of all non-hydrogen atoms with data $>3\sigma$ converged with $R = 0.0298$ and $R_w = 0.0475$. Interchanging enantiomers in this noncentric space group improved refinement indices by ~1%, rendering the latter enantiomer a more reasonable choice. A difference Fourier map now showed two peaks near the rhenium atom in positions expected for the two trans hydride atoms. Final refinement was carried out by varying all non-hydrogen atoms anisotropically and the hydride ligands isotropically while holding hydrogens attached to carbon fixed with thermal parameters of 5.0 Å^2. Table III lists final parameters.

X-ray Structural Determination of $CpRe(PPh_3)H_4$ (3). Colorless crystals of $CpRe(PPh_3)H_4$ were obtained by evaporation of a Et_2O solution. A crystal was mounted on a glass fiber and 25 reflections with values of χ between 5° and 60° were used to determine a triclinic unit cell. Crystal parameters are shown in Table I and are consistent with either space group $P1$ or $P\bar{1}$. Collection of a hemisphere of 3390 unique data with $F_o > 3\sigma$ from $4 < 2\theta < 50°$ was followed by the successful Patterson map solution of the structure in centric space group $P\bar{1}$. Hydrogen atoms on the phenyl groups and Cp ring were placed in idealized locations and their positions and thermal parameters refined along with those of the non-hydrogen atoms. A difference Fourier map now revealed four peaks within bonding position to the metal center corresponding to the expected locations of the hydride ligands. Final refinement of the positions of all atoms, the anisotropic thermal parameters of the non-hydrogen atoms, and the isotropic thermal parameters of the hydrogen atoms revealed the structure shown in Figure 6. Table IV lists final parameters.

Acknowledgement is made to the U.S. Department of Energy (DE-FG02-86ER13569), to the Alfred P. Sloan Foundation, and to the Camille and Henry Dreyfus Foundation for their support of this work.

Supplementary Material Available: Figures S1–S4, NMR spectra of 1, and tables of data collection parameters, hydrogen positional parameters, thermal parameters, least-squares planes, and bond angles and distances (26 pages); tables of structure factors (61 pages). Ordering information is given on any current masthead page.

N–N Double Bond Cleavage and the Ortho Metalation of Azoarenes Using $Ru_3(NPh)(CO)_{10}$

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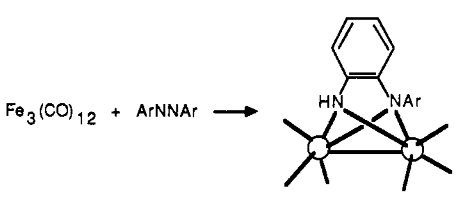
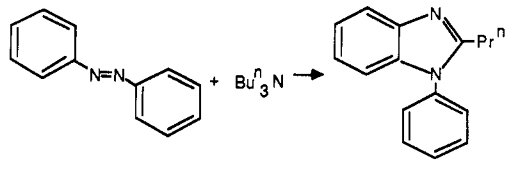
The reaction of $Ru_3(NAr)(CO)_{10}$ with azoarenes under CO results in the cleavage of the N–N double bond to yield $Ru_3(NAr)_2(CO)_9$ and ArNCO. In the absence of CO the insertion into one of the C–H bonds ortho to the azo functional group also occurs. The product distribution is sensitive to the para substituent on the azobenzene, with electron-withdrawing groups favoring N=N bond cleavage, while ortho metalation is favored with electron-donating groups. A single-crystal X-ray crystallographic study of one of the clusters containing an ortho-metalated azoarene, $HRu_3(NPh)(CH_3OC_6H_3NNC_6H_4OCH_3)(CO)_8$ [$P\bar{1}$ space group, $a = 9.237$ (4) Å, $b = 10.917$ (6) Å, $c = 17.199$ (6) Å, $\alpha = 100.47$ (3)°, $\beta = 99.80$ (3)°, $\gamma = 90.59$ (4)°, $Z = 2$], revealed a closed trinuclear cluster containing a triply bridging NPh, a semibridging carbonyl, an ortho-metalated azoarene, and a bridging hydride trans to the carbon of the ortho-metalated ring. Spectroscopic methods indicate the cluster interconverts in solution at room temperature among three isomers. Reaction of $HRu_3(NPh)(CH_3OC_6H_3NNC_6H_4OCH_3)(CO)_8$ with carbon monoxide leads to N–N double bond cleavage, while the reaction with excess azoarene yields a new cluster containing two ortho-metalated azoarenes. The analogous reaction of $Ru_3(NPh)(CO)_{10}$ with *N*-phenylbenzaldimine was also examined and found to give only the product resulting from ortho metalation of the phenyl ring.

Introduction

The reaction of azoarenes with metal complexes has been extensively studied.[1] One of the most common avenues of reaction involves metalation of one of the C–H bonds ortho to the azo functional group. Recently, the symmetric cleavage of the N–N double bond has also been reported with complexes of some of the early transition metals.[2-4] More complex rearrangements involving both of the above processes along with the additional formation of a C–N bond are known[5-10] and have resulted in complexes containing the *N*-phenyl-*o*-phenylenediamine ligand (eq 1). In one recent study,[11] this rearrangement was found in a useful ruthenium carbonyl catalyzed reaction (eq 2).



(1)



(2)

We report here the results of our study on the reaction of $Ru_3(NPh)(CO)_{10}$ with azoarenes. The nature of the products is sensitive to reaction conditions as well as to the substituents on the azoarene. Under certain conditions, new trinuclear clusters containing ortho-metalated

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azoarenes have been isolated in high yields, while N–N bond cleavage occurs under different conditions. Some parts of this study have been communicated previously.[12]

Experimental Section

$Ru_3(NPh)(CO)_{10}$,[13] 4,4′-$XC_6H_4NNC_6H_4X$[14] (X = NO_2, Cl, OCH_3), and PhCHNPh[15] were prepared according to published procedures. Azobenzene, purchased from Aldrich, and carbon monoxide, purchased from Matheson, were used without further purification. Hexane, heptane, and nonane were dried by distillation from sodium. 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 or an IBM AC-300 spectrometer. The aromatic regions in the ^1H NMR spectra consisted of complex multiplets, and only the range of values are reported. Mass spectra data was obtained by fast atom bombardment on a VG 7070 E-HF equipped with a VG Analytical 11/250 data system using *m*-nitrobenzyl alcohol as a matrix. Phenyl isocyanate was separated and analyzed by using a Packard Model 427 gas chromatograph equipped with an OV 101 column purchased from Alltech.

Reaction of $Ru_3(NPh)(CO)_{10}$ with Azoarenes in Refluxing Heptane under CO. The reactions between $Ru_3(NPh)(CO)_{10}$ and the various 4,4′-disubstituted azoarenes were performed under similar conditions. In a typical synthesis, $Ru_3(NPh)(CO)_{10}$ (21.4 mg, 0.032 mmol) was reacted with 5 equiv of the desired azoarene (X = NO_2, 40.1 mg, 0.147 mmol) in refluxing heptane (12 mL) under a CO atmosphere until infrared spectroscopy indicated that all of the $Ru_3(NPh)(CO)_{10}$ had been consumed. During the reaction with azobenzene, phenyl isocyanate was detected by infrared spectroscopy and gas chromatography. Reaction times were dependent on the surface area of the solution with smaller areas (70-mL Schlenk tube used as reaction vessel) yielding shorter reaction times (7–8 h). The solution changed from orange to red during the reaction and usually remained clear. Filtration in air, followed by chromatography on a silica gel column, yielded the cluster products as crystalline solids. The following paragraphs provide specific workup details and yields for each azoarene studied and analytical and spectral data for new compounds.

a. 4,4′-Dinitroazobenzene. A 10% solution of CH_2Cl_2 in hexane was used as the eluent. Only one band eluted from the column giving $Ru_3(NPh)(NC_6H_4NO_2)(CO)_9$ (Id) in 96% yield (24.0 mg, 0.031 mmol). IR (hexane): ν_{CO} 2099 w, 2077 s, 2053 s, 2026 s, 2019 s, 1994 m, 1984 w cm^{-1}. ^1H NMR (CD_2Cl_2): complex multiplet between 7.98 and 6.86 ppm. Anal. Calcd for $C_{21}H_9N_3O_{11}Ru_3$: C, 32.14; H, 1.16; N, 5.36. Found: C, 32.30; H, 1.25; N, 5.38. Mass spectrometry showed a parent ion at *m/z* 785 (^{102}Ru).

b. 4,4′-Dichloroazobenzene. Hexane was used as the eluent: band 1, unreacted 4,4′-dichloroazobenzene; band 2, orange $Ru_3(NPh)(NC_6H_4Cl)(CO)_9$[13] (Ic), 88% yield; band 3, mixture of several trace compounds back-flushed off column by using 100% CH_2Cl_2.

c. Azobenzene. Hexane was used as the eluent: band 1, mixture of $Ru_3(NPh)_2(CO)_9$ and unreacted azobenzene. Purification was achieved by subliming the azobenzene away from the cluster under vacuum at 90 °C. Final yield of purified $Ru_3(NPh)_2(CO)_9$[16] (Ib) was 81%: band 2, unreacted $Ru_3(NPh)(CO)_{10}$.

d. 4,4′-Dimethoxyazobenzene. A 20% solution of CH_2Cl_2 in hexane was used as the eluent: band 1, trace amount of $H_2Ru_3(NPh)(CO)_9$;[16] band 2, red $Ru_3(NPh)(NC_6H_4OCH_3)(CO)_9$ (Ia) 78% yield. IR (hexane): ν_{CO} 2094 w, 2072 s, 2049 s, 2020 s, 2015 s, 2012 s, 1988 m, 1977 w cm^{-1}. ^1H NMR (CD_2Cl_2): complex multiplet between 7.11 and 6.59 ppm, CH_3O singlet at 3.73 ppm. Anal. Calcd for $C_{22}H_{12}N_2O_{10}Ru_3$: C, 34.33; H, 1.57; N, 3.64. Found: C, 35.41; H, 2.07; N, 3.46. Mass spectrometry showed a parent ion at *m/z* 770 (^{102}Ru).

Reaction of $Ru_3(NPh)(CO)_{10}$ with 4,4′-Dimethoxyazobenzene in Refluxing Hexane. $Ru_3(NPh)(CO)_{10}$ (70.0 mg, 0.104 mmol) and 4,4′-dimethoxyazobenzene (75.0 mg, 0.310 mmol) were allowed to react in refluxing hexane (40 mL) for 22 h under nitrogen. Infrared spectroscopy detected a weak absorption at 2262 cm^{-1} which indicated a small amount of aryl isocyanate had formed during the course of the reaction. The final solution was filtered in air and chromatographed on a silica gel column using a solution of 20% CH_2Cl_2 in hexane. Eight bands eluted from the column, but only four contained an appreciable amount of material. The first band contained unreacted $Ru_3(NPh)(CO)_{10}$ (17.1 mg, 0.025 mmol) while the second band contained $Ru_3(NPh)(NC_6H_4OCH_3)(CO)_9$ (Ia) isolated as red crystals in 17% yield (13.5 mg, 0.018 mmol). The third band was bright red and contained $HRu_3(NPh)(CH_3OC_6H_3NNC_6H_4OCH_3)(CO)_8$ (IIa) isolated in 59% yield (52.6 mg, 0.061 mmol) as red crystals from a concentrated hexane solution by slow cooling at −25 °C. IR (hexane): ν_{CO} 2083 s, 2048 s, 2042 s, 2012 s, 2002 s, 1987 s, 1920 m, 1905 m. ^1H NMR (CD_2Cl_2): complex multiplet between 7.67 and 6.32 ppm, CH_3O peaks (relative intensity) at 3.99 (49), 3.95 (37), and 3.87 (100) ppm, metal hydride peaks present at −14.45 (12), −15.90 (3), and −19.56 (12) ppm, hexane peaks present at 1.17 and 0.81 ppm. Crystallographic analysis (vide infra) indicated one hexane molecule per two cluster molecules in the crystalline lattice. Anal. Calcd for $C_{28}H_{19}N_3O_{10}Ru_3\cdot{}^1/_2C_6H_{14}$: C, 41.21; H, 2.90; N, 4.65. Found: C, 41.26; H, 2.95; N, 4.73. Mass spectrometry showed a parent ion at *m/z* 863 (^{102}Ru). The fourth band contained unreacted 4,4′-dimethoxyazobenzene while the remaining four bands contained metal carbonyls in trace amounts (<0.5 mg).

Reaction of $Ru_3(NPh)(CO)_{10}$ with Azobenzene in Refluxing Heptane under N_2. $Ru_3(NPh)(CO)_{10}$ (20.6 mg, 0.031 mmol) and $C_6H_5NNC_6H_5$ (29.8 mg, 0.164 mmol) were degassed under an N_2 atmosphere, and heptane (12 mL) was added. The solution was refluxed for 3.5 h and filtered in air to remove insoluble brown decomposition material. Chromatography on a silica gel column yielded four bands. The first band contained $Ru_3(NPh)_2(CO)_9$[16] (Ib) in 56% yield. The second and third bands contained unreacted azobenzene and $Ru_3(NPh)(CO)_{10}$, respectively. The fourth band was brown, and removal of the solvent yielded a red brown oil proposed to be $HRu_3(NPh)(C_6H_4NNC_6H_5)(CO)_8$ (IIb) in 25% yield. (6.3 mg, 0.008 mmol). IR (hexane): ν_{CO} 2083 s, 2050 s, 2042 s, 2013 s, 2001 s, 1988 m, 1922 m, 1904 m cm^{-1}. ^1H NMR (CD_2Cl_2): complex multiplet between 7.7 and 6.5 ppm and hydride peaks located at −14.31 and −19.44 ppm. Mass spectrometry showed a parent ion at *m/z* 802 (^{102}Ru).

Reaction of $HRu_3(NPh)(CH_3OC_6H_3NNC_6H_4OCH_3)(CO)_8$ with 4,4′-Dimethoxyazobenzene. $HRu_3(NPh)(CH_3OC_6H_3NNC_6H_4OCH_3)(CO)_8$ (47.9 mg, 0.056 mmol) and 4,4′-dimethoxyazobenzene (68.0 mg, 0.281 mmol) were degassed in a Schlenk tube, and hexane (30 mL) was added. The solution was refluxed for 43 h, during which time the clear red solution turned very cloudy. Filtration in air yielded a red filtrate and a brown precipitate [IR (THF): ν_{CO} 2105 w, 2038 s, 1997 vs, 1972 s, 1870 w cm^{-1}]. The red filtrate was chromatographed on a silica gel column with 20% CH_2Cl_2 in hexane as an eluent. The first band contained $Ru_3(NPh)(NC_6H_4OCH_3)(CO)_9$ (Ia), isolated in 35% yield (15.2 mg, 0.020 mmol) as red crystals after removal of the solvent. The second band contained recovered $HRu_3(NPh)(CH_3OC_6H_3NNC_6H_4OCH_3)(CO)_8$ (IIa) (6.3 mg, 0.0073 mmol), and the third band contained unreacted azoarene. The fourth and fifth bands contained trace amounts (<0.5 mg) of two unknown red metal carbonyls that were not further characterized. The sixth band was bright yellow, and removal of the solvent yielded a golden brown solid proposed to be $Ru(CO)_2(CH_3OC_6H_3NNC_6H_4OCH_3)_2$[17] (5.7 mg, 0.009 mmol). IR (hexane): ν_{CO} 2027 s, 1975 s cm^{-1}. Mass spectrometry showed a parent ion at *m/z* 644 (^{102}Ru). The seventh band was bright red, and $H_2Ru_3(NPh)(CH_3OC_6H_3NNC_6H_4OCH_3)_2(CO)_6$ (IV) was isolated in 22% yield (13.0 mg, 0.012 mmol) as red crystals by slow cooling a concentrated hexane solution. IR (hexane): ν_{CO} 2098 s, 2037 s, 2027 s, 2007 s, 1990 s, 1851 m cm^{-1}. ^1H NMR (CD_2Cl_2): multiplet between 8.11 and 6.31 ppm (19), CH_3O signals at 3.92 (3), 3.87 (3), 3.84 (3), and 3.27 (3) ppm, hexane signals at 1.55, 1.27, and

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0.88 ppm, and hydride signals at −14.68 (1) and −15.93 (1) ppm. Mass spectrometry showed a parent ion at m/e 1049 (^{102}Ru) followed by the loss of 6 CO and a M − azoarene peak at m/e 807 followed by the loss of 6 CO. Anal. Calcd for $C_{40}H_{33}N_5O_{10}Ru_3 \cdot C_6H_{14}$: C, 48.77; H, 4.16; N, 6.18. Found: C, 48.54; H, 4.18; N, 6.15. The last band to elute contained a trace amount (1.2 mg) of an unknown yellow carbonyl. IR (hexane): ν_{CO} 2098 m, 2031 vs, 2006 m, 1984 s, 1874 w cm^{-1}.

Pyrolysis of $HRu_3(NPh)(CH_3OC_6H_3NNC_6H_4OCH_3)(CO)_8$ (IIa) under CO. $HRu_3(NPh)(CH_3OC_6H_3NNC_6H_4OCH_3)(CO)_8$ (21.1 mg, 0.025 mmol) was dissolved in heptane (20 mL) and placed under an atmosphere of CO. The reaction solution was refluxed for 5.5 h and monitored by infrared spectroscopy which indicated the formation of 4-$CH_3OC_6H_4NCO$ and new cluster products. The final clear red-orange solution was chromatographed on a silica gel column using 20% CH_2Cl_2 in hexane as an eluent. The first band to elute contained a trace amount of $Ru_3(NPh)(CO)_{10}$. $Ru_3(NPh)(NC_6H_4OCH_3)(CO)_9$ (Ia) was isolated in 80% yield (15.3 mg, 0.020 mmol) as red crystals from the second band. The third band contained recovered starting material (3.8 mg, 0.004 mmol).

Reaction of $Ru_3(NPh)(CO)_{10}$ with PhCHNPh. $Ru_3(NPh)(CO)_{10}$ (50.0 mg, 0.074 mmol) and PhCHNPh (67.0 mg, 0.370 mmol) were degassed in a Schlenk tube and placed under an atmosphere of CO. Heptane (25 mL) was added, and the solution was brought to reflux for 7 h. During this time the bright yellow solution slowly turned deep clear red. When infrared spectroscopy indicated that all of the starting cluster had been consumed, the CO atmosphere was replaced by blowing a slow stream of N_2 over the refluxing solution for 15 min. The clear solution was cooled to room temperature and chromatographed on a silica gel column with hexane as the eluent. The first band contained $H_2Ru_3(NPh)(CO)_9$[16] in less than 5% yield. The second band was bright red, and $HRu_3(NPh)(C_6H_4CHNPh)(CO)_8$ (III) was isolated in 71% yield (42.0 mg, 0.053 mmol) as red crystals after removal of the solvent. IR (hexane): ν_{CO} 2082 s, 2049 s, 2038 s, 2012 s, 2002 s, 1989 s, 1922 m, 1903 m cm^{-1}. ^{1}H NMR (CD_2Cl_2): complex multiplet between 8.0 and 6.3 ppm and hydride peaks at −14.77 (8) and −19.85 (10) ppm. Anal. Calcd for $C_{27}H_{16}N_2O_8Ru_3$: C, 40.57; H, 2.02; N, 3.50. Found: C, 40.52; H, 2.06; N, 3.40. Mass spectrometry showed a parent ion at m/z 802 (^{102}Ru). The third band contained a trace amount of a yellow metal carbonyl tentatively proposed to be $H_2Ru_3(NPh)(C_6H_4CHNPh)_2(CO)_6$ (V) only on the basis of comparison of infrared spectroscopy with that of $H_2Ru_3(CH_3OC_6H_3NNC_6H_4OCH_3)_2(CO)_6$ (IV). IR (hexane): ν_{CO} 2095 s, 2035 s, 2023 s, 2003 s, 1981 s, 1956 w, 1848 w cm^{-1}. This compound was never isolated in large enough quantities for elemental analysis or ^{1}H NMR.

Pyrolysis of $HRu_3(NPh)(C_6H_4CHNPh)(CO)_8$ (III). $HRu_3(NPn)(C_6H_4CHNPh)(CO)_8$ (8.6 mg, 0.011 mmol) dissolved in nonane (10 mL) was placed in a 120 °C oil bath for 25 min. The initially clear red solution quickly became cloudy brown. After filtration to remove the insoluble brown precipitate, chromatography of the red brown solution yielded four bands. The first three contained $H_2Ru_3(NPh)(CO)_9$,[16] $Ru_3(NPh)(CO)_{10}$, and starting material respectively in trace amounts. The last band contained a trace amount of an unknown yellow metal carbonyl. IR (hexane): ν_{CO} 2077 w, 2047 s, 2039 s, 2028 s, 2021 w, 1990 w cm^{-1}.

Reaction of $HRu_3(NPh)(C_6H_4CHNPh)(CO)_8$ (III) with CO. $HRu_3(NPh)(C_6H_4CHNPh)(CO)_8$ (40.0 mg, 0.49 mmol) dissolved in nonane (20 mL) was placed under an atmosphere of CO and into a 120 °C oil bath for 10 min. The bright red solution quickly turned clear bright yellow. Chromatography yielded one colored band containing $Ru_3(NPh)(CO)_{10}$ (3.7 mg, 0.047 mmol) in 96% yield.

X-ray Crystallographic Study. Red crystals of $HRu_3(NPh)(CH_3OC_6H_3NNC_6H_4OCH_3)(CO)_8$ (IIa) were grown by slow cooling of a concentrated hexane solution of the cluster. Details of the structural analysis (Table I) are similar to those of closely related compounds studied in our laboratory.[18] A preliminary peak search indicated the crystal was triclinic, and the $P\bar{1}$ space group was chosen. During data collection the three check reflections showed a 5.6% decay of intensity. A linear correction was applied to all the data.

Table I. Summary of Crystallographic Data

Crystal Parameters	
cryst system	triclinic
space group	$P\bar{1}$
formula	$C_{31}H_{26}N_3O_{10}Ru_3$
fw, g mol^{-1}	903.78
a, Å	9.237 (4)
b, Å	10.917 (6)
c, Å	17.199 (6)
α, deg	100.47 (3)
β, deg	99.80 (3)
γ, deg	90.59 (4)
V, Å^3	1679 (3)
Z	2
ρ(calcd), g cm^{-3}	1.79
temp, °C	23
abs coeff, cm^{-1}	13.64
cryst dimens, mm	0.10 × 0.35 × 0.40
trans factors, max to min, %	99.8–87.8
abs correctn applied	empirical (ψ scans)
Measurement of Intensity Data	
diffractometer	Enraf-Nonius CAD-4
radiation	Mo Kα (λ = 0.71073 Å)
monochrometer	graphite crystal
programs used	Enraf-Nonius CAD-4-SDP programs
method of structure soln	heavy-atom method
scan type	ω–2θ
scan range, deg	0° ≤ 2θ ≤ 56°
reflctns measd	+h, ±k, ±l
no. of unique reflctns	8081
no. of reflctns used	6757
cutoff	1σ
p	0.05
extinctn coeff	7.55 × 10^{-8}
R	0.036
R_w	0.045
error in observn of unit weight	1.245

After the location of all non-hydrogen atoms a difference Fourier calculation revealed a peak that was consistent for a hydride. This was added to the atom list and isotropically refined. The idealized positions for all other hydrogens were added to the list but not refined. All non-hydrogen atoms were refined anisotropically. The final difference Fourier map indicated no significant features. The values of the atomic scattering factors used in the calculations were taken from the usual tabulation,[19] and the effects of anomalous dispersion were included for the non-hydrogen atoms. The positional parameters, bond distances, and bond angles are listed in Tables II–IV.

Results

The Reaction of Azoarenes with $Ru_3(NPh)(CO)_{10}$. Reaction of $Ru_3(NPh)(CO)_{10}$ with azoarenes for 7–15 h in refluxing heptane under an atmosphere of CO (Scheme I) gave $Ru_3(NPh)(NC_6H_4X)(CO)_9$ (I) in yields ranging from 78 to 96%, with the highest yields being achieved when X was an electron-withdrawing group. Also formed in the reaction was 4-XC_6H_4NCO, which was detected by gas chromatography and infrared spectroscopy. The $Ru_3(NPh)(NAr)(CO)_9$ clusters were identified by fast atom bombardment mass spectrometry, elemental analysis, and spectroscopic comparison with known analogues synthesized by different routes.[13,16,20] In all cases the cluster

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Table II. Positional Parameters

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Ru1	0.04750 (3)	0.31629 (2)	0.14090 (1)	C4C	0.5059 (4)	0.2342 (4)	0.4754 (2)
Ru2	0.24719 (3)	0.14716 (3)	0.16816 (1)	C5C	0.4374 (5)	0.3028 (4)	0.5334 (2)
Ru3	0.30388 (3)	0.38448 (3)	0.26179 (1)	C6C	0.3441 (5)	0.3940 (4)	0.5123 (2)
NA	0.1308 (3)	0.2529 (2)	0.2454 (1)	OC	0.6002 (3)	0.1421 (3)	0.4896 (2)
C1A	0.0602 (4)	0.2257 (3)	0.3080 (2)	C7C	0.6253 (6)	0.1145 (5)	0.5682 (3)
C2A	0.1089 (4)	0.1330 (4)	0.3498 (2)	C11	−0.0906 (5)	0.4441 (4)	0.1637 (2)
C3A	0.0413 (6)	0.1093 (5)	0.4118 (3)	O11	−0.1846 (4)	0.5093 (3)	0.1729 (2)
C4A	−0.0727 (5)	0.1788 (5)	0.4332 (3)	C12	0.0567 (5)	0.3422 (4)	0.0345 (2)
C5A	−0.1209 (5)	0.2706 (5)	0.3933 (3)	O12	0.0660 (5)	0.3548 (3)	−0.0283 (2)
C6A	−0.0560 (4)	0.2942 (4)	0.3301 (2)	C13	−0.1149 (4)	0.1990 (4)	0.1051 (2)
NB	0.2003 (3)	0.5122 (3)	0.3417 (2)	O13	−0.2144 (4)	0.1327 (3)	0.0841 (2)
C1B	0.0994 (5)	0.6081 (3)	0.3238 (2)	C21	0.3377 (5)	0.1220 (4)	0.0740 (2)
C2B	0.1102 (5)	0.6668 (4)	0.2610 (2)	O21	0.3867 (5)	0.1111 (4)	0.0173 (2)
C3B	0.0111 (6)	0.7613 (4)	0.2450 (3)	C22	0.1104 (4)	0.0196 (3)	0.1138 (2)
C4B	−0.0965 (6)	0.7903 (4)	0.2909 (3)	O22	0.0318 (4)	−0.0607 (3)	0.0807 (2)
C5B	−0.1055 (6)	0.7298 (2)	0.3524 (3)	C23	0.3624 (5)	0.0349 (4)	0.2285 (2)
C6B	−0.0088 (5)	0.6410 (4)	0.3702 (3)	O23	0.4196 (4)	−0.0397 (4)	0.2581 (2)
OB	−0.2078 (5)	0.8762 (4)	0.2784 (2)	C31	0.4568 (4)	0.2922 (4)	0.2212 (2)
C7B	−0.2063 (8)	0.9372 (7)	0.2173 (5)	O31	0.5754 (3)	0.2708 (4)	0.2117 (2)
NC	0.2230 (4)	0.5033 (3)	0.4156 (2)	C32	0.4391 (5)	0.5199 (4)	0.2634 (2)
C1C	0.3188 (4)	0.4129 (3)	0.4330 (2)	O32	0.5214 (4)	0.5974 (3)	0.2645 (2)
C2C	0.3877 (4)	0.3437 (3)	0.3728 (2)	H	0.204 (5)	0.420 (4)	0.171 (2)
C3C	0.4831 (4)	0.2560 (4)	0.3963 (2)				

Table III. Bond Distances (Å)

	A. Within HRu_3N core		
Ru1–Ru2	2.669 (1)	Ru3–H	1.78 (4)
Ru1–Ru3	2.865 (1)	Ru1–NA	2.072 (2)
Ru2–Ru3	2.784 (1)	Ru2–NA	2.051 (2)
Ru1–H	1.77 (4)	Ru3–NA	2.086 (2)
	B. Metal Ligand Distances		
Ru1–C11	1.933 (4)	Ru2–C23	1.956 (4)
Ru1–C12	1.917 (4)	Ru3–C31	1.900 (4)
Ru1–C13	1.905 (4)	Ru3–C32	1.919 (4)
Ru2–C21	1.924 (4)	Ru3–NB	2.128 (3)
Ru2–C22	1.870 (4)	Ru3–C2C	2.063 (3)
	C. Ligand Distances		
NA–C1A	1.423 (4)	NC–C1C	1.372 (5)
C1A–C2A	1.380 (5)	C1C–C2C	1.414 (4)
C1A–C6A	1.381 (5)	C1C–C6C	1.397 (4)
C2A–C3A	1.384 (5)	C2C–C3C	1.375 (5)
C3A–C4A	1.366 (7)	C3C–C4C	1.405 (5)
C4A–C5A	1.353 (7)	C4C–OC	1.366 (5)
C5A–C6A	1.389 (5)	C4C–C5C	1.381 (5)
NB–NC	1.273 (4)	C5C–C6C	1.381 (5)
NB–C1B	1.450 (5)	OC–C7C	1.419 (5)
C1B–C2B	1.369 (5)	C11–O11	1.142 (5)
C1B–C6B	1.392 (5)	C12–O12	1.130 (4)
C2B–C3B	1.419 (6)	C13–O13	1.130 (4)
C3B–C4B	1.376 (7)	C21–O21	1.131 (5)
C4B–OB	1.414 (6)	C22–O22	1.133 (4)
C4B–C5B	1.358 (7)	C23–O23	1.126 (5)
C5B–C6B	1.366 (6)	C31–O31	1.154 (4)
OB–C7B	1.345 (7)	C32–O32	1.127 (5)

products retained the original μ_3-NPh ligand.

When the same reaction was conducted under nitrogen, the starting material was consumed in only 3.5 h, indicating CO inhibited the reaction. The yields of $Ru_3(NPh)(NC_6H_4X)(CO)_9$ also decreased under nitrogen and at lower reaction temperatures. Thus with 4,4′-dimethoxyazobenzene, $Ru_3(NPh)(NC_6H_4OCH_3)(CO)_9$ (Ia) was isolated in 17% yield after 22 h of reaction under nitrogen. The major product of this reaction was instead an isomeric mixture of a new ortho-metalated cluster, $HRu_3(NPh)(CH_3OC_6H_3NNC_6H_4OCH_3)(CO)_8$ (IIa, IIa′, and IIa″), isolated in 59% yield. Pyrolysis of this ortho-metalated cluster for 6.5 h in refluxing heptane under an atmosphere of CO gave an 80% conversion to $Ru_3(NPh)(NC_6H_4OCH_3)(CO)_9$ (Ia) and 4-$CH_3OC_6H_4NCO$. Alternatively, further reaction of the ortho-metalated cluster with excess 4,4′-dimethoxyazobenzene in refluxing hexane under nitrogen for 43 h produced a bis-ortho-metalated azoarene compound, $H_2Ru_3(NPh)(CH_3OC_6H_3NNC_6H_4OCH_3)_2(CO)_6$ (IV), in 22% yield along with $Ru_3(NPh)(NC_6H_4X)(CO)_9$ in 35% yield. Characterization of the new ortho-metalated species is described below.

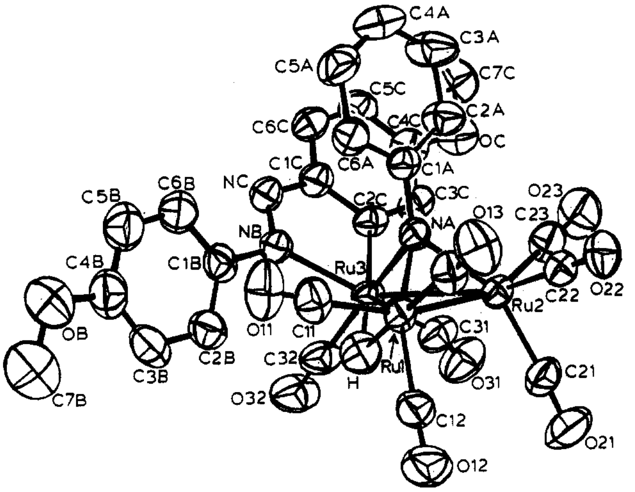
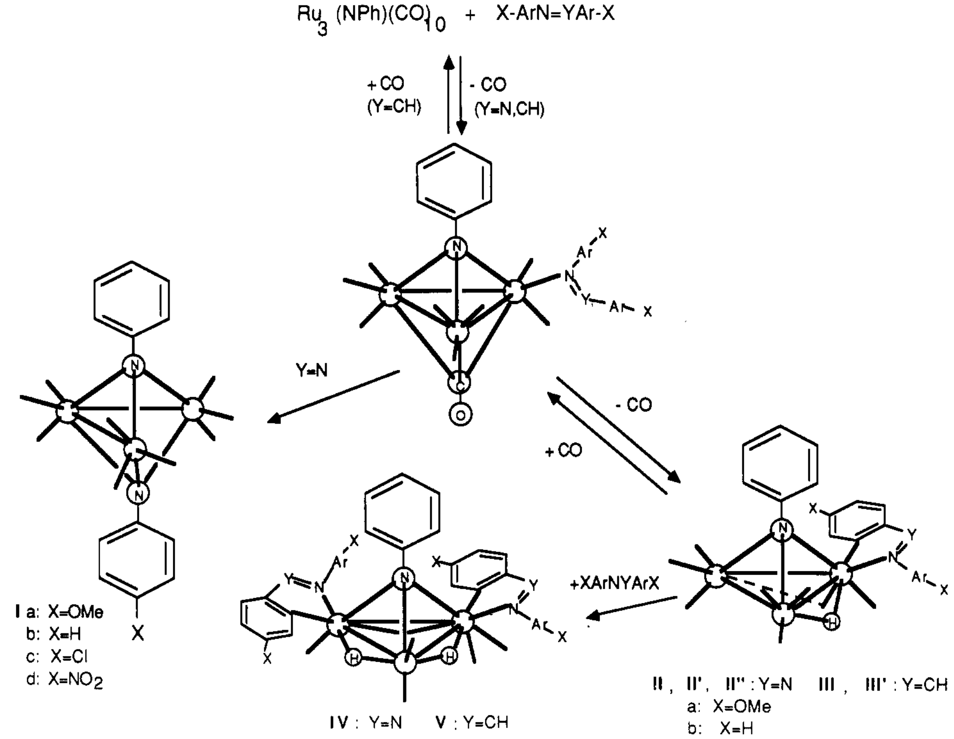


Figure 1. View of $HRu_3(NC_4H_5)(CH_3OC_6H_3NNC_6H_4OCH_3)(CO)_8$ showing the atomic labeling scheme.

Characterization of $HRu_3(NPh)(CH_3OC_6H_3NNC_6H_4OCH_3)(CO)_8$ (IIa). A single-crystal X-ray crystallographic study was performed on this cluster. Figure 1 shows a view of the structure with the atomic labeling scheme, and selected bond distances and angles are given in Tables III and IV, respectively. The ruthenium–ruthenium bond distances vary between 2.669 (1) and 2.865 (1) Å with the longest edge being bridged by the hydride atom. Seven of the eight carbonyl ligands are coordinated to the metals in a linear, terminal fashion. The M–C bond distances range from 1.870 (4) (Ru2–C22) to 1.956 (4) Å (Ru2–C23). the remaining carbonyl (C31) is bent (Ru3–C31–O31 = 157.1 (3)°) toward Ru2 with the Ru2–Ru3–C31 angle equal to 58.9 (1)°. The imido ligand is capping the face of the metal triangle with M–NA bond distances varying between 2.051 (2) and 2.086 (2) Å. The hydride ligand was located and found to be bridging the Ru1–Ru3 edge with an average Ru1(3)–H bond distance of 1.78 (4) Å and a Ru1–H–Ru3 bond angle of 108 (2)°. The hydride was 0.90 (4) Å from the plane of metal atoms and trans

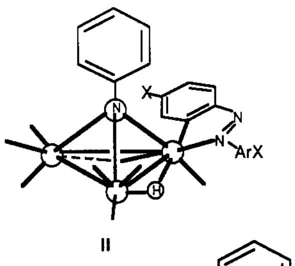
Scheme I



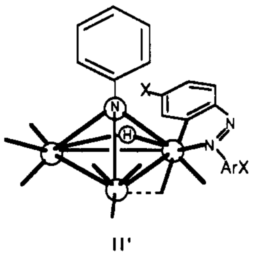
to the carbon (C2C) of the ortho-metalated aromatic ring with the H-Ru3-C2C angle equal to 171 (1)°.

The azobenzene ligand is bound in a chelating fashion similar to that observed for other transition-metal azobenzene complexes.[21-24] The free $C_6H_4OCH_3$ ring, B, is twisted by an angle of 30.3° from the plane of the five-membered chelate ring. The magnitude of this twist is comparable to those previously observed for other metalated azoarene ligands. The metal-bound $C_6H_3OCH_3$ ring is nearly coplanar (dihedral angle 5.1°) with the chelate ring. The NB—NC separation (1.273 (4) Å) is consistent with the presence of an N=N double bond and is characteristic of coordinated azoarene ligands where one of the nitrogen atoms is involved in a σ-bond to a metal atom.[25] The two N-C distances (NB-C1B = 1.450 (5) and NC-C1C = 1.372 (5) Å) differ significantly with the longer distance being to the free $C_6H_4OCH_3$ ring. This pattern has been observed in related complexes and is expected due to the lesser degree of conjugation between the twisted phenyl group and the chelate ring. The Ru3-C2C and Ru3-NB distances of 2.063 (3) and 2.128 (3) Å are reasonable for low-valent ruthenium bonded to sp^2 carbon and nitrogen bonds.[21,26]

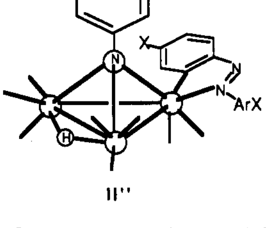
In the solid-state structure of $HRu_3(NPh)(CH_3OC_6H_3NNC_6H_4OCH_3)(CO)_8$ (Figure 1), only one semibridging carbonyl ligand is observed. In solution, however, the infrared spectrum shows two absorptions, 1920 and 1905 cm^{-1}, that may be attributed to a semibridging CO. The ^1H NMR spectrum is complex and suggests that in solution the hydride can bridge any of the Ru–Ru bonds producing three possible isomers, II, II′, and II″, shown below. There are three signals present in the hydride region at −14.45, −15.90, and −19.56 ppm in a 12:3:12 ratio. In II, the hydride is trans to the carbon of the metalated aromatic ring; in II′, it is trans to the coordinated nitrogen; and in II″, the hydride is bridging the two rutheniums that are not chelated by the azoarene. There are also three signals present at 3.99, 3.95, and 3.87 ppm in a 49:37:100 ratio attributed to inequivalent methoxy groups. Since the methoxy group on the aromatic ring bound to the coordinated nitrogen should not be strongly influenced by the hydride location, its chemical shift should be similar in each isomer. We tentatively assign the peak at 3.87 ppm to this group in all three isomers. On the other hand, the chemical shift of the methoxy group on the metalated ring should be more sensitive to the structure of the isomer. From the hydride region, these three methoxy signals are expected to appear in a 4:1:4 ratio, but only two signals in an approximate 5:4 ratio are apparent.



II



II′



II″

A spin saturation transfer experiment at 25 °C demonstrated chemical exchange between the possible hydride sites. At this temperature, two of the hydride locations are equally populated (−14.45 and −19.56 ppm). With the

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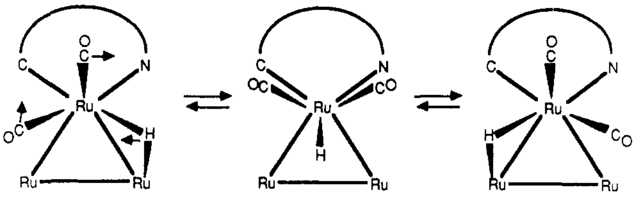
Table IV. Selected Bond Angles (deg)

A. Within HRu_3N Core			
Ru2-Ru1-Ru3	60.27 (1)	Ru3-Ru2-C23	105.8 (1)
Ru2-Ru1-NA	49.33 (7)	NA-Ru2-C21	151.2 (2)
Ru2-Ru1-C11	158.7 (1)	NA-Ru2-C22	102.7 (1)
Ru2-Ru1-C12	104.7 (1)	NA-Ru2-C23	107.1 (1)
Ru2-Ru1-C13	95.4 (1)	Ru-Ru3-Ru2	56.36 (1)
Ru2-Ru1-H	36 (1)	Ru1-Ru3-NA	46.22 (6)
Ru3-Ru1-NA	46.64 (7)	Ru1-Ru3-NB	96.37 (7)
Ru3-Ru1-C11	105.5 (1)	Ru1-Ru3-C2C	137.29 (8)
Ru3-Ru1-C12	117.7 (1)	Ru1-Ru3-C31	105.1 (1)
Ru3-Ru1-C13	143.7 (1)	Ru1-Ru3-C32	123.8 (1)
RU3-Ru1-H	36 (1)	Ru1-Ru3-H	36 (1)
NA-Ru1-C11	109.4 (1)	Ru2-Ru3-NA	47.18 (7)
NA-Ru1-C12	152.7 (2)	Ru2-Ru3-NB	138.37 (7)
NA-Ru1-C13	97.2 (1)	Ru2-Ru3-C2C	101.62 (9)
NA-Ru1-H	83 (1)	Ru2-Ru3-C31	58.9 (1)
Ru1-Ru2-Ru3	63.37 (1)	Ru2-RU3-C32	133.8 (1)
Ru1-Ru2-NA	49.99 (7)	Ru2-Ru3-H	79 (1)
Ru1-Ru2-C21	103.9 (1)	NA-Ru3-NB	91.2 (1)
Ru1-Ru2-C22	90.0 (1)	NA-Ru3-C2C	91.3 (1)
Ru1-Ru2-C23	156.8 (1)	NA-Ru3-C31	104.1 (1)
Ru3-Ru2-NA	48.24 (7)	NA-Ru3-C32	169.5 (1)
Ru3-Ru2-C21	113.6 (1)	NA-Ru3-H	82 (1)
Ru3-Ru2-C22	148.9 (1)		
B. Ligand-Metal-Ligand			
NB-Ru3-C2C	76.8 (1)	C11-Ru1-C12	96.0 (2)
NB-Ru3-C31	158.6 (1)	C11-Ru1-C13	88.4 (2)
NB-Ru3-C32	86.7 (1)	C11-Ru1-H	95 (1)
NB-Ru3-H	97 (1)	C12-Ru1-C13	93.3 (2)
C2C-Ru3-C31	87.8 (1)	C12-Ru1-H	85 (1)
C2C-Ru3-C32	98.2 (1)	C13-Ru1-H	177 (1)
C2C-Ru3-H	171 (1)	C21-Ru2-C22	87.2 (2)
C31-Ru3-C32	80.8 (2)	C21-Ru2-C23	99.3 (2)
C31-Ru3-H	100 (1)	C22-Ru2-C23	92.6 (2)
C32-Ru3-H	88 (1)		
C. Metal Carbonyls			
Ru1-C11-O11	172.1 (4)	Ru2-C22-O22	177.3 (3)
Ru1-C12-O12	177.7 (4)	Ru2-C23-O23	172.7 (4)
Ru1-C13-O13	177.7 (3)	Ru3-C31-O31	157.1 (3)
Ru2-C21-O21	176.9 (5)	Ru3-C32-O32	178.2 (3)
D. Ligand Angles			
Ru3-NB-NC	117.9 (2)	Ru1-NA-Ru2	80.68 (8)
Ru3-NB-C1B	128.9 (2)	Ru1-NA-Ru3	87.14 (9)
Ru3-C2C-C1C	110.7 (2)	Ru2-NA-Ru3	84.57 (9)
Ru3-C2C-C3C	132.5 (2)	Ru1-NA-C1A	130.9 (2)
NB-C1B-C2B	120.0 (4)	Ru2-NA-C1A	132.8 (2)
NB-C1B-B6B	120.3 (3)	Ru3-NA-C1A	124.4 (2)
NB-NC-C1C	113.5 (3)	C4B-OB-C7B	117.1 (5)
NC-C1C-C2C	120.7 (3)	C4C-OC-C7C	117.3 (4)
NC-C1C-C6C	116.8 (3)	Ru1-H-Ru3	108 (2)

assumption of similar longitudinal relaxation times (T_1) for the hydrides,[27] an approximate chemical exchange rate for the two positions was calculated to be 0.10 ± 0.02 s^{-1}.[28] One possible pathway of isomerization could involve a hydride migration concurrent with the semibridging ligand becoming terminal and a terminal carbonyl ligand becoming semibridging as shown in Scheme II.

Characterization of $HRu_3(NPh)(C_6H_4CHNPh)(CO)_8$ (III). Fast atom bombardment mass spectrometry, elemental analysis, and spectroscopic comparison to the closely related, structurally characterized, ortho-metalated azoarene cluster is the basis for the formulation and proposed structure III for $HRu_3(NPh)(C_6H_4CHNPh)(CO)_8$. The imine proton that appears at 8.49 ppm in the free ligand could not be assigned in the ortho-metalated cluster.

Scheme II



II II'

The presence of two absorptions attributed to semibridging carbonyls in the infrared spectrum and the presence of two hydride signals in the ^1H NMR indicate $HRu_3(NPh)(C_6H_4CHNPh)(CO)_8$ has similar behavior in solution as that of $HRu_3(NPh)(CH_3OC_6H_3NNC_6H_4OCH_3)(CO)_8$ (II).

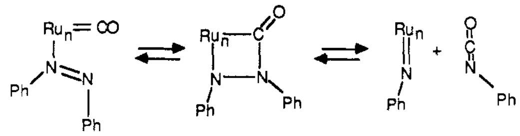
Characterization of $H_2Ru_3(NPh)(CH_3OC_6H_3NNC_6H_4OCH_3)_2(CO)_6$ (IV). Elemental analysis and fast atom bombardment mass spectrometry suggest a molecular formula of $H_2Ru_3(NPh)(CH_3OC_6H_4NNC_6H_4OCH_3)_2(CO)_6$ (IV). An absorption at 1851 cm^{-1} in the infrared spectrum indicates that at least one bridging carbonyl ligand is present. In the ^1H NMR spectrum, there are two hydrides of equal intensity at −14.69 and −15.94, four methoxy signals of equal intensity between 3.92 and 3.27 ppm, and a complex pattern of peaks in the aromatic region. A possible structure consistent with the spectroscopic data is shown in Scheme I, where one hydride is trans to a coordinated nitrogen while the other is trans to a carbon on the second ortho-metalated aromatic ring.

Ortho Metalation of PhCHNPh. Reaction of $Ru_3(NPh)(CO)_{10}$ with *N*-phenylbenzaldimine for 7 h in refluxing heptane under an atmosphere of carbon monoxide yielded clean conversion to a new ortho-metalated cluster, $HRu_3(NPh)(C_6H_4CHNPh)(CO)_8$ (III). To isolate the product, the CO was replaced with N_2 while the reaction was hot, and the mixture was then cooled to room temperature. If the reaction was cooled under the carbon monoxide atmosphere, rapid re-formation of starting materials occurred, indicating clean reversibility. This reactivity differs markedly from the closely related azoarene analogue in which reaction with carbon monoxide yielded N-N bond cleavage (Scheme I). The reaction of $Ru_3(NPh)(CO)_{10}$ with *N*-phenylbenzaldimine was performed under carbon monoxide to stabilize $Ru_3(NPh)(CO)_{10}$ from thermal decomposition.[13]

Discussion

The reaction of $Ru_3(NPh)(CO)_{10}$ with azoarenes results either in the cleavage of the N-N double bond or in the insertion into one of the C-H bonds ortho to the azo functional group. The results suggest that the two products are formed in parallel reaction paths, possibly from a common intermediate, as shown in Scheme I. Initial (and reversible) CO substitution by the nitrogen lone pair of the azoarene would be consistent with the observed CO inhibition. Unfortunately neither this compound nor any other intermediate was observed with use of photolysis, Me_3NO, or thermal activation.

Subsequent steps leading to N═N bond cleavage could involve a metathesis-like reaction of the N═N bond with the Ru—C bond which clearly has some π character to it (eq 3). The N-C bond-forming step shown in eq 3 may



(3)

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[27] The apparent longitudinal relaxation times (T_1) measured by inversion recovery while saturating the exchanging hydride were 0.8 and 1.0 s. The small concentration of isomer IIa″ prohibited us from establishing its role (and rate) in the isomerization.

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come about from the intramolecular nucleophilic attack of the β-N lone pair on an adjacent CO. It is possible that the conversion may occur on more than one of the metal atoms involving a five-membered ring intermediate instead of four. Recently, Cotton and co-workers[3] reported the reaction between azobenzene and the Nb–Nb doubly bonded dimer $Nb_2Cl_6(Me_2S)_3$ formed the metathesis product $[NbCl_2(Me_2S)(NPh)]_2(\mu\text{-}Cl)_2$. Also, Hegedus and co-workers[4] found that photolysis of $Cr(CO)_5[C(OMe)Me]$ and azoarenes yielded products that could be explained via metathesis intermediates. Previous routes to the bis(phenylimido) clusters of ruthenium have been reported,[8,13,16,20] and $Ru_3(NPh)_2(CO)_9$ has been crystallographically characterized.[29]

The formation of an ortho-metalated cluster during the reaction is dependent on the electronic character of the azoarene ligand and on the reaction conditions. With electron poor aromatic rings such as 4,4′-dinitroazobenzene, ortho metalation is never observed, while with electron-rich aromatic rings, N–N bond cleavage is preferred over ortho metalation only in the presence of CO. These substituent effects parallel those found for the related reaction of azoarenes with palladium compounds[30] that indicated the metal was acting as an electrophile. The fact that the presence of CO favors the formation of the bis(phenylimido) clusters seems to be explained by the reversible nature of the ortho metalation reaction (which involves CO loss). When the ortho-metalated species is reacted with carbon monoxide in refluxing heptane, the N–N bond cleavage products $Ru_3(NPh)(NC_6H_4X)(CO)_9$ and 4-XC_6H_4NCO are produced. Also formed in the reaction is a trace amount of $Ru_3(NPh)(CO)_{10}$ along with a small amount of decomposition material. The best yield of $Ru_3(NPh)(NC_6H_4X)(CO)_9$ obtained from this reaction was 80%. In contrast to the reactivity of the ortho-metalated azoarene cluster, the analogous ortho-metalated *N*-phenylbenzaldimine species III reacts with carbon monoxide to quantitatively regenerate the free ligand and $Ru_3(NPh)(CO)_{10}$. No C–N bond cleavage products were detected, which supports the suggestion that the β-N lone pair (eq 3) attacks an adjacent CO.

It is interesting to compare these results with the reaction of $Ru_3(CO)_{12}$ itself with azobenzene, which was previously reported to yield mono- and dinuclear products from cluster degradation along with $Ru_3(NPh)_2(CO)_9$ (20% yield).[8,20] The triply bridging ligand of $Ru_3(NPh)(CO)_{10}$ appears to prevent cluster fragmentation since only trinuclear products are formed in its reaction with azoarenes. The robust nature of clusters containing the μ_3-NR ligand under certain conditions has been noted previously.[12,31–34] Despite these observations, the μ_3-NR ligand has been a commonly proposed intermediate in catalytic reductions (with H_2 or CO) of nitroaromatics.[34–40] More on the reactive nature of the phenylimido ligand was recently demonstrated by Geoffroy and co-workers[34,35] in a stoichiometric carbene–phenylimido coupling involving $Fe_3(NPh)_2(CO)_8[C(OEt)Ph]$ giving $Fe_3(NPh)(CO)_{10}$ and PhN=C(OEt)Ph under mild conditions [22 °C, CO (1 atm), 8 days]. However, the seemingly analogous CO–phenylimido coupling of $Fe_3(NPh)_2(CO)_9$ at 70 atm and 80 °C for 12 h yielded no isocyanate. Likewise, we have found that $Ru_3(NPh)_2(CO)_9$ is stable toward high CO pressures (170 atm) even at 165 °C. If one less μ_3-NPh group is present, as in $Ru_3(NPh)(CO)_{10}$, fragmentation to $Ru(CO)_5$ and PhNCO occurs slowly (6.5 h) at 170 atm of CO and 120 °C.[41] Clearly, the important factors governing the stability of μ_3-NPh groups have yet to be fully determined.

It is interesting observation that the two fundamental bond activations observed in this study, N–N double bond cleavage and cleavage of the C–H bond ortho to the azo group, are the same two bonds activated in the ruthenium-catalyzed conversion shown in eq 2.[11]

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Registry No. Ia, 107820-83-7; Ib, 51233-18-2; Ic, 102869-62-5; Id, 104198-82-5; IIa, 107820-85-9; IIb, 107820-86-0; III, 107820-88-2; IV, 107820-89-3; V, 107820-90-6; $Ru_3(NPh)(CO)_{10}$, 51185-99-0; $Ru(CO)_2(CH_3OC_6H_3NNC_6H_4OCH_3)_2$, 107820-87-1; PhCHNPh, 538-51-2; 4,4′-dinitroazobenzene, 3646-57-9; 4,4′-dichloroazobenzene, 1602-00-2; azobenzene, 103-33-3; 4,4′-dimethoxyazobenzene, 501-58-6.

Supplementary Material Available: Tables of temperature factors, H-atom positions, and bond angles (5 pages); a listing of structure factors (28 pages). Ordering information is given on any current masthead page.

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