitute on the cluster because of steric hindrances. It also might not substitute on the anionic cluster because it is nucleophile.

(2) Reaction with Nitrosonium Tetrafluoroborate.

Thes last two statements seem to imply that a small electrophile would probably react very easily with the cluster. One common small electrophile is the nitrosonium ion, NO^+. This cation has been shown to replace a CO on both $(C_5H_5)Re(CO)_3$[4] and $(C_5Me_5)Re(CO)_3$[5] by electrophilic substitution forming monocationic complexes. Since NO^+ substitutes so easily on the $Re(CO)_3$ group in the above two organometallic complexes, reaction of this electrophile with the cluster would be a good place to continue the study of the aforementioned analogy.

Addition of $[NO][BF_4]$ to a dichloromethane solution of $Re_8C(CO)_{24}^{2-}$ does produce a reaction to apparently form $Re_8C(CO)_{23}(NO)^-$. Through the course of the reaction, the strong carbonyl stretching frequencies for $Re_8C(CO)_{24}^{2-}$ at 2013 and 2005

cm^{-1} disappear and are replaced by two new strong bands at 2028 and 2020 cm^{-1}. The peak for the coordinated nitrosyl stretch was found to be a very weak, broad band occurring at 1749 cm^{-1} in dichloromethane and at 1745 cm^{-1} in tetrahydrofuran.

This reaction goes quicker with PPN$^+$ as a counter ion rather than N(CH$_2$CH$_3$)$_4$$^+$ because the tetraethylammonium salt of Re$_8$C(CO)$_{24}$$^{2-}$ is only slightly soluble in dichloromethane. When tetraethylammonmium is used as the counter ion, excess [NO][BF$_4$] must be added to the solution to force the reaction to completion. This reaction, however, does not work in acetonitrile in which the tetraethylammonium salt of the cluster is very soluble. Similarily, it has been shown that another cluster, [Os$_4$(CO)$_{12}$H$_3$$^-$], does not react with [NO][BF$_4$] in acetonitrile, but does react in dichloromethane. Instead, a solvent molecule substitutes for a carbon monoxide on the cluster since it is in excess and is also a fairly good ligand.[13] A similar competitive inhibition by solvent molecules probably makes the reaction of Re$_8$C(CO)$_{24}$$^{2-}$ and [NO][BF$_4$] not occur in acetonitrile. Unlike [Os$_4$(CO)$_{12}$H$_3$$^-$], however, no change in the infrared spectrum of the solution occured during twenty two hours of reaction, implying that not only had a nitrosonium ion, but an acetonitrile molecule also had not replaced a carbon monoxide on the cluster. In addition, since it is difficult to remove all the water from acetonitrile, a few microliters of water in the solvent would be enough to destroy all the [NO][BF$_4$],

thus, giving the cluster nothing to react with.

Another problem occurred during the work-up of the reactions of $Re_8C(CO)_{24}{}^{2-}$ with $[NO][BF_4]$ in dichloromethane: the product could not be crystallized. Instead of the nitrosylated octa-rhenium cluster crystallizing out of solution, the nitrosylated hepta-rhenium cluster, $[Re_7C(CO)_{20}(NO)][PPN]$, crystallized. During the course of the reaction of $[Re_8C(CO)_{24}][PPN]$ with $[NO][BF_4]$, $[PPN][BF_4]$ is formed in the solution. Since nothing precipitated out of solution during any of these reactions, $[PPN][BF_4]$ must be soluble in dichlorormethane and, therefore, was not removed from the solution before crystallization. Consequently, it reacted with the nitrosylated octa-rhenium cluster to remove a $Re(CO)_3$ cap producing the nitrosylated hepta-rhenium cluster, $Re_7C(CO)_{20}(NO)^{2-}$, as was seen by the replacement of the 2028 and 2020 cm^{-1} infrared peaks with bands at 1997 and 1986 cm^{-1} (vide supra). The other product of this decomposition reaction (i.e. the one containing the removed $Re(CO)_3$ unit) stayed in solution and was not determined.

Because it is involved in the decomposition of $Re_8C(CO)_{23}(NO)^-$, $[PPN][BF_4]$ was synthesized for the purpose of testing its solubility properties with the intent of finding a solvent that can separate it from the cluster. The compound was prepared by mixing separate aqueous solutions of $[PPN][Cl]$ and $[Na][BF_4]$ which immediately formed a precipitate. After extraction of the precipitate into dichloromethane,

the solution was dried over MgSO4, and then the solvent was removed in a vacuum leaving a white powder. This powder was found to be impure by microanalysis. The impurity was probably dichloromethane which had not been removed during the drying of the solvent. Due to the impurity, the powder was recrystallized in approximately a five to one mixture of chlorobenzene and hexane by heating the mixture until all the solid dissolved and then cooling to -20 °C. White crystals of the $[PPN][BF_4]$ were shown to have a sharp melting point at 234 °C and were also found to be analytically pure. Subsequent solubility tests showed that $[PPN][BF_4]$ is insoluble in tetrahydrofuran, but the product cluster, however, is quite soluble in THF. However, when a residue of $[Re_8C(CO)_{23}(NO)^-][PPN]$ is dissolved in THF, partial decomposition does occur even though some $[PPN][BF_4]$ quickly precipitates out of solution. Since THF is a good coordinating solvent and can easily replace open coordination sites on the removed cap, the decomposition probably can occur at a much quicker rate even though the $[PPN][BF_4]$ is insoluble in tetrahydrofuran.

Luckily, important characterization data such as mass spectra can be obtained on products without having the crystals of the product. Therefore, a fast-atom bombardment mass spectrum was done on a residue of the tetraethylammonium salt of $Re_8C(CO)_{23}(NO)^-$. The negative ion scan gave the fragmention pattern for the anionic cluster (Figure 2). The group of peaks around 2182 m/z correspond to the product cluster without the counter ion. The peaks at 1911 m/z are due

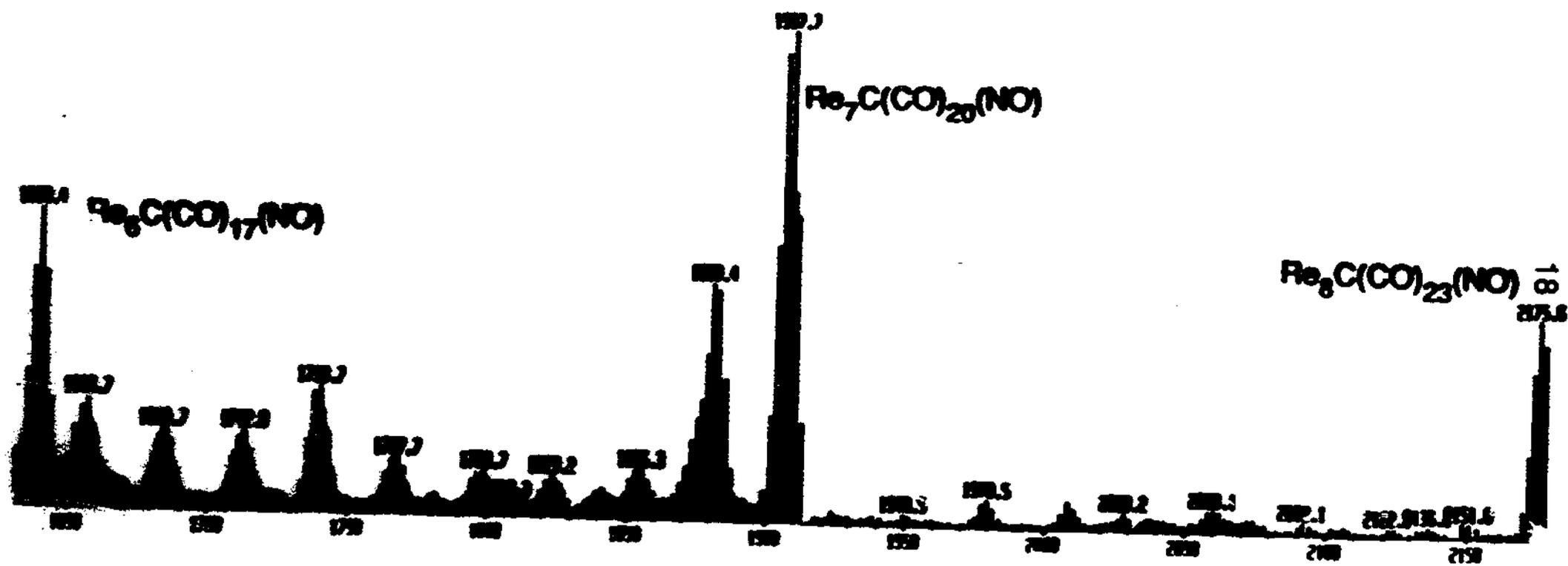Figure 2. The negative ion FAB mass spectrum of $[Re_8C(CO)_{23}(NO)][N(C_2H_5)_4]$.

-13 CO

$Re_8C(CO)_{24}^-$

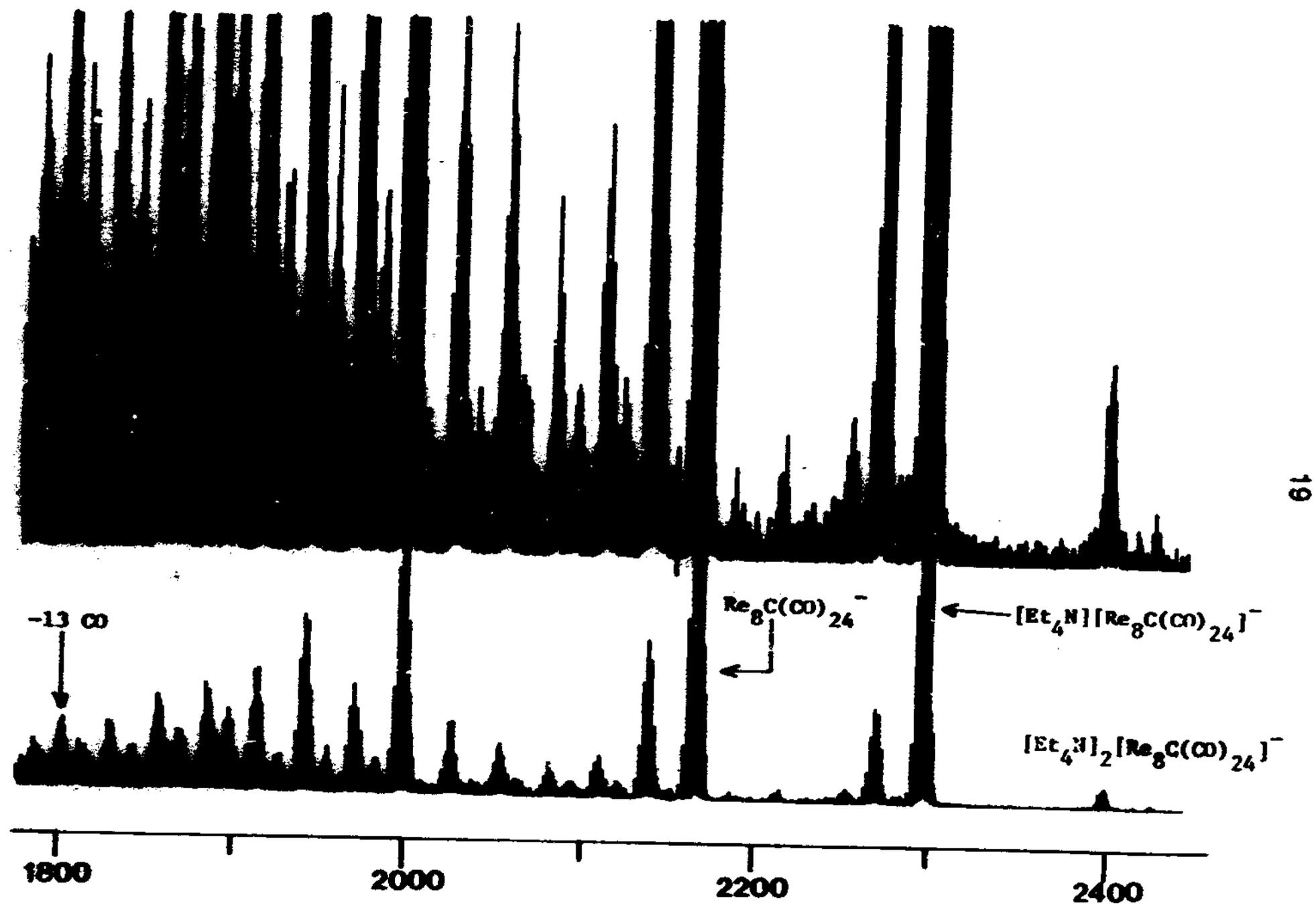$[Et_4N][Re_8C(CO)_{24}]^-$

$[Et_4N]_2[Re_8C(CO)_{24}]^-$

1800   2000   2200   2400

Figure 3. The negative ion FAB mass spectrum of $[Re_8C(CO)_{24}][NEt_4]_2$.

to the product cluster without one capping $Re(CO)_3$. Successive peaks 28 m/z apart below 1911 m/z correspond to nine consecutive losses of carbon monoxide. The peak at 1640 m/z corresponds to the octahedral frame of the cluster: $Re_6C(CO)_{17}(NO)$.

These peaks in the product mass spectrum can also be assigned to the starting material, $[Re_6C(CO)_{24}][NEt_4]_2$. However, the infrared spectrum indicated that no starting material remained, and also the negative ion mass spectrum of the product (Figure 2) was found to be different from that of the starting material (Figure 5).[26] Both mass spectra were taken of tetraethylammonium salts of the clusters allowing comparisons to be made between the two. Both spectra do show a group of peaks around 2175 m/z corresponding to the clusters without counter ions and also groups of peaks between 1900 and 1800 m/z that correspond to consecutive losses of carbon monoxide. These, however, are the only similarities between the spectra. The mass spectra of $[Re_6C(CO)_{24}][NEt_4]_2$ shows a large peak at 2000 m/z which does not appear in the mass spectrum of $[Re_6C(CO)_{23}(NO)][NEt_4]$. Similarily, the mass spectrum of the product has a group of intense peaks around 1910 m/z correspondng to the loss of a rhenium tricarbonyl cap from the cluster. A large peak in this range does not appear in the mass spectrum of the starting material, implying that the starting material will not lose a cap as easily as the product. There are also several other peaks that differentiate the two mass spectra, giving further evidence that the product obtained was not the starting

material, $[Re_6C(CO)_{24}][NEt_4]_2$.

Since the peaks are commonly in groups of five to eight large bands, a peak for a released carbon monoxide can not be diferentiated that of a released nitrosyl ligand. Thus, the mass spectrum of the product does not allow the determination of the location of substitution. However, assignments of smaller cluster fragments such as with six or seven rheniums can be made with the nitrosyl intact. The known decomposition of $Re_8C(CO)_{23}(NO)^-$ to $Re_7C(CO)_{21}(NO)^{2-}$ and the known location of the nitrosyl ligand on the latter cluster allow for these assignments to be made with the nitrosyl intact.[27]

Direct comparisons of spectral data for nitosylation products of $CpRe(CO)_3$ and $Re_8C(CO)_{24}^{2-}$ can not be made. The nitrosylated cluster is an anion while the nitrosylated monometallic compound is a cation. Also, with $CpRe(CO)_3$ all three carbon monoxide ligands are equivalent on the NMR time scale at room temperature.[28] Therefore, it does not matter which carbonyl the NO^+ replaces. However, at room temperature there are two different groups of NMR equivalent carbonyls: eighteen on the octahedron and six on the caps.[29] To make direct comparisons between the cyclopentadienyl ring and the hepta-rhenium cluster as six electron donors to a $Re(CO)_2(NO)$ group, the NO^+ would have to substitute on the cap of the cluster. However, it is known that the NO^+ does not substitute onto the cap of the cluster. This is known because $Re_8C(CO)_{23}(NO)^-$ decomposes to $Re_7C(CO)_{20}(NO)^{2-}$ in solution and the NO ligand was found to be on the octahedron by

variable temperature NMR studies.[27]

Even though direct comparisons can not be made, relative comparisons can be made between the nitrosylation products of $CpRe(CO)_3$ and $Re_8C(CO)_{24}^{2-}$. As would be expected, the carbonyl frequencies for both compounds shift to higher energy upon substitution of carbon monoxide with NO^+. For example, the carbonyl stretching frequencies at 2020 and 1925 cm^{-1} for $CpRe(CO)_3$ shift to 2105 and 2049 cm^{-1} upon reaction of the compound with NO^+. Likewise, those frequencies for $CpRe(CO)_2(NO)^+$ are also higher in energy than those found for $Re_8C(CO)_{23}(NO)^-$ at 2028 and 2020 cm^{-1}. Because less electron density can be back donated by the metal to coordinated carbon monoxides as the charge on the complex becomes more positive, therefore, less electron density can be donated by the CO to the metal because of synergic bonding. Thus, the stretching frequencies for the CO ligands in a cationic complex would be at higher energy than in a similar anionic complex. The NO stretching frequency for $CpRe(CO)_2(NO)^+$ appearing at 1815 cm^{-1} is also higher in energy than that for the cluster at 1749 cm^{-1} which is to be expected for the same reason.[4] Both NO stretching frequencies are in the range for terminally bound nitrosyls.[23]

(3) Reactions with Tetrafluoroborate salts of Aryl Diazonium Ions.

Since the electrophilic NO^+ seemed to react quite easily with the octa-rhenium cluster, it might be possible for other electrophiles

to react just as readily with the cluster. Another class of electrophiles that have been found to react with $CpRe(CO)_3$ are the substituted phenyl diazonium ions. The substituted phenyl diazonium ions that have been reacted with $CpRe(CO)_3$ have the form $^+N=N-C_6H_4R$ and $^+N=N-C_6H_3R'_2$ where R includes para-methyl, para-methoxy, and ortho-trifluoromethyl and R' is a methyl group on the phenyl ring in either the 2,6 or 3,5 disubstituted arrangement. These reactions, however, were not performed by direct addition of the diazonium ion to a solution of the cluster, but rather, by initially photolyzing a THF solution of $CpRe(CO)_3$ to remove a CO and then addition of the diazonium salt.[6]

Due to the previous problems that occurred while trying to remove a carbon monoxide from the cluster by photolysis, direct addition of different diazoium ions to dichloromethane solutions of the cluster was tried instead. Three different phenyl diazonium ions of the formula para-$^+N=N-C_6H_4R$ where R = H, CH_3 and NMe_2 were tried. No reaction occurred with the addition of the dimethyl amine derivative in dichloromethane or acetone, but reactions did occur with the other two.

A trial reaction was done with $[N=N-C_6H_5][BF_4]$ and $[Re_6C(CO)_{24}]$ $[PPN]_2$ to see if the two would react quickly in dichloromethane. After three hours in solution together, the strong carbonyl frequencies for $[Re_6C(CO)_{24}]$ $[PPN]_2$ at 2003 and 2011 cm^{-1} were replaced by two new peaks at 2016 and 2026 cm^{-1}. This

confirmed that diazonium ions would react in a similar manner as $[NO][BF_4]$.

Reaction was then tried with $[N=N-C_6H_4CH_3][BF_4]$ and $[Re_8C(CO)_{24}]$ $[PPN]_2$. An excess of the diazonium was added to a dichloromethane solution of the cluster. After one day of reaction, the infrared peaks for the starting material had disappeared and were replaced by strong peaks at 2016 and 2029 cm^{-1}, a shoulder at 2025 cm^{-1}, a weak peak at 1958 cm^{-1}, and a medium, broad peak at 1918 cm^{-1}. After removal of the dichloromethane, the residue was washed with water to remove excess diazonium salt. The residue was then dissolved in eight milliliters of acetone and carefully layered with about twenty milliliters of ethanol. The solid that eventually came out of solution did not have the infrared peaks of the original product suggesting that decomposition had occurred in solution.

Due to the failure of the crystallization attempt, the above reaction was tried again. This time four equivalents of the same diazonium ion had to be added to force the reaction to completion. In addition, the carbonyl stretching frequencies of the product were different than the first attempt. The product carbonyl peaks were found to be at 2052, 2037, 1941, and 1910 cm^{-1}. All four peaks were strong in intensity and the last two were also broad bands. A fast-atom bombardment negative ion mass spectrum was obtained on a portion of the product residue (Figure 4). All of the peaks, however, were very weak, but several peaks were discernible. The group of
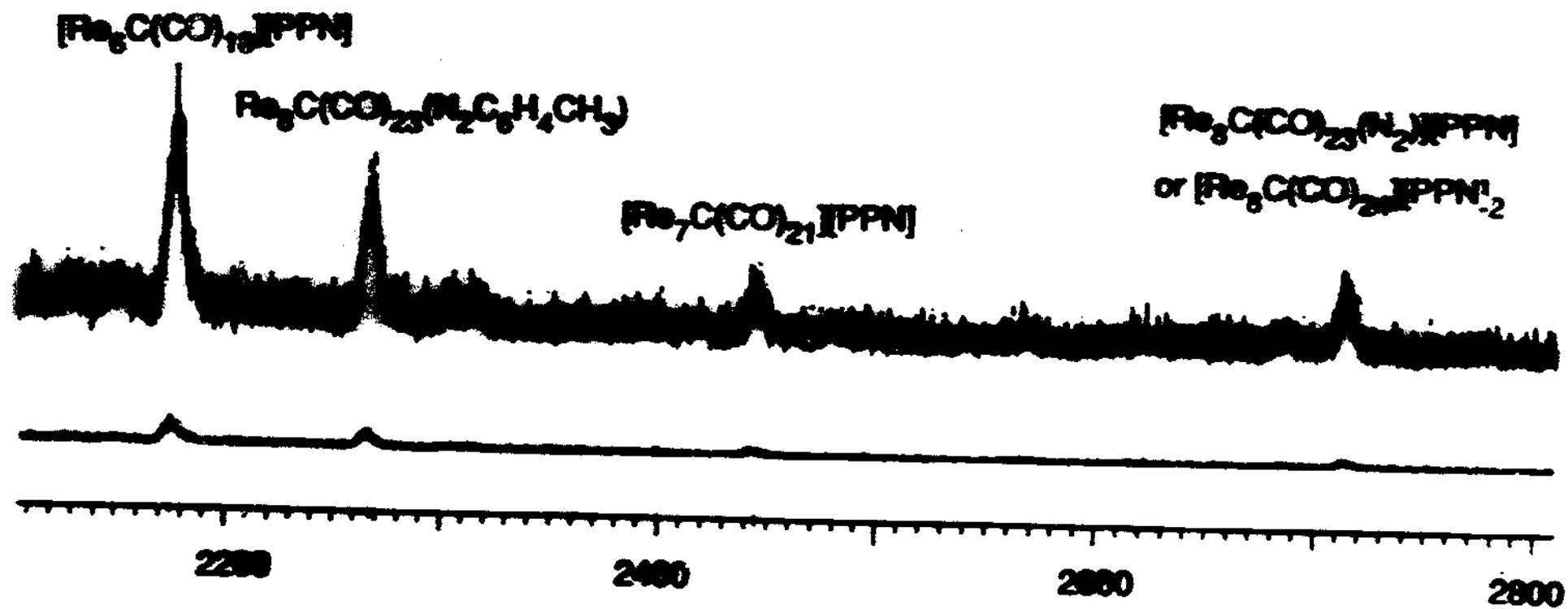
Figure 4. The negative ion FAB mass spectrum of $[Re_8C(CO)_{23}(N_2C_6H_4CH_3)][PFN]$.

peaks around 2718 m/z corresponds to a monosubstituted cluster with the loss of $C_6H_4CH_3$. The peaks around 2447 m/z correspond to the product cluster with the loss of $Re(CO)_2(N_2C_6H_4CH_3)$. Peaks about 2271 m/z is the product cluster minus the counter ion, PPN$^+$. The last large group of peaks at 2176 m/z corresponds to the ion at 2447 m/z with the removal of a $Re(CO)_3$ group.

The mass spectrum of this product seems to suggest that the cluster is only monosubstituted, however, the infrared seems to suggest that the compound might actually be disubstituted. The infrared of the first reaction with $[N=N-C_6H_4CH_3][BF_4]$ is quite similar to that of $[Re_6C(CO)_{23}(NO)][PPN]$. It might be possible that one of the carbon monoxides on the cluster was replaced by a dinitrogen from one of the diazonium ions which would shift the carbonyl stretching frequencies to higher energy as is seen. However, a mass spectrum would not show the difference between a carbon monoxide and a dinitrogen. The mass spectrum did seem to suggest that the diazonium ion had substituted onto the cap of the cluster. One reason that this electrophile might have substituted on the cap instead of on the octahedron like NO$^+$ is steric hindrances. Since the diazonium cation is much larger than the nitrosonium ion, it would be effected more by the size and bulk of the cluster. A diazonium ion might have originally substituted on the octahedron, but steric hindrances might have removed the tolyl group, thereby creating a dinitrogen ligand.

It is also interesting to note that as the electron donating

ability of the para ligand increases, the rate of the reaction seems to slow down. Since the para ligands like dimethyl amine and methyl groups donate electrons to the phenyl ring, the positive charge of the diazonium ions becomes more delocalized and, consequently, the ligand becomes less electrophilic. This trend is understandable since the cluster seems to react well with more electrophilic compounds, and less with more nucleophilic compounds.

(B) $[Re_7C(CO)_{20}(NO)][PPN]_2$.

(1) Preparation.

Addition of a slight excess of $[NO][BF_4]$ to a dichloromethane solution of $[Re_7C(CO)_{21}][PPN]_3$ changed the color of the solution from red to brown in about ten minutes. After two hours of stirring, the strong carbonyl stretching frequencies of $Re_7C(CO)_{21}{}^{2-}$ at 1978 and 1968 cm^{-1} had been replaced by two new peaks at 1997 and 1986 cm^{-1}. The solution was then filtered to remove any excess $[NO][BF_4]$, which is essentially insoluble in dichloromethane. After the filtrate was concentrated down to about two milliliters, about fifteen milliliters of methanol was carefully layered on top. Brown air stable crystals of $[Re_7C(CO)_{20}(NO)]$ $[PPN]_2$ were isolated after allowing the layer diffuse at room temperature for two days. The yield was 50.5%. In addition to the two strong peaks mentioned above, the infrared spectrum of this product also showed two weak peaks in the carbonyl range appearing at 2050 and 1911 cm^{-1}.

Another method of preparing $[Re_7C(CO)_{20}(NO)][PPN]_2$ is to attempt to crystallize $[Re_8C(CO)_{23}(NO)][PPN]$ by layering methanol on top of a dichloromethane solution of the nitrosyl substituted octa-rhenium cluster. As was mentioned previously, excess $[PPN][BF_4]$ in solution will react with $[Re_8C(CO)_{23}(NO)][PPN]$ to remove a $Re(CO)_3$ cap, thus forming $[Re_7C(CO)_{20}(NO)][PPN]_2$. When a more coordinating solvent such as tetrahydrofuran is used, the decapitation goes cleaner and quicker, giving an analytically pure sample of $[Re_7C(CO)_{20}(NO)][PPN]_2$. This method, however, is not the easiest or the best method of preparing $[Re_7C(CO)_{20}(NO)][PPN]_2$, but it does work nonetheless.

(2) Elucidation of the NO stretching frequency.

To be sure that the nitrosonium had indeed substituted for a carbon monoxide on the cluster, the NO stretching frequency had to be found for $[Re_7C(CO)_{20}(NO)][PPN]_2$. Very concentrated solutions of the compound had to be studied to find this frequency since there are nitrosyl twenty carbonyls and only one nitrosyl. The frequency in wave numbers was originally thought to have been found at 1712 cm^{-1} in dichloromethane. However, this peak can almost always be found in infrared spectra using dichloromethane as a solvent. Using a very concentrated solution of the nitrosylated cluster in dichloromethane, the peak was later found to be at 1693 cm^{-1}. To be sure that this was indeed the peak, the infrared of this compound was run in several other

media. The peak was found at 1697 cm^{-1} using a KBr pellet, at 1695 cm^{-1} in tetrahydrofuran, and at 1699 cm^{-1} in acetonitrile, thus confirming that the peak found in dichloromethane was due to the nitrosyl on the compound and not the solvent.

Frequencies for terminal NO stretches on mononuclear coordination complexes commonly occur in the 1600 to 1850 cm^{-1} range.[23] For metal carbonyl clusters, terminally bound nitrosyls have infrared bands usually between 1650 and 1800 cm^{-1}. On the other hand, bridging nitrosyls, like bridging carbonyls, will have infrared bands at lower frequencies than the terminal nitrosyls.[15-19] A neutral cluster like $H_3Os_4(CO)_{11}(NO)$ in which the nitrosyl is terminally bound (as found by crystallography) has an NO stretch at 1735 cm^{-1} [17], whereas the bridging nitrosyl in $[Os_{10}C(CO)_{24}(\mu_2\text{-}NO)]^-$ has its NO stretching frequency at 1603 cm^{-1} [15].

The nitrosyl stretching frequencies for both $[Re_7C(CO)_{20}(NO)]$ $[PPN]_2$ and $[Re_8C(CO)_{23}(NO)][PPN]$ fall in the range for terminally bound ligands. The NO stretch for the hepta-rhenium cluster is at lower energy which is to be expected because this cluster is a dianion where as the octa-rhenium cluster is a monoanion. The NO stretching frequency of $[Re_8C(CO)_{23}(NO)][PPN]$ in dichloromethane is 56 cm^{-1} higher than $[Re_7C(CO)_{20}(NO)][PPN]_2$. Infrared spectrometry, however, does not give the location of the NO ligand in a compound, and crystallography could not help to discern one nitrosyl from the twenty or more carbonyls on the clusters. As was previously mentioned, a NMR

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variable temperature study has been done to show that the nitrosyl is on one of the rheniums of the octahedron opposite the cap in $[Re_7C(CO)_{20}(NO)][PPN]_2$.[27]
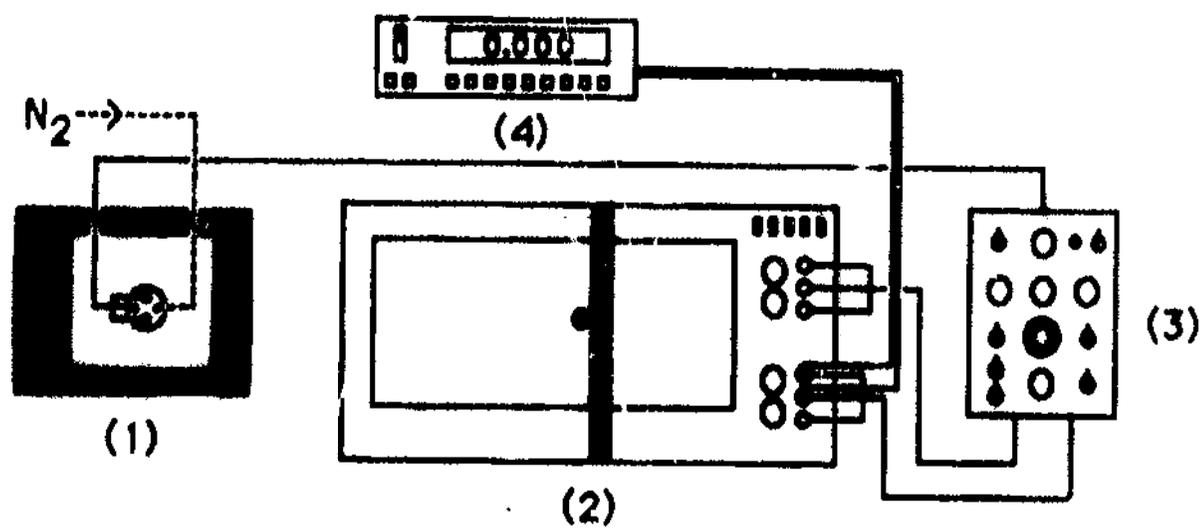
(C) Cyclic Voltammetry.

(1) Introduction.

The electrochemical technique of cyclic voltammetry (CV) has become very popular with inorganic chemists within recen. years.[30] Since cyclic voltammetry is a form of polarography, current is plotted as a function of voltage which is being cycled at a constant rate, thus the name. Therefore, when a compound is oxidized or reduced a current is generated that shows up as a peak on the voltammogram. A current is also generated when the oxidized or reduced species is reduced or oxidized back to its original form. These two peaks will give the potential at which the electrochemical process took place. In addition, the number of electrochemical changes a compound can undergo will also be shown by a cyclic voltammogram. CV studies can also give insight into the reversibility of an electrochemical process and whether the reduction or oxidation is a one or two electron process. More complicated electrochemical information about a compound or system can also be determined using CV.[31]

(2) The System.

Since so much information about a compound can be obtained from a cyclic voltammogram, a cyclic voltammetry system (Figure 5) was set up to study the electrochemistry of novel clusters. The

(1)   Electrochemical cell on stir plate (black).

(2)   Houston Instruments Omnigraphic 100 Series Recorder

(3)   Bioanalytical Systems CV1B Voltammograph

(4)   Fluke model 8040A Multimeter

Figure 5. A block diagram of the cyclic voltammetry system.

potential generator is a Bioanalytical Systems CV1B cyclic voltammograph. This device has controls to change the scan rate, the starting point of the scan, the potential range and window, the direction of the scan, and attenuation of the vertical scale. The voltammograms are recorded on a Houston Instruments Omnigraphic Series 100 Recorder, which is wired directly to the voltammograph, has scaled vertical and horizontal controls to keep the peaks on the chart paper. However, since neither the CV1B cyclic voltamograph nor the recorder has a voltmeter, determination of peak potentials was impossible because the starting and ending potentials for a scan were not known. Therefore, a Fluke 8040A model Multimeter voltmeter was attached to the horizontal voltage controls of the recorder to monitor potential as it is generated by the voltammograph. If needed, the voltmeter can also be attached to the vertical controls of the recorder to find exact peak height voltages which are directly proportional to the peak currents.

None of this instrumentation, however, is useful unless there is an electrochemical cell to place the compounds. The cell itself is made out of glass and held by a special holder so that the wires that attach to the electrodes will reach. (A top view of the cell is shown in Figure 5 and an expanded top view is in Figure 6.) The cell holder is placed on top of a stir plate so that the solution can be stirred between scans to remove any concentration gradient created during a scan. The cap for the cell has two large and two small holes in it. The two large holes are for the reference and working electrodes. The reference electrode
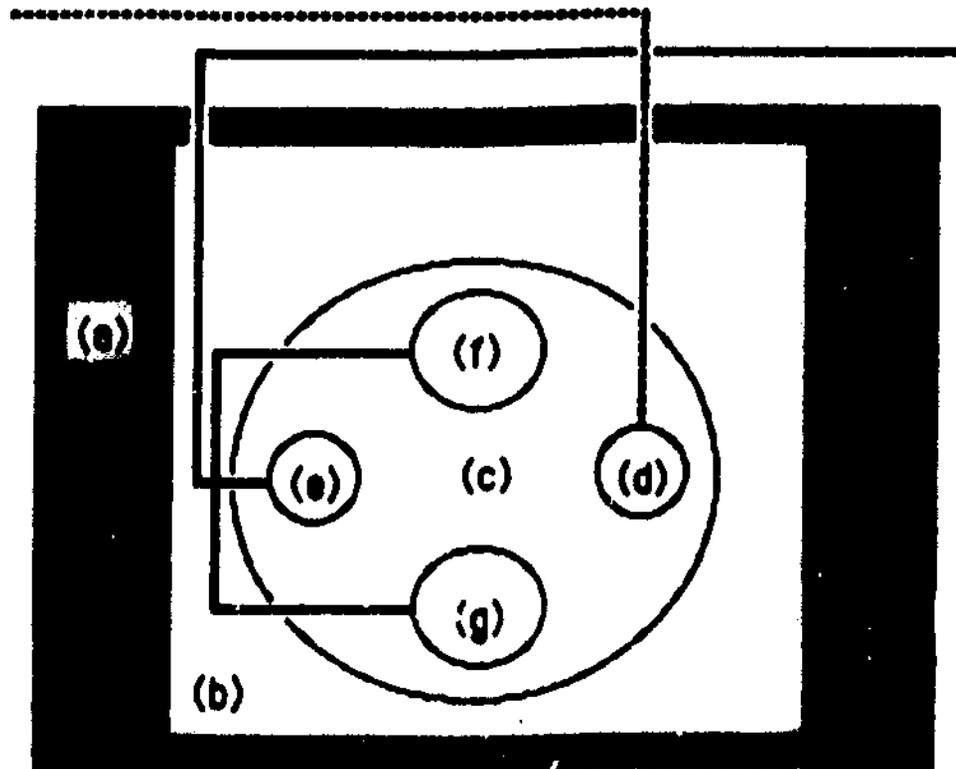
———————— Electrical wires from CV1B Voltammograph

················· Nitrogen line

(a)   Stir plate to make solution homogeneous between scans.

(b)   Cell holder

(c)   The cap on the cell

(d)   Nitrogen gas inlet

(e)   Platinum wire for auxiliary electrode

(f)   Bioanalytical Systems platinum working electrode

(g)   Bioanalytical Systems silver/silver chloride reference electrode

Figure 6. Top view of the electrochemical cell.

is a Bioanalytical Systems Ag/AgCl electrode that is 3.0 M in chloride ions. When not in use, the reference electrode is stored in an aqueous solution of 3.0 M sodium chloride. The working electrode is a Bioanalytial System platinum voltammetry electrode. The two small holes are for the auxiliary electrode and a inert gas inlet. The auxiliary electrode is a platinum wire that is permanently encased in the cap. The purpose of the auxiliary electrode is to prevent large currents from passing through the reference electrode and also to provide a current to the working electrode to sustain any electrolysis that occurs there.[31] The inert gas inlet makes it possible to bubble nitrogen through the solution between scans to remove oxygen, which will show up in a cyclic voltammogram. The solution is kept under a blanket of nitrogen during scans.

(3) Compounds with known Electrochemical Properties.

Once the system was set up, several different compounds with known electrochemical properties were studied by cyclic voltammetry. The first compound studied was ferrocene as a 1.0 mM solution in dichloromethane with 0.10 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. The $E_{1/2}$ for ferrocene was found at 0.491 volts versus the Ag/AgCl reference electrode with a ΔE_p = 102 mV suggesting that the couple is not reversible. The same conditions were tried with acetonitrile rather than dichloromethane as solvent (Figure 7). The $E_{1/2}$ for the ferrocene/ferrocenium couple was found to be 0.438 V vs. Ag/AgCl in this solvent with a ΔE_p = 45 mV.
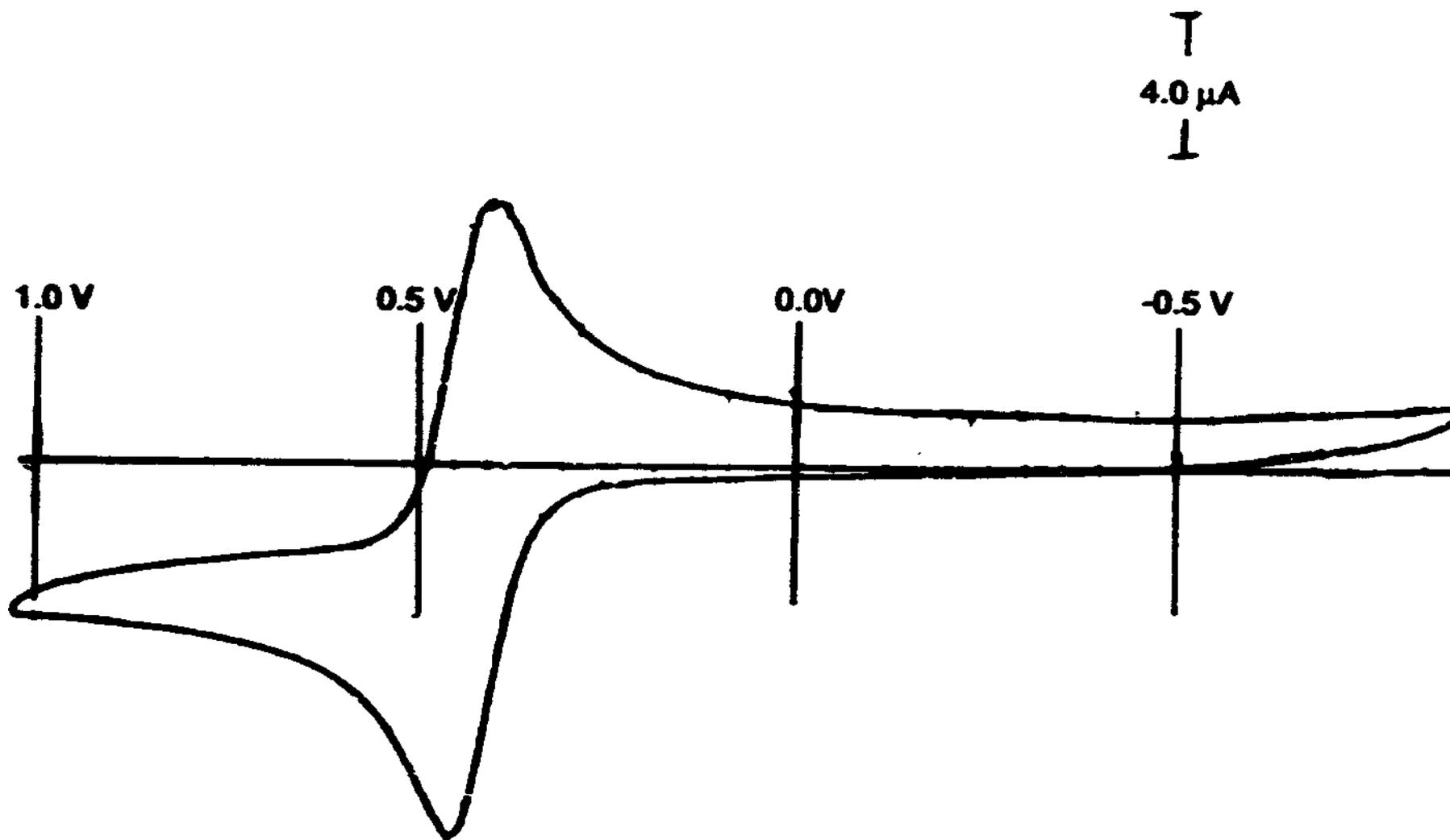
Figure 7. The cyclic voltammogram of 1.9 mM ferrocene in CH_3CN.

Since the voltammograph was going to be used to study the electrochemistry of rhenium clusters, two previously characterized clusters were run under the same conditions as had been originally done. The two clusters run were $[Re_7C(CO)_{21}][PPN]_3$ and $[Re_8C(CO)_{24}][PPN]_2$ as 0.3 mM solutions in dichloromethane with 0.1 M TBAP as supporting electrolyte. Two oxidation peaks were found for $[Re_7C(CO)_{21}][PPN]_3$ at $E_{1/2}$ = 0.351 V and 0.025 V with ΔE_p = 83.5 mV and 69.5 mV respectively. One large oxidation peak was found for $[Re_8C(CO)_{24}][PPN]_2$ at $E_{1/2}$ = 0.778 V with ΔE_p = 79 mV. Other waves for this cluster were hard to see over the backround.

The $E_{1/2}$ for the ferrocene/ferrocenium couple in acetonitrile compares well with the value of 0.46 V from the literature.[32] Differences between the two may be because the literature value was found with half the concentration of ferrocene and twice the concentration of electrolyte, tetrabutylammonium tetrafluoroborate in this case. The authors used a platinum electrode and a silver/silver chloride reference. They, however, do not specify the chloride concentration in the reference electrode. An electrode saturated in chloride ion gives a different potential than one that is 3.0 M in chloride ion.[33] Although oxidation potential for ferrocene in acetonitrile seems to be correct, the three $E_{1/2}$ values obtained for the two clusters were each about 0.10 volts low of the originally found results.[34] Due to the lack of detailed experimental information given about these cyclic voltammograms, it is hard to determine where

errors might lie.

It was noticed during the scans with the two clusters and the ferrocene that the supporting electrolyte seemed to contain some impurities that were appearing in the scans. However, due to instability of perchlorate salts at high temperatures, the electrolyte could not safely dried at high temperatures after recrystallization. Therefore, the supporting electrolyte was changed to tetrabutylammonium hexafluorophosphate (TBAPF$_6$), which can be easily recrystallized and dried.

Since most of the clusters studied by CV were to be done in dichloromethane solutions with 0.10 TBAPF$_6$ as supporting electrolyte, it was of interest to find what the scan limits of this system were. This was done by running the solvent with the 0.10 TBAPF$_6$ and 0.2 mM ferrocene to find where the background became too large to decipher a peak. For positive voltages, the background began to grow at 1.10 V, but peaks could probably still be studied with potentials up to about 1.30 V (Figure 8). On the negative side, the background started to increase at -0.77 V (Figure 9). A compound with a reduction potential beyond -0.90 V could not be studied with this system especially at concentrations comparable to those used with the clusters.

(4) The Electrochemistry of [Re$_7$C(CO)$_{20}$(NO)][PPN]$_2$.

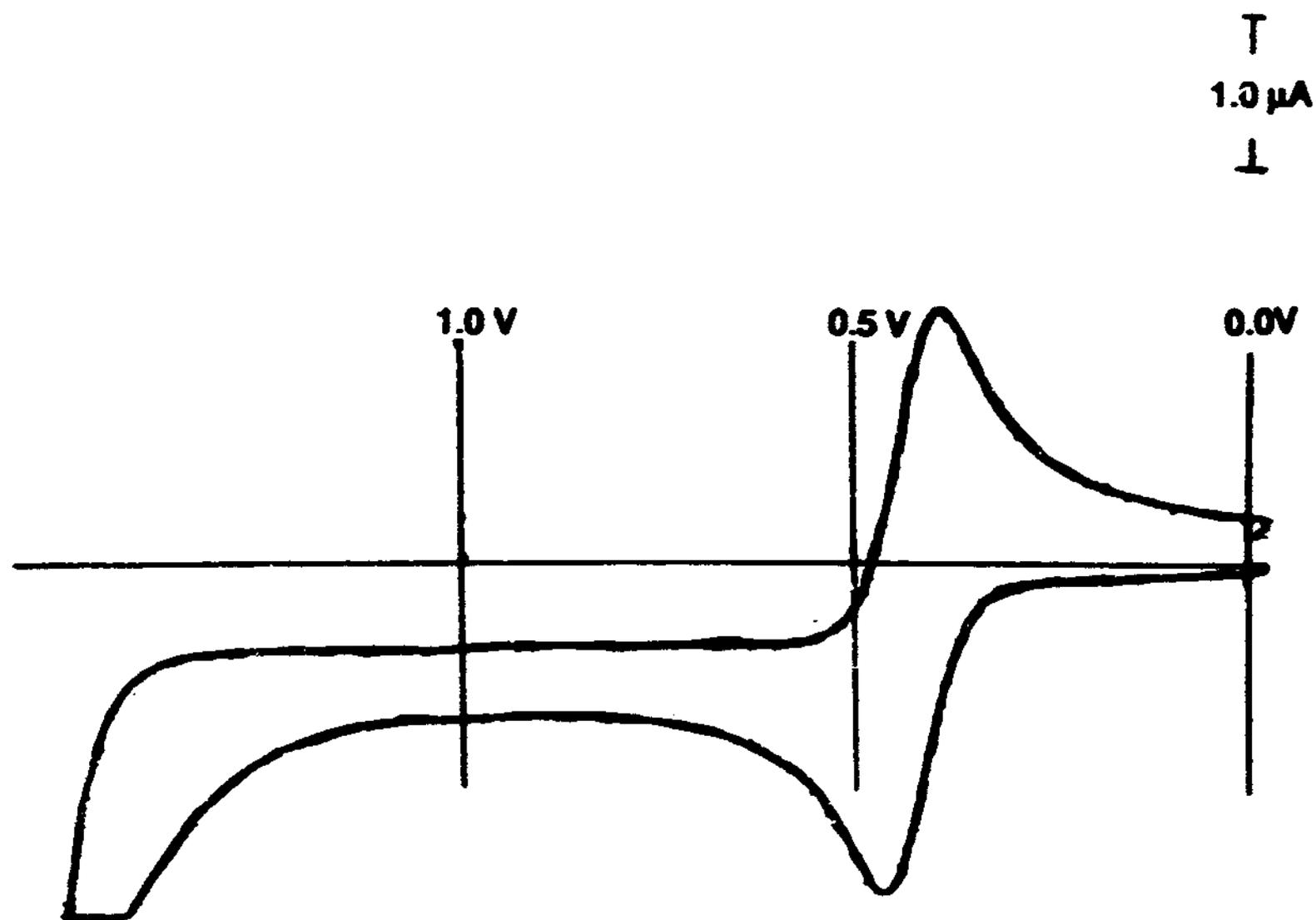The electrochemical properties of the nitrosyl substituted cluster, [Re$_7$C(CO)$_{20}$(NO)][PPN]$_2$, were studied on the voltammograph. A

Figure 8. The cyclic voltammogram of 0.2 mM ferrocene in CH_2Cl_2 showing the positive edge for scanning in this system.
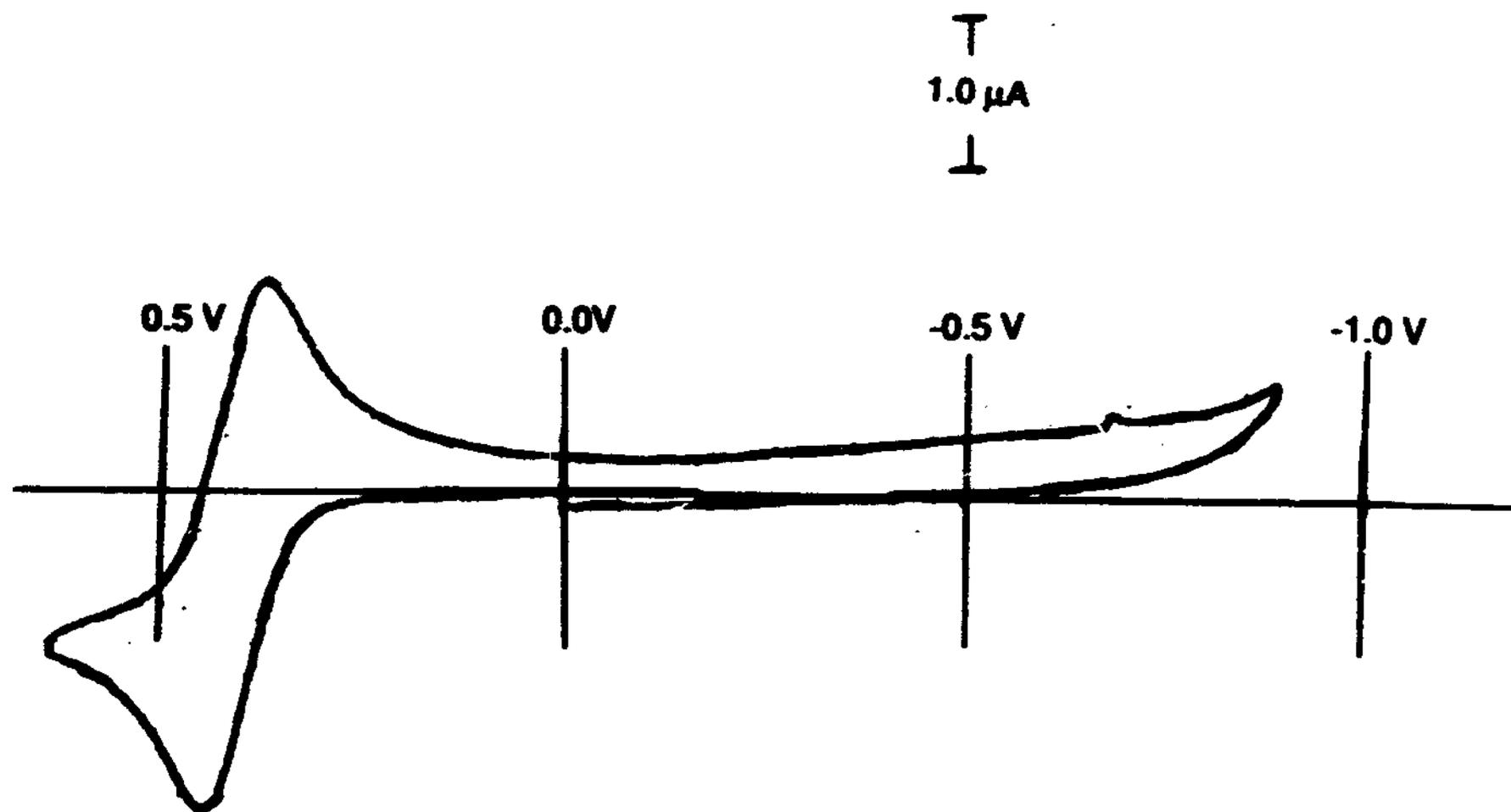
1.0 μA

0.5 V 0.0V -0.5 V -1.0 V

Figure 9. The cyclic voltammogram of 0.2 mM ferrocene in CH_2Cl_2 showing the beginning of the negative edge for scanning in this system.

0.20 mM dicloromethane solution of the cluster containing 0.10 M TBAPF$_6$ was studied. This compound was found to undergo two oxidations (Figure 10). The first wave occurred at E$_{1/2}$ = 0.244 V with peak separation of ΔE$_p$ = 79 mV. The second wave occurred at E$_{1/2}$ = 0.462 V with ΔE$_p$ = 74 mV. The intensity of the peaks in the second oxidation wave was found to be about 1.5 times larger than the peaks for the first oxidation.

The ΔE$_p$ values for the two oxidation waves of [Re$_7$C(CO)$_{20}$(NO)] [PPN]$_2$ show that these processes are not totally reversible. ΔE$_p$ values for reversible couples are 59/n mV where n is the number of electrons involved in the process.[31] Any ΔE$_p$ value greater than 59 mV suggests only partial reversiblity for any process and a value less than 59 mV usually suggests that the couple is not a one electron process. However, the ferrocene/ferrocenium couple in acetonitrile was found to have a ΔE$_p$ = 45 mV (Figure 7), but this couple is known to be a one electron oxidation.[34] This small ΔE$_p$ value can probably be attributed to instrumental error. Commonly, ΔE$_p$ values for one electron processes which are less than 59 mV are due to an overcompensation for the IR drop in the solution.[30] However, this system does not contain a device that compensates for IR drops that occur in nonaqueous solutions. In addition to ΔE$_p$ values as useful measures of the reversibility of a redox couple, the ratio of the cathodic peak height to
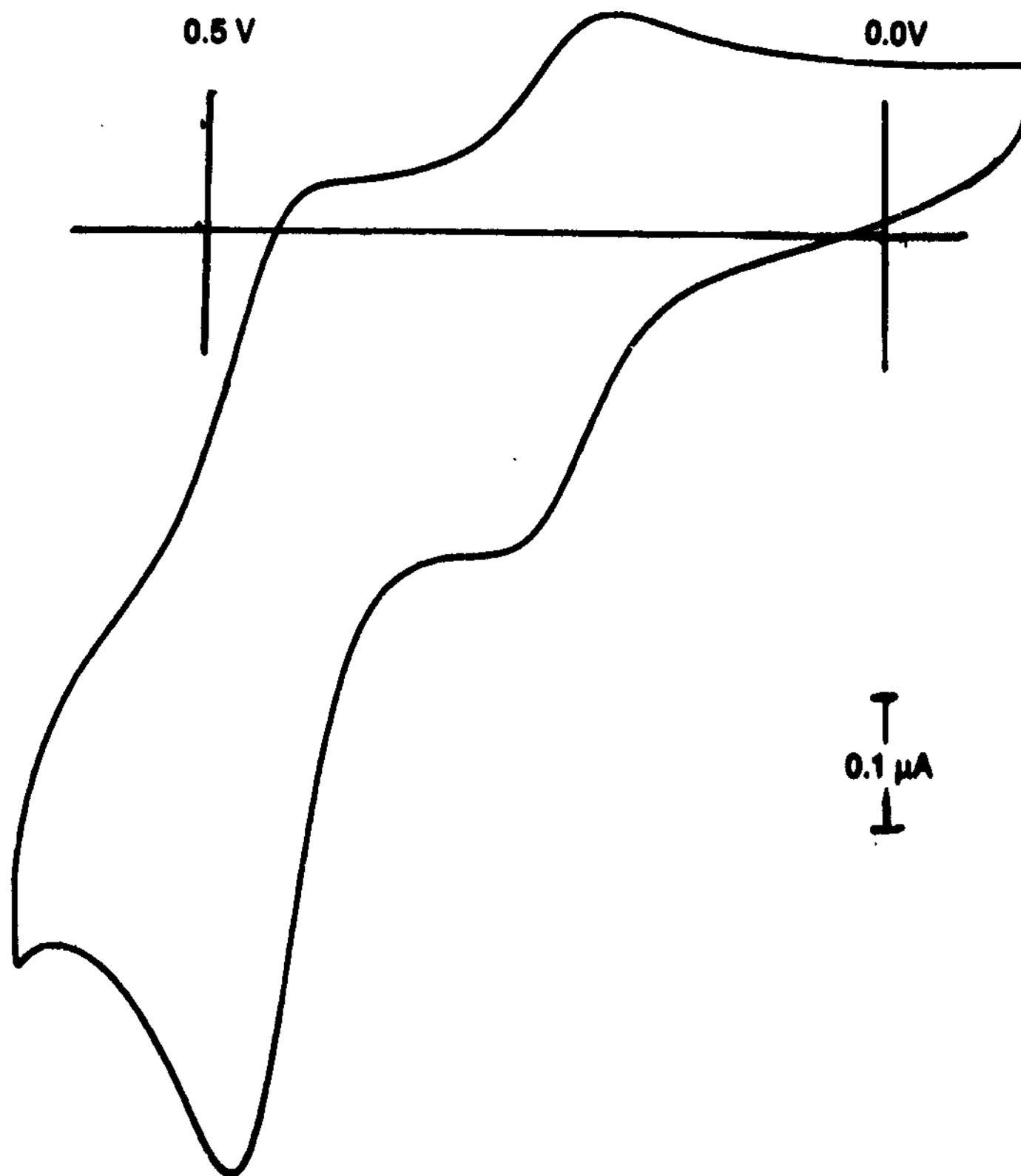
0.5 V   0.0V

0.1 μA

Figure 10. The cyclic voltammogram of 0.2 mM [Re$_7$C(CO)$_{20}$(NO)][PPN]$_2$

in CH$_2$Cl$_2$ showing both oxidation waves.

anodic peak height is also a good measure of reversiblity. If this ratio is exactly one, then the system is completely reversible. However, i_c/i_p values for both peaks were found to be 0.6, stressing the point that these oxidation processes are not completely reversible.

The relative sizes of the peaks can give also an insight into whether or not the peaks are due to one electron or two electron processes. In this study with $[Re_7C(CO)_{20}(NO)][PPN]_2$, the size of the second oxidation wave in comparison to the first oxidation wave seems to imply that process involved in the second oxidation is not a one electron process. However, since the ratio of peak heights is approximately 1.5 to 1 and 1.5 electron processes are probably not possible, it is hard to determine whether the second wave wave is due to a two electron or one electron oxidation. The ΔE_p value seems to put this peak in the partially irreversible one electron category, but it could also be a partially irreversible two electron process.

If the potential is cycled over the second oxidation wave many times (Figure 11), the height of the anodic peak decreases while the height of the cathodic peak increases. If there was an increase in the concentration of the oxidized species about the electrode, this would mean that there would be more of that oxidized species to be reduced at the electrode, thus giving a larger cathodic peak. Consequently, there would also be less of the reduced species in the vicinity of the electrode to be oxidized and the anodic peak would gradually become smaller. Thus, there must be an increase in the concentration of the
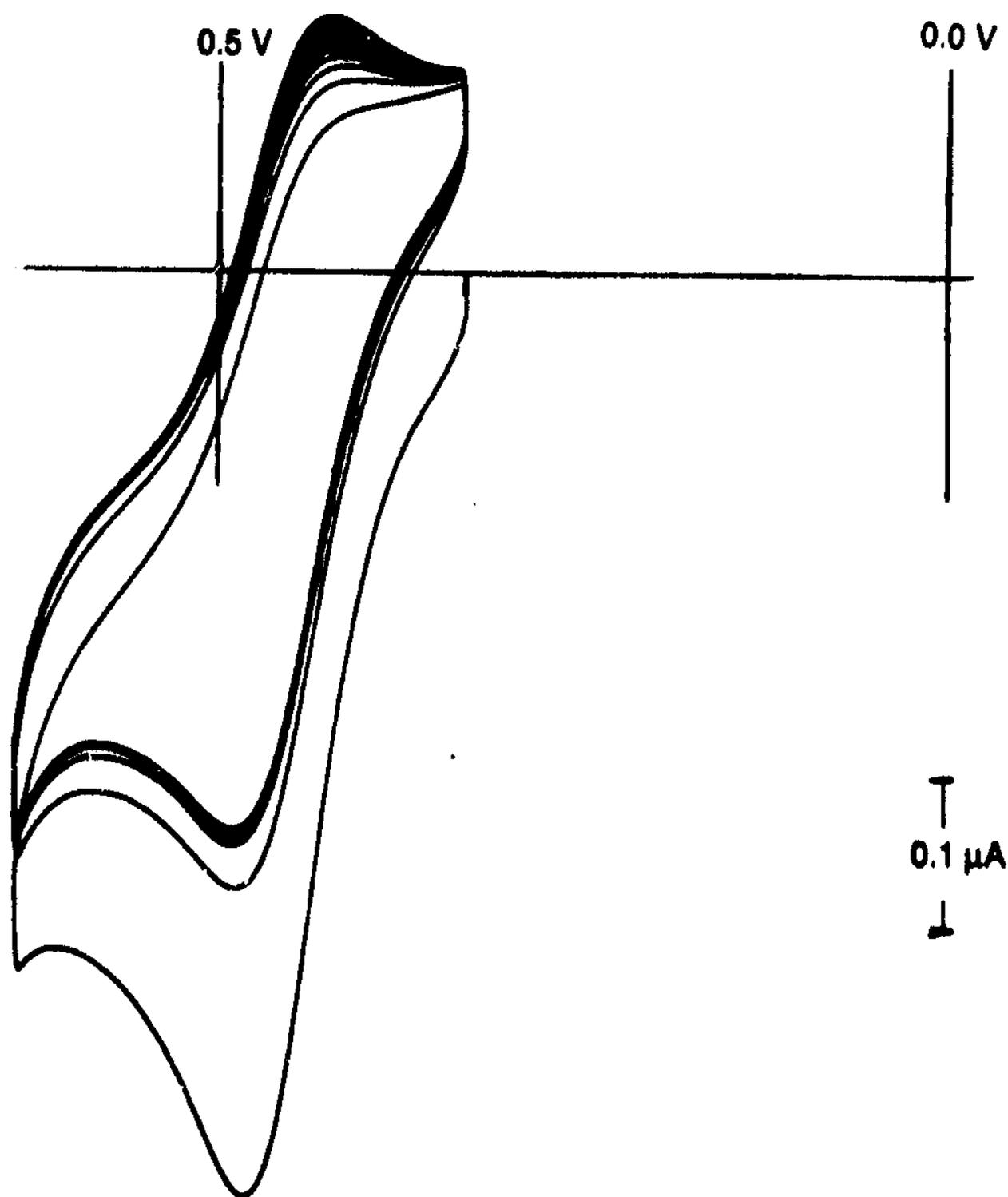
Figure 11. The cycling of the potential over the second oxidation wave of $[Re_7C(CO)_{20}(NO)][PPN]_2$ showing the decrease of the anodic peak and the increase of the cathodic peak.

oxidized species created by the second oxidation of $Re_7C(CO)_{20}(NO)][PPN]_2$. Therefore, the oxidized species that is in solution after the second oxidation wave is more stable than the species created after the first oxidation.

(5) Ferrocene as an Internal Standard.

It has been proposed that ferrocene be used as an internal reference for cyclic voltammetry. This is done by adding ferrocene to the systems after they have been studied, and then running one more scan to find at what potential the ferrocene/ferrocenium couple occurs. This method, however, demands that the couple be electrochemically reversible (i.e having a ΔE_p = 59 mV). The reasons that the authors propose ferrocene as an internal reference are that its oxidation wave "is reproducible, provides a basis for judging electrochemical reversibility, and allows for a quantitative comparison of reduction potentials measured in various solvents".[30]

Addition of 3.6 milligrams of ferrocene to the same 10 mL dichloromethane solution of $[Re_7C(CO)_{20}(NO)][PPN]_2$ used to study its electrochemistry created a 0.2 mM ferrocene solution. The ferrocene couple in this solution was found to occur at $E_{1/2}$ = 0.391 V with a ΔE_p value of 138 mV. With reference to the ferrocene couple, the two oxidation waves for $[Re_7C(CO)_{20}(NO)][PPN]_2$ have $E_{1/2}$ values of -0.147 V for the wave at lower potential and 0.091 V for the wave at higher potential. In this case, however, the ferrocene might not be able to be used as an internal standard because the oxidation of ferrocene was

found not to be completely reversible in this solution.

In a 1.0 mM solution of ferrocene in dichloromethane with 0.1 M TBAP as supporting electro.yte, the ferrocene/ferrocenium couple was previously found to occur at 0.491 V. If the supporting electrolyte is changed to $TBAPF_6$ and the concentration of ferrocene is changed to 0.2 mM (to match the concentration of the studied clusters), the oxidation wave occurs at $E_{1/2}$ - 0.462 V with ΔE_p - 74 mV (Figures 8 and 9). Since the supporting electrolyte should not effect the potential of the oxidation, the concentration obviously does. However, in the paper that proposed ferrocene as an internal standard, it is not specified what concentration of ferrocene should be used as a standard for comparison.[30] The authors are probably consistent at what concentration of ferrocene they use, and subsequent users of this method probably should be also. As a side note, it is also obvious that the presence of $[Re_7C(CO)_{20}(NO)][PPN]_2$ in solution effects the potential at which the ferrocene/ferrocenium couple occurs. Monitoring these kinds of effects, however, might be the reason that ferrocene should be used as an internal reference.

IV. BIBLIOGRAPHY

(1)   Green, M.H.L.; Wilkinson, G. J. Chem. Soc. 1958, 4314 - 4317.

(2)   Pruett, R.L.; Morehouse, E.L. Chem. Ind. (London) 1958, 980.

(3)   Caulton, K. Coord. Chem. Rev. 1981, 38, 1 - 43.

(4)   Gladysz, J.A.; Knobler, C.B.; Patton, A.T.; Strouse, C.E. J. Am. Chem. Soc. 1983, 105, 5804 - 5811.

(5)   Fischer, E.O.; Stramotz, H. Z. Naturforsch. 1968, 23b, 278 - 279.

(6)   Barrientos-Penna, C.F.; Einstein, F.W.B.; Jones, T.; Sutton, D. Inorg. Chem. 1982, 21, 2578 - 2585.

(7)   Nesmeyanov, A.N.; Kolobova, N.E.; Makarov, Yu. V.; Lokshin, B.V.; Rusach, E.B. Bull. Acad Sci. USSR. Div. Chem. Sci. 1976, 3, 612 - 615.

(8)   Tam, W.; Wong, W.-K.; Gladysz, J.A. J. Am. Chem. Soc. 1979, 101, 1589 - 1591.

(9)   Kolobova, N.E.; Valueva, Z.P.; Solodova, M. Ya. Izv. Akad. Nauk. SSSR Ser. Khim. 1980, 2387 - 2391.

(10)   Henly, T.J.; Shapley, J.R. Organometallics 1988, 7, 441 - 448.

(11)   Hayward, C.M.T.; Shapley, J.R. Organometallics 1988, 7, 448 - 452.

(12)   Johnson, B.F.G.; Lewis, J.; Nelson, W.J.H.; Puga, J.; Braga, D.; Henrick, K.; McPartlin, M. J. Organomet. Chem. 1984, 266, 173 - 189.

(13)   Johnson, B.F.G.; Lewis, J.; Nelson, W.J.H.; Puga, J.; Henrick, K.; McPartlin, M. J. Chem. Soc. Dalton Trans. 1983, 1203 - 1206.

(14) Johnson, B.F.G.; Lewis, J.; Nelson, W.J.H.; Puga, J.; McPartlin, M.; Sironi, A. J. Organomet. Chem. 1983, 253, C5 - C7.

(15) Johnson, B.F.G.; Lewis, J.; Nelson, W.J.H.; Puga, J.; Braga, D.; Henrick, K.; McPartlin, M. J. Chem. Soc., Chem. Commun. 1982, 1083 - 1084.

(16) Anson, C.E.; Ditzel, E.S.; Fajardo, M.; Holden, H.D.; Johnson, B.F.G.; Puga, J.; Raithby, P.R. J. Chem. Soc., Dalton Trans. 1984, 2723 - 2727.

(17) Puga, J.; Sanchez-Delgado, R.; Braga, D. Inorg. Chem. 1985, 24, 3971 - 3974.

(18) Bhaduri, S.; Johnson, B.F.G.; Lewis, J.; Watson, D.J.; Zuccaro, C. J. Chem. Soc., Dalton Trans. 1979, 557 - 561.

(19) Johnson, B.F.G.; Lewis, J.; Nelson, W.J.H.; Puga, J.; Braga, D.; Raithby, P.R.; McPartlin, M.; Clegg, W. J. Organomet. Chem. 1983, 243, C13 - C16.

(20) Johnson, B.F.G.; Lewis, J.; Nelson, W.J.H.; Puga, J.; Raithby, P.R.; Schroder, M.; Whitmire, K.H. J. Chem. Soc., Chem. Commun. 1982, 610 - 612.

(21) Fjare, D.E.; Gladfelter, W.L. J. Am. Chem. Soc. 1981, 103, 1572 - 1574.

(22) Gourdon, A.; Jeanin, Y. J. Organomet. Chem. 1985, 282, C39 - C42.

(23) Eisenberg, R.; Meyer, C.D. Acc. Chem. Res. 1975, 8, 26 - 34.

(24) Gladfelter, W.L.; Geoffroy, G.L. Adv. Organomet. Chem. 1980, 18, 207 - 273.

(25) Ozin, G.A. Catal. Rev.-Sci. Eng. 1977, 16, 191 - 289.

(26) Hayward, C.M.T.; Ph.D. Thesis, University of Illinois, Urbana, 1984.

(27) Hayward, C.M.T.; Folkers, J.P.; Shapley, J.R. submitted for publication.

(28) Cozak, D.; Butler, I.S. Spectrosc. Lett. 1976, 9, 673 - 679.

(29) Ciani, G.; D Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. J. Chem. Soc., Chem. Commun. 1982, 705.

(30) Gagne, R.R.; Koval, C.A.; Lisenky, G.C. Inorg. Chem. 1980, 19, 2854 - 2855.

(31) Kissinger, P.T.; Heineman, W.R. J. Chem. Ed. 1983, 60, 702 - 706.

(32) Grobe, J.; Zimmerman, H. Z. Naturforsch. 1981, 36b, 301 - 306.

(33) Skoog, D.A. "Principles of Instrumental Analysis"; 3rd ed., Saunders College Publishing: Philadelphia, Pa., 1985, p. 601.

(34) Faulkner, L.R.; He, P. Anal. Chem. 1986, 58, 517 - 523.