Acknowledgment. We thank the U.S. Army Research Office for the support of this work.

Supplementary Material Available: Listings of the positional and thermal parameters from the final cycle of refinement (Tables I and II), the interatomic distances (Table III), and bond angles (Table IV) (6 pages); a list of observed and calculated structure factors (Table V) (19 pages). Ordering information is given on any current masthead page.

Nitrogen–Nitrogen Double-Bond Scission of Azoarenes by $Ru_3(NAr)(CO)_{10}$. Structure and Catalytic Activity of $H_2Ru_3(NAr)_2(CO)_8$

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Summary: Azoarenes react with $Ru_3(NAr)(CO)_{10}$ giving $Ru_3(NAr)(NAr')(CO)_9$ in high yields. These bis(imido) clusters react with H_2 to give $H_2Ru_3(NAr)(NAr')(CO)_8$, which can be used to catalyze the hydrogenation of olefins.

The cleavage of strong multiple bonds using polynuclear metal complexes is an interesting facet of cluster reactivity. Small molecules such as CO and NO are the sources for the main-group atoms in carbido[3] and nitrido[4] clusters, while larger molecules such as acetylenes[5] and coordinated acyl groups[6] have led to the alkylidyne ligand. In this communication we describe the use of a trinuclear ruthenium cluster to cleave the N–N double bond in azoarenes, the use of the product as a homogeneous catalyst for olefin hydrogenation, and the structure of a new hydrido cluster obtained from the active solutions. The symmetric cleavage of azoarenes is uncommon.[7-9]

The reaction of $Ru_3(NAr)(CO)_{10}$[10,11] with azoarenes was complete in refluxing hexane in 20–24 h (or 6 h in heptane). It was dependent upon the nature of the para substituent on the azoarene with electron-withdrawing groups improving the yield of the bis(imido) clusters (eq 1). Typically, the yields were greater than 50% with 4,4′-dinitroazobenzene forming $Ru_3(NPh)(NC_6H_4NO_2)(CO)_9$ in 85% isolated yield. Both infrared spectroscopy and gas chromatography were used to verify that the second half of the azoarene was converted into an arene isocyanate. An important observation was the complete selectivity for the formation of the unsymmetric product. None of the original arylimido ligand was displaced as the isocyanate. Although inhibited by CO, suggesting that CO dissociation is important in the mechanism, reactions run under an atmosphere of CO gave improved yields (77–97% in refluxing heptane for ~12 h).[12]

$$Ru_3(NAr)(CO)_{10} + Ar'NNAr' \rightarrow Ru_3(NAr)(NAr')(CO)_9 + Ar'NCO \quad (1)$$

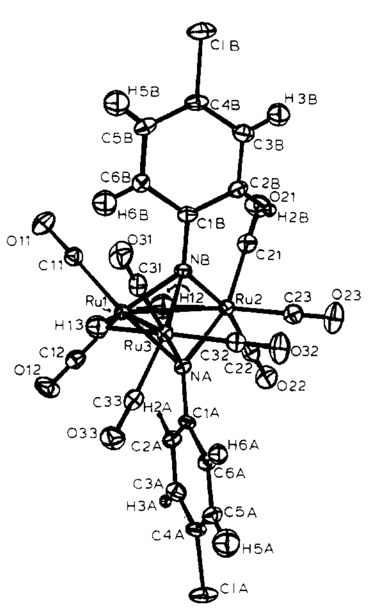
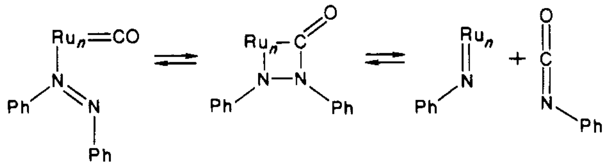


Figure 1. View of $H_2Ru_3(NC_6H_4Cl)_2(CO)_8$ showing the atom labels. Selected distances (Å): Rul–Ru2, 2.686 (1); Rul–Ru3, 2.673 (1); Ru2–Ru3, 3.322 (1); Rul–NA, 2.100 (3); Ru2–NA 2.092 (3); Ru3–NA, 2.077 (3), Rul–H12, 1.74 (5); Rul–H13, 1.64 (4); Ru2–H12, 1.89 (5); Ru3–H13, 1.90 (4). Selected angles (deg): Ru2–Rul–Ru3, 76.62 (1); Rul–NA–Ru2, 79.7 (1); Ru2–NA–Ru3, 105.7 (1); Rul–NA–C1A, 128.2 (2); Ru2–NA–C1A, 122.3 (2); Rul–H12–Ru2, 95 (2); Rul–H13–Ru3, 98 (2), H12–Rul–H13, 164 (2); NA–Ru3–NB, 70.4 (1); C32–Ru3–H13, 177 (1).

Two recent reports of N–N double-bond scission in azoarenes involved a metathesis-like reaction. Cotton and co-workers reported[8] the formation of $[NbCl_2(Me_2S)(NPh)]_2(\mu\text{-}Cl)_2$ in the reaction between azobenzene and the Nb–Nb doubly bonded dimer $Nb_2Cl_6(Me_2S)_3$. Hegedus and co-workers found[9] that photolysis of $Cr(CO)_5[C(OMe)Me]$ and azoarenes led to products that could be explained via metathesis intermediates. One view (eq 2) of the current reaction could involve metathesis of the N–N double bond with the Ru–C bond which clearly has some π character to it. It is also possible that the conversion may occur on more than one of the metal atoms, possibly through an intermediate with a five-membered ring instead of four.



(2)

The two triply bridging arylimido ligands are responsible for the robust nature of these clusters. One use of other such stabilizing ligands has been to maintain the integrity of the cluster throughout a catalytic reaction. This has been reported in several cases using phosphinidene (PR), alkylidyne (CR), or sulfur stabilized homo- or heteronu-

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[12] In the absence of CO, $Ru_3(NAr)(CO)_{10}$ will slowly decompose in refluxing heptane. In a typical synthesis, $Ru_3(NAr)(CO)_{10}$ (21.4 mg, 0.032 mmol) and 4,4′-dinitroazobenzene (40.1 mg, 0.147 mmol) was dissolved in 12 mL of heptane in a 40-mL Schlenk tube. A slow stream of CO was passed over the refluxing solution, and the reaction was monitored by infrared spectroscopy. This particular reaction was complete after 13 h, and the product $Ru_3(NPh)(NC_6H_4NO_2)(CO)_9$ was purified by chromatography on silica gel (eluent, 8% CH_2Cl_2/hexane) and isolated in 97% yield. The para substituents studied were MeO, Me, H, Cl, and NO_2.

clear carbonyl clusters in reactions such as the hydrogenation and hydroformylation of olefins and the transalkylation of amines.[13-15] We examined the activity of these bis(imido) clusters and found that under 3 atm of H_2 at 98 °C catalytic olefin hydrogenation occurred, but the solutions rapidly turned from red to orange. From these solutions a new hydrido cluster was isolated that contained only terminal carbonyl absorptions in the infrared spectrum and an unusually low-field (−8.7 ppm) chemical shift for a hydride.[16] A low-temperature (−95 °C), single-crystal X-ray crystallographic analysis[17] of $H_2Ru_3(NC_6H_4Cl)_2(CO)_8$ revealed a structure (Figure 1) that is very similar to the starting nonacarbonyl.[18] The systematic asymmetry of the bridging hydrogen atoms (average Ru1–H12(13) = 1.69 (5) Å; average Ru2(3)–H12(13) = 1.90 (5) Å) may be the cause of the unusual chemical shift. The dihydrides could be prepared in the absence of olefin, and the reverse reaction occurred quantitatively under CO (3 atm) at 110 °C. It appears as if the equilibrium constant for reaction 3 is not far from unity and, therefore, similar to that found from studies of related ruthenium[19] and iron[20] systems containing bridging alkylidyne ligands.

$$Ru_3(NC_6H_4X)_2(CO)_9 + H_2 \rightleftharpoons CO + H_2Ru_3(NC_6H_4X)_2(CO)_8 \quad (3)$$

When the catalysis was conducted by using the dihydrides, the reactions remained visually homogeneous, and the rate was typically 0.5 turnover/min at 98 °C and 3 atm of H_2.[21] Two crossover experiments, monitored by HPLC, indicated that no scrambling of the arylimido ligands occurred during the reaction. Catalysis by an equimolar mixture of $H_2Ru_3(NPh)_2(CO)_8$ and $H_2Ru_3(NC_6H_4OMe)_2(CO)_8$ failed to yield any of the crossover product $H_2Ru_3(NPh)(NC_6H_4OMe)(CO)_8$. Further, a sample of this unsymmetric cluster catalyzed the hydrogenation without forming either of the two symmetric clusters. The catalytic rates of these three clusters were the same within our current experimental error. It must be stressed that these experiments alone do not prove that the cluster remains intact throughout the reaction. Further studies that are necessary to establish the details of the mechanism are underway.

Acknowledgment. This work was supported by a grant (CHE-8410999) from the National Science Foundation.

Supplementary Material Available: Tables of crystallographic data, bond distances, bond angles, general temperature factor expressions, and positional and thermal parameters (9 pages); a listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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(16) Anal. Calcd for $H_2Ru_3(NC_6H_4Cl)_2(CO)_8$: C, 30.78; H, 1.29; N, 3.59. Found: C, 30.48; H, 1.28; N, 3.48. IR (cm^{-1}, hexane): 2108 w, 2092 s, 2033 vs, 2013 w, 1977 s. ^1H NMR (CD_2Cl_2, ppm): 7.04, 7.01, 6.66, 6.63 (phenyl region), −8.76 (hydride region). Mass spectrum (m/e, ^{102}Ru, ^{37}Cl): 786 (parent ion).

(17) X-ray diffraction data for $C_{20}H_{10}Cl_2N_2O_8Ru_3$: M_r 782.3; d(calcd) = 2.092 g/cm³; crystal system = monoclinic; space group = $P2_1/n$; T = −94 (2) °C; a = 10.969 (5) Å, b = 12.991 (7) Å, c = 17.642 (5) Å; β = 99.78 (2)°; V = 2478 (3) Å³; Z = 4; μ = 20.37 cm^{-1} (empirical correction applied); radiation = Mo Kα; scan range = 0–50°; reflections collected = 5815 unique, 4307 with $F_o > 1.0\ \sigma(F_o)$; R = 0.0257; R_w = 0.0296.

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(21) A typical reaction involves 0.007 mmol of cluster and 0.35 mmol of 3,3-dimethylbutene in 10.0 mL of heptane. Hexane was used as the internal GC standard. Since some of the volatile olefin and alkane escaped during the monitoring process, the rate was based on the actual amount of alkane detected by gas chromatography. All of the olefin was consumed during the reaction. While detailed kinetic studies are underway, preliminary studies indicated the reaction is sensitive to the pressure of hydrogen and was inhibited by the addition of CO. HPLC monitoring of the reaction indicated that the dihydrido cluster was present throughout the catalysis. At the end of the reaction only a small amount (3%) of the dihydrido cluster was lost by the cleavage of one of the arylimido ligands to form aniline (or the substituted derivative) and the known cluster $H_2Ru_3(NAr)(CO)_9$.[10] Pure samples of this species also catalyzed the reaction, but the rate was no faster than that for the bis(imido) clusters.

Photoinduced Ring Expansion of Cyclobutyliron σ-Complexes: An Example of Rearrangement of an Aryl Group from Saturated Carbon to a Transition Metal To Give a Carbene Complex

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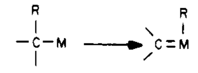
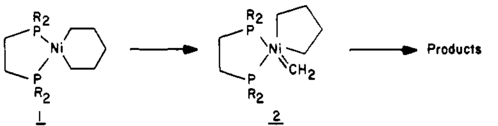
Summary: Photolysis of dicarbonyl(η^5-cyclopentadienyl)(1-methoxybenzocyclobutenyl)iron (**10**) gives a mixture of two rearranged carbene complexes (**11** and **12**) in a ratio of 73/27. These products are suggested to arise respectively from rearrangement of phenyl and benzyl from C-1 to coordinatively unsaturated iron. From the product ratio, it is concluded that aryl rearranges a bit faster than benzyl. The rearrangement is irreversible up to 77 °C. Photolysis of dicarbonyl(η^5-cyclopentadienyl)(1-*p*-thiocresylbenzocyclobutenyl)iron (**13**) also leads to a new product that is tentatively assigned structure **14**. If correct, this is the first example of a thiocresyl-induced rearrangement of this type. An X-ray crystal structure of **11** is reported.

Rearrangement of alkyl groups from saturated carbon to electron-deficient transition metals (eq 1) has recently

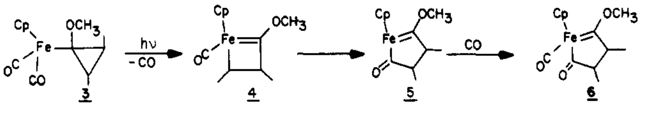


$$-\underset{|}{\overset{\overset{\displaystyle R}{|}}{C}}-M \longrightarrow \;>C{=}\overset{\overset{\displaystyle R}{|}}{M} \qquad (1)$$

been extended from Grubbs' original report[1] that deuterium-labeling studies on the decomposition of 1 were most consistent with intermediacy of the carbene complex 2 to our suggestion[2] that the photoinduced conversion of



3 to 6 proceeds via 4 and our finding[3] that photolysis of



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