

Figure 3. Nuclear magnetic resonance spectra of $[\text{Ru}(\text{NOX})_3(\text{BC}_6\text{H}_5)_2]$: (a) ^{13}C NMR (proton decoupled); (b) ^1H NMR.

complex.¹¹ The electronic spectrum of the ruthenium clathrochelate reveals a complex charge-transfer band centered at $25\,100\text{ cm}^{-1}$ ($\epsilon = 18\,000\text{ L}/(\text{mol cm})$; CH_2Cl_2) (Figure 1). The analogous iron complex generates a qualitatively similar spectrum with a band centered at $22\,300\text{ cm}^{-1}$ ($\epsilon = 17\,000\text{ L}/(\text{mol cm})$).

Cyclic voltammetric studies of $[\text{Ru}(\text{NOX})_3(\text{BC}_6\text{H}_5)_2]$ reveal a quasi-reversible couple with $E_{1/2} = +1.28\text{ V}$ ($\Delta E_p = 70\text{ mV}$; $I_{p,c}/I_{p,a} = 0.89$; scan rate = 100 mV/s)²¹ (Figure 2). In comparison, cyclic voltammetric studies of the iron clathrochelate complex in methylene chloride revealed a quasi-reversible couple with $E_{1/2} = +1.12\text{ V}$ ($\Delta E_p = 80\text{ mV}$; $I_{p,c}/I_{p,a} = 0.92$; scan rate = 100 mV/s). Oxidative electrolysis of a methylene chloride solution of $[\text{Ru}(\text{NOX})_3(\text{BC}_6\text{H}_5)_2]$, where a platinum-mesh electrode was held at a potential value of $+1.43\text{ V}$, resulted in a transfer of $>>1$ electron/molecule. Cyclic voltammetry of the electrolyzed solution illustrated that the original clathrochelate complex had undergone extensive decomposition, most likely occurring via an ECE mechanism involving rupture of the ligand superstructure. This is comparable to the behavior of the analogous iron complexes reported previously.¹³

The ^1H NMR spectrum of $[\text{Ru}(\text{NOX})_3(\text{BC}_6\text{H}_5)_2]$ shows two broad methylene resonances (1.71 and 2.88 ppm vs TMS), both of which integrate to account for 12 hydrogen atoms (Figure 3). These resonances were assigned to the hydrogen atoms bonded to the γ - and β -carbons of the oxime. Two multiplets at chemical shift values of 7.36 and 7.89 ppm were assigned to the phenyl hydrogen atoms. These resonances integrate to values of four and six hydrogen atoms, respectively. The proton-decoupled ^{13}C NMR spectrum of the ruthenium clathrochelate revealed six peaks. The two peaks that appeared at chemical shift values of 21.54 and 25.41 ppm were assigned to the γ - and β -carbons of the oximes. Examination of the proton-coupled ^{13}C NMR spectrum allowed assignment of the peaks at 127.37, 127.90, and 131.77 ppm to phenyl carbon atoms bonded to hydrogen atoms. The remaining peak at 147.86 ppm is assigned to the azomethine carbon. The ^{13}C resonance for the carbon atom bonded directly to the boron atom was not observed. This is most likely due to quadrupole broadening caused by the adjacent boron atom.²²

Conclusions

In order to further explore the chemistry of transition-metal clathrochelate complexes based on dioxime/boron bicyclic macrocyclic ligands, the first example of an in situ template synthesis of a ruthenium(II) clathrochelate was successfully conducted. Since ruthenium complexes are generally much more substitutionally inert than analogous iron complexes,²³ it was anticipated that the electrochemical generation of a ruthenium(III) clathrochelate complex might be a possibility, if the mechanism of

the analogous iron(III) clathrochelate complex decomposition involves a simple ligand dissociation subsequent to complex oxidation. However, the exhaustive oxidative electrolysis of a ruthenium(II) clathrochelate complex solution resulted in the decomposition of the complex, in a manner very similar to that observed for analogous iron(II) clathrochelate complexes.¹³ These observations, coupled with the fact that an analogous cobalt(III) clathrochelate complex is stable,¹⁰ indicate that, for the iron and ruthenium complexes, the clathrochelate ligand probably undergoes decomposition subsequent to complex oxidation, possibly due to the substantially more positive oxidation potentials associated with ruthenium and iron clathrochelate complexes relative to the analogous cobalt clathrochelate complex. For the generation of stable ruthenium(III/II) redox couples, clathrochelate ligands that lower the redox potential of the ruthenium(III/II) couples to values closer to the values for cobalt(III/II) couples will be investigated.

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Registry No. 1, 102575-59-7; NOXH_2 , 492-99-9; phenylboric acid, 98-80-6.

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Reaction of Nitrosoarenes with Trinuclear Metal Carbonyl Clusters of Iron, Ruthenium, and Osmium

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Bridging ligands play an important role in cluster chemistry often by adding stability to the particular group of metals to which they are attached. Certain four-electron-donor ligands such as PR_3 , S ,⁴⁻⁸ and other group 16 elements⁹ have found many such applications. Organoimido ligands (RN) on metal carbonyl clusters have been less well studied, in part, because of the low yields that typically characterize their synthesis.¹⁰⁻²⁶ We report

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Table I. Infrared Spectral Data

product	IR (hexane) ν_{CO} , cm^{-1}
$\text{Ru}_3(p\text{-ClC}_6\text{H}_4\text{N})(\text{CO})_{10}$	2103 w, 2072 s, 2033 s, 2028 sh, 2015 m, 2011 m, 1744 m
$\text{Ru}_3(p\text{-ClC}_6\text{H}_4\text{N})_2(\text{CO})_9$	2097 w, 2076 s, 2052 s, 2025 m, 2019 m, 2015 m, 1992 m, 1982 w
$\text{Ru}_3(\text{C}_6\text{H}_5\text{N})(\text{CO})_{10}$	2102 w, 2070 s, 2031 s, 2028 sh, 2012 m, 2010 m, 1743 m
$\text{Ru}_3(\text{C}_6\text{H}_5\text{N})_2(\text{CO})_9$	2095 w, 2074 s, 2050 s, 2023 m, 2016 m, 2012 m, 1989 m, 1979 w
$\text{Ru}_3(p\text{-CH}_3\text{C}_6\text{H}_4\text{N})(\text{CO})_{10}$	2102 w, 2070 s, 2031 s, 2027 sh, 2012 m, 2009 m, 1743 m
$\text{Ru}_3(p\text{-CH}_3\text{C}_6\text{H}_4\text{N})_2(\text{CO})_9$	2094 w, 2072 s, 2049 s, 2020 m, 2015 m, 2010 m, 1988 m, 1977 w
$\text{Ru}_3(p\text{-CH}_3\text{OC}_6\text{H}_4\text{N})(\text{CO})_{10}$	2101 w, 2069 s, 2030 s, 2027 sh, 2011 m, 2008 m, 1743 m
$\text{Ru}_3(p\text{-CH}_3\text{OC}_6\text{H}_4\text{N})_2(\text{CO})_9$	2092 w, 2071 s, 2048 s, 2019 m, 2014 m, 2009 m, 1987 m, 1976 w

in this paper the reaction of nitrosoarenes with group 8 metal carbonyls to give the new osmium trimers $\text{Os}_3(\text{ArN})(\text{CO})_{10}$ and $\text{Os}_3(\text{ArN})_2(\text{CO})_9$ and much improved yields of the known ruthenium trimer $\text{Ru}_3(\text{ArN})(\text{CO})_{10}$. Also, we report an improved synthesis of the known cluster $\text{Ru}_3(\text{ArN})_2(\text{CO})_9$ using nitroarenes.

Experimental Section

$\text{Ru}_3(\text{CO})_{10}$,²⁷ $\text{Os}_3(\text{CO})_{12}$,²⁸ and $p\text{-XC}_6\text{H}_4\text{NO}$ ($\text{X} = \text{Cl}$,²⁹ CH_3 ,³⁰ CH_3O ²⁹) were prepared according to published procedures. $p\text{-XC}_6\text{H}_4\text{NO}_2$ ($\text{X} = \text{Cl}$, H , CH_3 , CH_3O) and $\text{C}_6\text{H}_5\text{NO}$ were purchased from Aldrich and, unless noted otherwise, were used without further purification. $\text{C}_6\text{H}_5\text{NO}$ was sublimed at $\sim 75^\circ\text{C}$ prior to use. Tetrahydrofuran (THF) was dried by distillation from sodium-benzophenone ketyl under N_2 . $\text{C}_6\text{H}_5\text{NO}_2$ was distilled from P_2O_{10} . Hexane was dried by distillation from sodium. CO was purchased from Matheson and used without further purification. Infrared spectra were recorded on a Mattson Cygnus 25 FTIR spectrometer equipped with a HgCdTe detector. ^1H NMR data were obtained on a Nicolet NFT 300-MHz spectrometer. The chemical shifts of the major peaks of the complex multiplets are reported without assignment to specific hydrogens on the phenyl rings. All mass spectral data are calculated by using ^{102}Ru and ^{192}Os .

Reaction of $p\text{-XC}_6\text{H}_4\text{NO}$ with $\text{Ru}_3(\text{CO})_{12}$. Since all of the reactions of $\text{Ru}_3(\text{CO})_{12}$ with para-substituted nitrosobenzenes were performed under similar reaction conditions, the experimental details of only one of these reactions will be discussed. $\text{Ru}_3(\text{CO})_{12}$ (61.9 mg, 9.68×10^{-2} mmol) and $p\text{-ClC}_6\text{H}_4\text{NO}$ (61.8 mg, 4.40×10^{-1} mmol) were placed under a N_2 atmosphere in a Schlenk tube equipped with a stir bar. THF (15 mL) was added, and the vessel was heated to 57°C . As the solution was warmed, it turned from bright orange to clear dark brown. The reaction was monitored by infrared spectroscopy and was stopped when the intensity of the $\mu_3\text{-CO}$ stretch of the product ($\sim 1730\text{ cm}^{-1}$) maximized. Carbon dioxide was evolved during the reaction and was detected by IR spectroscopy. Reaction times for the various nitrosobenzenes varied between 70 and 80 min. The solvent was removed, and hexane was added to the resulting brown oil. The solution was filtered in air, and the brown precipitate was washed with hexane until the washes were colorless. The brown precipitate was an unknown metal carbonyl. IR (THF): ν_{CO} 2112 w, 2040 s (br), 1986 s (br). ^1H NMR (CD_2Cl_2): multiplet from 7.37 to 7.01 ppm. The golden brown filtrate was chromatographed on a silica gel column using hexane as an eluent. In each reaction four bands eluted from the column; the order and yields of the products were dependent on the para substituent. Equation 1 shows the

yields, and Table I contains the spectroscopic data for the $\text{Ru}_3(p\text{-XC}_6\text{H}_4\text{N})(\text{CO})_{10}$ and $\text{Ru}_3(p\text{-XC}_6\text{H}_4\text{N})_2(\text{CO})_9$ products. The order of elution and analytical data for the new compounds are listed below by para substituent.

$\text{X} = \text{Cl}$. Band 1: orange $\text{Ru}_3(\text{CO})_{12}$ (15.0 mg, 2.35×10^{-2} mmol). Band 2: green $p\text{-ClC}_6\text{H}_4\text{NO}$. Band 3: lemon yellow $\text{Ru}_3(p\text{-ClC}_6\text{H}_4\text{N})(\text{CO})_{10}$. Mass spectrum: m/z 711 (parent ion). ^1H NMR (acetone- d_6): δ 7.21 (s). Anal. Calcd for $\text{C}_{16}\text{H}_4\text{NO}_{10}\text{Ru}_3\text{Cl}$: C, 27.11; H, 0.57; N, 1.98. Found: C, 27.42; H, 0.77; N, 1.92. Band 4: brown unknown (<1.0 mg). IR (hexane): ν_{CO} 2092 m, 2088 m, 2069 m, 2049 s, 2036 s, 2015 m, 2005 s cm^{-1} .

$\text{X} = \text{H}$. Band 1: orange $\text{Ru}_3(\text{CO})_{12}$. Band 2: blue $\text{C}_6\text{H}_5\text{NO}$. Band 3: lemon yellow $\text{Ru}_3(\text{C}_6\text{H}_5\text{N})(\text{CO})_{10}$.^{17,18} Band 4: green unknown oil. IR (hexane): ν_{CO} 2089 s, 2053 s, 2045 vs, 2027 m, 2003 vs, 1905 m, 1885 w cm^{-1} . ^1H NMR (CD_2Cl_2): δ 8.32, 8.29, 8.16, 8.13, 7.58, 7.56, 7.54, 7.51, 7.48, 7.43, 7.41.

$\text{X} = \text{CH}_3$. Band 1: orange $\text{Ru}_3(\text{CO})_{12}$. Band 2: green $p\text{-CH}_3\text{C}_6\text{H}_4\text{NO}$. Band 3: orange $\text{Ru}_3(p\text{-CH}_3\text{C}_6\text{H}_4\text{N})_2(\text{CO})_9$. Mass spectrum: m/z 768 (parent ion). ^1H NMR (CD_2Cl_2): δ 6.80, 6.78, 6.64, 6.61, 2.17 (3 H). A satisfactory elemental analysis for $\text{Ru}_3(p\text{-CH}_3\text{C}_6\text{H}_4\text{N})_2(\text{CO})_9$ has not been obtained. Band 4: lemon yellow $\text{Ru}_3(p\text{-CH}_3\text{C}_6\text{H}_4\text{N})(\text{CO})_{10}$. Mass spectrum: m/z 692 (parent ion). ^1H NMR (CD_2Cl_2): δ 6.98 (s, 4 H), 2.22 (s, 3 H). Anal. Calcd for $\text{C}_{17}\text{H}_7\text{NO}_{10}\text{Ru}_3$: C, 29.66; H, 1.05; N, 2.03. Found: C, 29.67; H, 1.01; N, 1.88.

$\text{X} = \text{CH}_3\text{O}$. Band 1: orange $\text{Ru}_3(\text{CO})_{12}$. Band 2: green $p\text{-CH}_3\text{OC}_6\text{H}_4\text{NO}$. Band 3: lemon yellow $\text{Ru}_3(p\text{-CH}_3\text{OC}_6\text{H}_4\text{N})(\text{CO})_{10}$. Mass spectrum: m/z 707 (parent ion). ^1H NMR (CD_2Cl_2): δ 7.05, 7.02, 6.67, 6.64, 3.76 (3 H). Anal. Calcd for $\text{C}_{17}\text{H}_7\text{NO}_{11}\text{Ru}_3$: C, 28.98; H, 1.00; N, 1.99. Found: C, 29.01; H, 1.08; N, 1.95. Band 4: orange $\text{Ru}_3(p\text{-CH}_3\text{OC}_6\text{H}_4\text{N})_2(\text{CO})_9$. Mass spectrum: m/z 800 (parent ion). ^1H NMR (CD_2Cl_2): δ 6.80, 6.77, 6.61, 6.58, 3.72 (3 H). Anal. Calcd for $\text{C}_{22}\text{H}_{14}\text{N}_2\text{O}_{11}\text{Ru}_3$: C, 34.63; H, 1.77; N, 3.51. Found: C, 35.45; H, 2.02; N, 3.71.

Reaction of $\text{C}_6\text{H}_5\text{NO}$ with $\text{Os}_3(\text{CO})_{12}$. $\text{Os}_3(\text{CO})_{12}$ (23.0 mg, 2.54×10^{-2} mmol) and $\text{C}_6\text{H}_5\text{NO}$ (2.8 mg, 2.57×10^{-2} mmol) were degassed under a N_2 atmosphere in a Schlenk tube equipped with a condenser and a stir bar. Octane (15 mL) was added, and the solution was brought to reflux. During the reaction, the solution changed from pale yellow to golden brown, and after 7 h at reflux, infrared spectroscopy indicated no $\text{Os}_3(\text{CO})_{12}$ remained. The solution was cooled to room temperature and filtered to yield a brown insoluble precipitate and a golden brown filtrate. The solution was chromatographed on a silica gel column using a 1:4 CH_2Cl_2 /hexane mixture as an eluent. The first band was pale yellow, and infrared spectroscopy indicated it was $\text{Os}_3(\text{CO})_{12}$ (11.0 mg, 1.22×10^{-2} mmol). The second band was yellow-orange, and removal of the solvent yielded orange crystals of $\text{Os}_3(\text{C}_6\text{H}_5\text{N})_2(\text{CO})_9$ in 19% yield. IR (hexane): ν_{CO} 2095 w, 2074 s, 2051 s, 2011 s, 2001 m, 1980 m, 1972 w cm^{-1} . ^1H NMR (CD_2Cl_2): 7.14, 7.12, 7.09, 6.94, 6.92, 6.90, 6.79, 6.76. Anal. Calcd for $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_9\text{Os}_3$: C, 25.10; H, 1.00; N, 2.79. Found: C, 24.70; H, 1.07; N, 2.61. The third band was yellow and removal of the solvent yielded yellow crystals of $\text{Os}_3(\text{C}_6\text{H}_5\text{N})(\text{CO})_{10}$ in 5% yield. IR (hexane): ν_{CO} 2105 w, 2074 s, 2028 s, 2020 sh, 2002 m, 1995 m, 1695 m cm^{-1} . Mass spectrum showed a parent ion at m/z 947 (^{192}Os).

Preparation of $\text{Os}_3(\text{C}_6\text{H}_5\text{N})_2(\text{CO})_9$. $\text{Os}_3(\text{CO})_{12}$ (50.0 mg, 5.51×10^{-2} mmol) and PhNO (30.0 mg, 2.86×10^{-1} mmol) were transferred to a Griffen-Worden reaction tube equipped with a stir bar, and octane (15 mL) was added. The tube was evacuated and flushed with 15 psig of CO five times before the reaction tube was pressurized to 50 psig of CO. The tube was heated to 126°C with an oil bath for 24 h, after which the clear golden yellow solution was allowed to cool to room temperature. As it cooled, yellow crystals precipitated from the solution. The reaction tube was depressurized, and the solution was filtered. The yellow crystals were identified by infrared spectroscopy to be unreacted $\text{Os}_3(\text{CO})_{12}$. The golden yellow filtrate was chromatographed on a silica gel column using hexane as an eluent. Two bands eluted from the column; the first band was pale yellow and contained additional unreacted $\text{Os}_3(\text{CO})_{12}$. After

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removal of the solvent using a rotovaporator, the two fractions of $\text{Os}_3(\text{CO})_{12}$ were combined, resulting in a 24% recovery of starting material. The second band was yellow-orange, and removal of the solvent yielded orange crystals of $\text{Os}_3(\text{C}_6\text{H}_5\text{N})_2(\text{CO})_9$ in 34% yield.

Reaction of $\text{C}_6\text{H}_5\text{NO}$ with $\text{Fe}_3(\text{CO})_{12}$. $\text{Fe}_3(\text{CO})_{12}$ (65.0 mg, 2.08×10^{-1} mmol) and $\text{C}_6\text{H}_5\text{NO}$ (54.0 mg, 5.14×10^{-1} mmol) were degassed under N_2 in a Schlenk tube equipped with a stir bar. THF (15 mL) was added, and the solution was submerged in an oil bath and heated to 48 °C for 105 min. During this time the solution changed from clear blue-green to cloudy brown-green. The THF was removed, and hexane was added to the resulting oil. The solution was filtered in air to yield a brown precipitate, which was insoluble in CH_2Cl_2 or acetone, and a green filtrate, which was chromatographed on a silica gel column using hexane as an eluent. The first band was green and contained unreacted $\text{Fe}_3(\text{CO})_{12}$. The second band was purple and contained the known $\text{Fe}_3(\text{C}_6\text{H}_5\text{N})_2(\text{CO})_9$ cluster in 2% yield. The third band was gold and contained trace amounts of an unknown carbonyl cluster. IR (hexane): ν_{CO} 2091 w, 2063 s, 2031 s, 2027 sh, 2013 m, 2001 s, 1983 m, 1969 w, cm^{-1} .

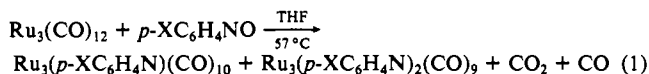
Preparation of $\text{Ru}_3(\text{XC}_6\text{H}_4\text{N})(\text{X}'\text{C}_6\text{H}_4\text{N})(\text{CO})_9$. All of the reactions were run under similar conditions, and only the experimental details for the formation of the unsymmetric cluster will be presented. See Table I for the infrared spectroscopic data of the symmetric clusters ($\text{X} = \text{X}' = \text{H}, \text{Cl}, \text{CH}_3$ or CH_3O) and eq 2 for the yields of these reactions. The ^1H NMR, mass spectral, and analytical data for some of the complexes have already been given.

$\text{X} = \text{H}, \text{X}' = \text{Cl}$. $\text{Ru}_3(\text{C}_6\text{H}_5\text{N})(\text{CO})_{10}$ (22.5 mg, 3.35×10^{-2} mmol) and $p\text{-ClC}_6\text{H}_4\text{NO}_2$ (41.0 mg, 2.95×10^{-1} mmol) were dissolved in heptane (10 mL), and the solution was transferred to a Griffen-Worden reaction vessel. The tube was evacuated and flushed with 15 psig of CO five times before it was pressurized to 50 psig of CO. The tube was heated to 125 °C with an oil bath, and the reaction was monitored by infrared spectroscopy. After 5.5 days, the $\mu_3\text{-CO}$ stretch of the starting material had disappeared, and the cloudy orange solution was cooled to room temperature. After the system was depressurized, the solution was filtered, and the orange filtrate was chromatographed on a silica gel column using hexane as an eluent. The first band to elute was orange $\text{Ru}_3(\text{CO})_{12}$ (1.0 mg, 1.56×10^{-3} mmol). The second band was bright orange $\text{Ru}_3(p\text{-ClC}_6\text{H}_4\text{N})(\text{C}_6\text{H}_5\text{N})(\text{CO})_9$, which was isolated in 59% yield as red crystals after removal of the solvent. IR (hexane): ν_{CO} 2096 w, 2075 s, 2051 s, 2024 s, 2018 m, 2013 m, 1991 m, 1981 w cm^{-1} . ^1H NMR (CD_2Cl_2): δ 7.13, 7.10, 7.08, 7.05, 6.95, 6.93, 6.90, 6.86, 6.84, 6.81, 6.78. The mass spectrum exhibits a parent ion at m/z 775 (^{102}Ru) followed by the loss of nine carbonyls. Anal. Calcd for $\text{C}_{21}\text{H}_9\text{ClN}_2\text{O}_9\text{Ru}_3$: C, 32.67; H, 1.18; N, 3.63; Cl, 4.59. Found: C, 32.85; H, 1.32; N, 3.54; Cl, 4.46. The third band was yellow, and removal of the solvent yielded a mixture of unreacted $p\text{-ClC}_6\text{H}_4\text{NO}_2$ and $\text{Ru}_3(\text{C}_6\text{H}_5\text{N})(\text{CO})_{10}$. Separation was achieved by subliming the nitrobenzene away from the cluster. A 10% recovery of pure $\text{Ru}_3(\text{C}_6\text{H}_5\text{N})(\text{CO})_{10}$ was obtained.

$\text{X} = \text{X}' = \text{Cl}$. Mass spectrum of $\text{Ru}_3(p\text{-ClC}_6\text{H}_4\text{N})_2(\text{CO})_9$: m/z (^{102}Ru) 809 (parent ion). ^1H NMR (CD_2Cl_2): δ 7.08, 7.05, 6.80, 6.78. Anal. Calcd for $\text{C}_{21}\text{H}_9\text{Cl}_2\text{N}_2\text{O}_9\text{Ru}_3$: C, 31.28; H, 1.00; N, 3.47. Found: C, 31.34; H, 0.91; N, 3.40.

Results and Discussion

Reaction of Nitrosoarenes with $\text{Ru}_3(\text{CO})_{12}$. The reaction between a nitrosoarene and $\text{Ru}_3(\text{CO})_{12}$ occurs under relatively mild conditions to give isolated yields of $\text{Ru}_3(\text{ArN})(\text{CO})_{10}$, which range from 40 to 61% depending on the para substituent (eq 1).

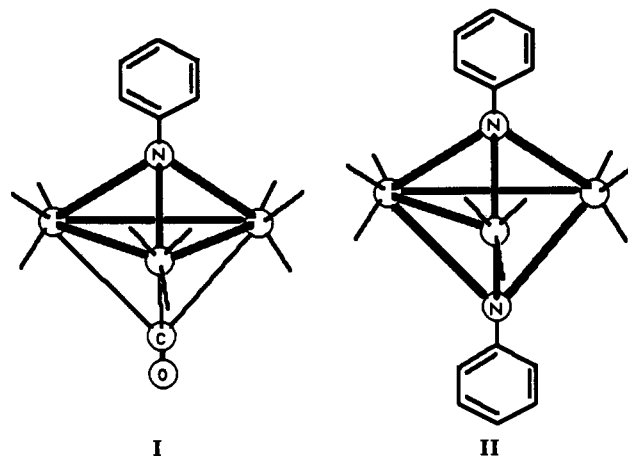


61% ($\text{X} = \text{Cl}$)	
46% ($\text{X} = \text{H}$)	
42% ($\text{X} = \text{CH}_3$)	3% ($\text{X} = \text{CH}_3$)
40% ($\text{X} = \text{OCH}_3$)	27% ($\text{X} = \text{OCH}_3$)

Previous reports on the synthesis of $\text{Ru}_3(\text{C}_6\text{H}_5\text{N})(\text{CO})_{10}$ using phenyl isocyanate¹⁷ or nitrobenzene^{17,18} required much more forcing reaction conditions and resulted in substantially lower yields (less than 20%). The success of the reaction using the nitrosoarene was surprisingly dependent on the solvent as well as the temperature. With $\text{C}_6\text{H}_5\text{NO}$, for example, when the temperature is kept below 60 °C with THF as the solvent, the major product is $\text{Ru}_3(\text{C}_6\text{H}_5\text{N})(\text{CO})_{10}$. If the solvent is changed to hexane or if the temperature is raised (refluxing THF), the major products are $\text{Ru}_3(\text{C}_6\text{H}_5\text{N})_2(\text{CO})_9$ and a hexane-insoluble, THF-soluble unknown metal carbonyl.

The yields of $\text{Ru}_3(\text{ArN})(\text{CO})_{10}$ and $\text{Ru}_3(\text{ArN})_2(\text{CO})_9$ formed in the reaction of $p\text{-XC}_6\text{H}_4\text{NO}$ with $\text{Ru}_3(\text{CO})_{12}$ are also dependent on the para substituent. When the para substituent is chloro or hydrogen, no bis(imido) cluster forms, but when the para substituent is methyl or methoxy, the isolated yield of the bis(imido) cluster becomes appreciable. Since the amount of reacted $\text{Ru}_3(\text{CO})_{12}$ after 70 min is the same when $\text{X} = \text{Cl}$ as when $\text{X} = \text{MeO}$, the first reaction ($\text{Ru}_3(\text{CO})_{12}$ and $p\text{-XC}_6\text{H}_4\text{NO}$) does not appear to be strongly influenced by the para substituent. However, once the $\mu_3\text{-NC}_6\text{H}_4\text{X}$ ligand is bound to the cluster, it may activate or deactivate it toward further reactions. The electronic influence of the para substituents can be seen by comparing the energies of the carbonyl stretches in the infrared spectrum. As the para substituent is changed from an electron-withdrawing chloro atom to an electron-donating methoxy group, all of the CO stretches for both the $\text{Ru}_3(\text{ArN})(\text{CO})_{10}$ and $\text{Ru}_3(\text{ArN})_2(\text{CO})_9$ clusters decrease in energy by 2–6 cm^{-1} .

Reaction of Nitrosobenzene with $\text{Os}_3(\text{CO})_{12}$. The successful application of nitrosoarenes to the synthesis of ruthenium arylimido clusters suggested other metal carbonyls might undergo similar reactions. The reaction of nitrosobenzene with $\text{Os}_3(\text{CO})_{12}$ leads to the formation of the new clusters $\text{Os}_3(\text{C}_6\text{H}_5\text{N})(\text{CO})_{10}$ (I) and



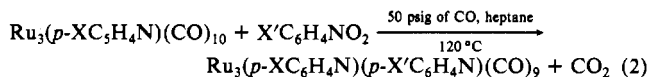
$\text{Os}_3(\text{C}_6\text{H}_5\text{N})_2(\text{CO})_9$ (II). This is particularly significant, since (unlike the iron and ruthenium systems) all attempts at synthesizing the osmium clusters using nitrobenzene failed.

The yields of the two osmium clusters are also dependent on the reaction conditions. $\text{Os}_3(\text{C}_6\text{H}_5\text{N})(\text{CO})_{10}$ can only be prepared if $\text{C}_6\text{H}_5\text{NO}$ is not present in a large excess and if the reaction is not allowed to go too long. Even under the most favorable conditions the yields of $\text{Os}_3(\text{C}_6\text{H}_5\text{N})(\text{CO})_{10}$ were very low. $\text{Os}_3(\text{C}_6\text{H}_5\text{N})_2(\text{CO})_9$ is best prepared by using an excess of $\text{C}_6\text{H}_5\text{NO}$ and by allowing the reaction to go for at least 24 h under 50 psig of CO. From our studies on the analogous ruthenium reactions, we have found that the $\text{M}_3(\text{ArN})(\text{CO})_{10}$ clusters are more thermally unstable at high temperatures than the bis(imido) clusters and will either decompose or, if it is present, react rapidly with excess ArNO to form $\text{M}_3(\text{ArN})_2(\text{CO})_9$ clusters. The decomposition rate of the $\text{M}_3(\text{ArN})(\text{CO})_{10}$ clusters may be inhibited by the presence of a few atmospheres of carbon monoxide. In the synthesis of $\text{Os}_3(\text{C}_6\text{H}_5\text{N})_2(\text{CO})_9$, the role of the carbon monoxide is to stabilize the intermediate $\text{Os}_3(\text{C}_6\text{H}_5\text{N})(\text{CO})_{10}$ so that it may react with excess $\text{C}_6\text{H}_5\text{NO}$ before it decomposes. If no carbon monoxide is present, not only does the yield of $\text{Os}_3(\text{C}_6\text{H}_5\text{N})_2(\text{CO})_9$ decrease but the amount of hexane-insoluble material increases substantially.

The structures of the two new osmium trimers are formulated on the basis of spectroscopic comparison to crystallographically characterized analogues from the literature. $\text{Os}_3(\text{C}_6\text{H}_5\text{N})(\text{CO})_{10}$ is proposed to have structure I, similar to those of $\text{Os}_3(\text{S})(\text{CO})_{10}$ ⁵ and $\text{Ru}_3(\text{C}_6\text{H}_5\text{N})(\text{CO})_{10}$.¹⁸ It is interesting to note the substantial lowering in energy of the $\mu_3\text{-CO}$ band from 1743 cm^{-1} in $\text{Ru}_3(\text{C}_6\text{H}_5\text{N})(\text{CO})_{10}$ to 1695 cm^{-1} in $\text{Os}_3(\text{C}_6\text{H}_5\text{N})(\text{CO})_{10}$. The proposed structure of $\text{Os}_3(\text{C}_6\text{H}_5\text{N})_2(\text{CO})_9$ (II) is based on the corresponding $\text{Os}_3(\text{S})_2(\text{CO})_9$ ⁶ and $\text{Ru}_3(\text{C}_6\text{H}_5\text{N})_2(\text{CO})_9$ ²¹ clusters.

Reaction of Nitrosobenzene with $\text{Fe}_3(\text{CO})_{12}$. The reaction of nitrosobenzene with $\text{Fe}_3(\text{CO})_{12}$ was performed to see whether this reagent was as successful in improving the yields of (arylimido)iron clusters as it was for the analogous ruthenium compounds. Preliminary studies of this reaction indicate that only very small amounts of $\text{Fe}_3(\text{C}_6\text{H}_5\text{N})_2(\text{CO})_9$ are formed along with a substantial amount of decomposition. The yields are no better than the known routes to $\text{Fe}_3(\text{ArN})_2(\text{CO})_9$.¹⁰⁻¹⁶

Reaction of $\text{Ru}_3(\text{XC}_6\text{H}_4\text{N})(\text{CO})_{10}$ with Nitroarenes. Sappa and Milone¹⁷ reported that the reaction of $\text{Ru}_3(\text{C}_6\text{H}_5\text{N})(\text{CO})_{10}$ with excess nitrobenzene in refluxing benzene gives $\text{Ru}_3(\text{C}_6\text{H}_5\text{N})_2(\text{CO})_9$ in 30% yield. We have found that substantially higher yields of the bis(imido) cluster may be obtained if the reaction is performed under 50 psig of CO (eq 2). Although the overall reaction of



- 56% (X = X' = Cl)
- 54% (X = X' = H)
- 45% (X = X' = OCH₃)
- 59% (X = H, X' = Cl)

$\text{Ru}_3(\text{C}_6\text{H}_5\text{N})(\text{CO})_{10}$ with nitrobenzene requires an additional mole of carbon monoxide to reduce the nitro group, we believe the carbon monoxide pressure serves an additional purpose. The starting $\text{Ru}_3(\text{C}_6\text{H}_5\text{N})(\text{CO})_{10}$ cluster decomposes in solution above 80 °C under a nitrogen atmosphere. If, however, a few atmospheres of carbon monoxide are present, this cluster is stabilized and even after several days at 120 °C in heptane does not appreciably decompose. Performing the reaction of a nitroarene with $\text{Ru}_3(\text{XC}_6\text{H}_4\text{N})(\text{CO})_{10}$ under these conditions allows the isolation of the bis(imido) clusters in yields ranging from 45 to 59%.

In an attempt to obtain an unsymmetric bis(imido) cluster (i.e. two different arylimido ligands) the reaction of $\text{Ru}_3(\text{C}_6\text{H}_5\text{N})(\text{C}$ -

$\text{O})_{10}$ with $p\text{-ClC}_6\text{H}_4\text{NO}_2$ was performed. The infrared, proton NMR, mass spectral, and analytical data of the resulting product were consistent with the formulation of unsymmetric $\text{Ru}_3(\text{C}_6\text{H}_5\text{N})(p\text{-ClC}_6\text{H}_4\text{N})(\text{CO})_9$. A small amount of $\text{Ru}_3(\text{CO})_{12}$ was also isolated, and a few very weak peaks consistent with $\text{Ru}_3(p\text{-ClC}_6\text{H}_4\text{N})_2(\text{CO})_9$ were apparent in the mass spectrum. It is interesting that only a very small amount of crossover had occurred under the forcing reaction conditions (5.5 days at 120 °C). This is certainly a testament to the ability of the $\mu_3\text{-NR}$ ligand to maintain the integrity of the trinuclear cluster.

Conclusions

Nitrosoarenes have been found to react with metal carbonyls of iron, ruthenium, and osmium to produce trinuclear clusters with arylimido ligands. With ruthenium, much improved yields of $\text{Ru}_3(\text{ArN})(\text{CO})_{10}$ are formed under mild conditions. With osmium, the new clusters $\text{Os}_3(\text{C}_6\text{H}_5\text{N})(\text{CO})_{10}$ and $\text{Os}_3(\text{C}_6\text{H}_5\text{N})_2(\text{CO})_9$ are formed, although the former is generated in only very low yields. With iron, $\text{Fe}_3(\text{C}_6\text{H}_5\text{N})_2(\text{CO})_9$ can be isolated from the reaction of nitrosobenzene with $\text{Fe}_3(\text{CO})_{12}$, but the yield is low and comparable to those of the previous methods of synthesis. With the reaction of $\text{Ru}_3(\text{ArN})(\text{CO})_{10}$ with nitroarenes under a CO atmosphere, much improved yields of the bis(imido) clusters, $\text{Ru}_3(\text{ArN})_2(\text{CO})_9$, can be obtained. This has allowed us to synthesize an interesting unsymmetrically substituted bis(imido) cluster, $\text{Ru}_3(\text{C}_6\text{H}_5\text{N})(\text{ClC}_6\text{H}_4\text{N})(\text{CO})_9$. The observation of the conversion of nitro- and nitrosoaromatics into a coordinated arylimido ligand may shed some light on the mechanism of the catalytic conversion of nitroaromatics into aryl isocyanates under high pressures of CO. Further study of the use of nitrosoarenes for preparing arylimido complexes is under way.

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