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Synthesis of Dimetallaazacyclobutenes via Reaction of Polynuclear Heteroaromatic Nitrogen Compounds with Triruthenium Dodecacarbonyl: Reactivity and Structural Elucidation

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The reactions of triruthenium dodecacarbonyl ($Ru_3(CO)_{12}$) with polynuclear heteroaromatic nitrogen compounds, such as quinoline, 1,2,3,4-tetrahydroquinoline, phenanthridine, and 9,10-dihydrophenanthridine, provided an entry to a series of dimetallaazacyclobutenes. The common structural feature among these complexes is the bonding of the nitrogen and the 2-carbon atoms of the heterocyclic ligand and a bridging hydride to one edge of the ruthenium cluster. Regardless of whether we started with the unsaturated or saturated nitrogen ring, we always found the formation of a carbon–nitrogen double bond in the dimetallaazacyclobutene structure. Under our reaction conditions, we found that quinoline gave the mono ligand complex $Ru_3(\mu\text{-H})(\mu\text{-}C_9H_6N)(CO)_{10}$ (1) even in the presence of excess ligand, while 1,2,3,4-tetrahydroquinoline (THQ) provided a mixed bis complex, 2, i.e., a quinoline ligand and 3,4-dihydroquinoline ligand, $Ru_3(\mu\text{-H})_2(\mu\text{-}C_9H_6N)(\mu\text{-}C_9H_8N)(CO)_8$. The THQ reaction also provided small amounts of the bis(quinoline) complex $Ru_3(\mu\text{-H})_2(\mu\text{-}C_9H_6N)_2(CO)_8$ (3) and $H_4Ru_4(CO)_{12}$ (4). Thus, dehydrogenation of the saturated nitrogen ring is a predominant reaction in the synthesis of these ruthenium clusters containing polynuclear heteroaromatic nitrogen compounds as ligands. The X-ray structure of the phenanthridine–triruthenium decacarbonyl complex $Ru_3(\mu\text{-H})(\mu\text{-}C_{13}H_8N)(CO)_{10}$ (5) was determined. Complex 5 crystallizes with four molecules in space group C_{2h}^5—$P2_1/c$ of the monoclinic system in a cell of dimensions $a = 11.805$ (6) Å, $b = 7.584$ (6) Å, $c = 27.747$ (6) Å, and $\beta = 91.13$ (3)°. The structure has been refined to an R index on F of 0.0184 for 2876 observations and 339 variables. The planar nitrogen ligand is situated approximately perpendicular to the triangle of ruthenium atoms while the dihedral angle between the plane of ruthenium atoms and the Ru(2), Ru(3), and H(1) atoms is only 32.5°. Several reactions of complexes 1 and 5 were performed and included hydrogenation and hydride reactions. Hydrogenation afforded the starting polynuclear heteroaromatic nitrogen ligand and tetrahydridotetraruthenium dodecacarbonyl, $H_4Ru_4(CO)_{12}$, while hydride reagents, $LiAlH_4$ or $LiBEt_3H$, showed no reactivity.

Introduction

We, as well as others, have found that a wide variety of transition-metal compounds[1a-g] catalyze the homogeneous, regiospecific hydrogenation of polynuclear heteroaromatic nitrogen and sulfur compounds. The mechanism of hydrogenation of the nitrogen heterocyclic ring involves prior coordination of the nitrogen compound to the catalytic metal center using either rhodium or ruthenium complexes.[1b,d]

These rhodium and ruthenium complexes were either mono- or tetranuclear, and thus it would be of interest to define more clearly the coordination of the polynuclear heteroaromatic nitrogen compounds to catalytic metal centers. We chose to study the ruthenium cluster, $Ru_3(CO)_{12}$, where several ruthenium metal centers were available for bonding to the nitrogen ring. Recently, several groups have reported on the reactions of polynuclear heteroaromatic nitrogen compounds with metal clusters. These include the studies of Yin and Deeming[2] with the triosmium cluster $Os_3(CO)_{12}$ and polynuclear heteroaromatic compounds such as pyridines and quinolines. The resultant substituted clusters have been characterized spectroscopically as a triangle of osmium atoms with the nitrogen heterocycle bound to an edge of the cluster via σ bonds to the nitrogen and the 2-carbon atoms. More recently, Laine et al.[3] substantiated the structure of both mono- and disubstituted quinoline–triosmium clusters by X-ray analysis and extended the examples to saturated nitrogen heterocyclic compounds such as piperidines and 1,2,3,4-tetrahydroquinoline. An excellent review of cyclometalated complexes with heterocyclic ligands, covering many other examples, was recently published by Constable.[4]

While our present study on the triruthenium cluster $Ru_3(CO)_{12}$ and its reactions with quinoline, 1,2,3,4-tetrahydroquinoline, phenanthridine, and 9,10-dihydrophenanthridine was underway, Laine et al.[3] and Lewis et al.[5] both reported the quinoline–triruthenium complex. Our present results extend the knowledge in the synthesis and reactivity of dimetallaazacyclobutene compounds of ruthenium with the above-mentioned nitrogen ligands. In addition, we report the X-ray crystal structure of the phenanthridine–triruthenium derivative $Ru_3(\mu\text{-H})(\mu\text{-}C_{13}H_8N)(CO)_{10}$ (5) as well as the reactions of the quinoline- and phenanthridine–triruthenium complexes 1 and 5, respectively, with hydrogen gas and hydride reagents.

Results and Discussion

The Reaction of Quinoline with Triruthenium Dodecacarbonyl ($Ru_3(CO)_{12}$). The reaction of triruthenium dodecacarbonyl ($Ru_3(CO)_{12}$) with excess quinoline provided only the mono-substituted four-membered

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[1] (a) Fish, R. H.; Thormodsen, A. D.; Cremer, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 5234. (b) Fish, R. H.; Tan, J. L.; Thormodsen, A. D. *J. Org. Chem.* **1984**, *49*, 4500. (c) Fish, R. H. *Ann N.Y. Acad. Sci.* **1983**, *415*, 292. (e) Fish, R. H.; Thormodsen, A. D.; Heinemann, H. *J. Mol. Catal.* **1985**, *31*, 191. (d) Fish, R. H.; Tan, J. L.; Thormodsen, A. D. *Organometallics* **1985**, *4*, 1743. (f) Lynch, T. J.; Banah, M.; McDougall, M.; Kaesz, H. D.; Porter, C. R. *J. Mol. Catal.* **1982**, *17*, 109. (g) Lynch, T. J.; Banah, M.; Kaesz, H. D.; Porter, C. R. *J. Org. Chem.* **1984**, *49*, 1266.

[2] Yin, C. C.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1975**, 2091.

[3] Eisenstadt, A.; Giandomenico, C. M.; Frederick, M. F.; Laine, R. M. *Organometallics* **1985**, *4*, 2033.

[4] Constable, E. C. *Polyhedron* **1984**, *3*, 1037.

[5] Foulds, G. A.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1985**, *294*, 123.

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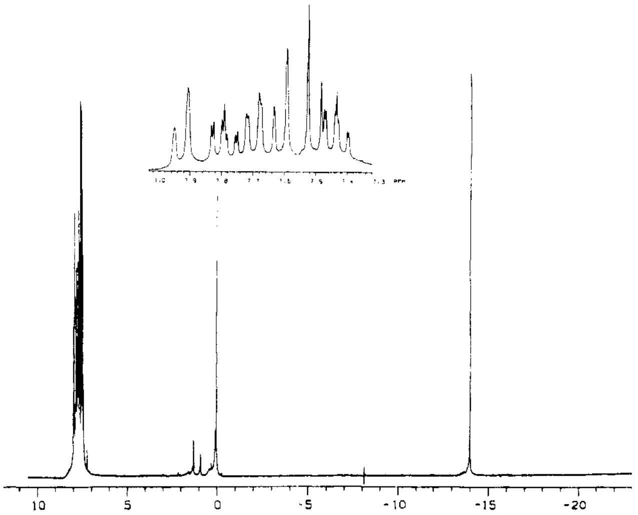
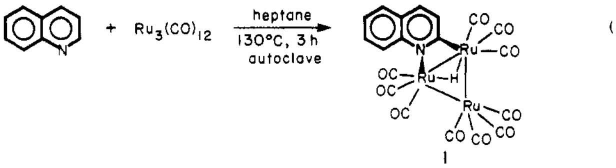


Figure 1. 200-MHz ^1H NMR spectrum of complex 1.

ring dimetallaazacyclobutene complex 1 in 69% yield (eq 1). The reaction was performed in a sealed autoclave, in order to prevent decomposition from loss of CO, in heptane at 130 °C for 2–3 h under argon. This result is in contrast to the recently reported result of Laine et al.[3] where they obtain the mono- and bis(quinoline)–ruthenium complex in a 1:2 ratio under similar conditions, but with methylcyclohexane as the solvent. In addition, Laine's group also found that the reaction product ratio was affected by a carbon monoxide atmosphere. This resulted in a 17:1 ratio of mono to bis complex and clearly indicates that the product ratio is extremely dependent upon the reaction conditions.



(1)

The orange-red complex 1 has been formulated from its ^1H and ^{13}C NMR and IR spectra as well as by elemental and mass spectral analyses and was consistent with the reported parameters.[3] The 200-MHz ^1H NMR spectrum of 1 (Figure 1) showed the absence of the 2-carbon proton, which appears as a doublet of doublets in the spectrum of free quinoline at 8.81 ppm. The proton of the 8-carbon atom remains evident in the spectrum of the quinoline derivative. As expected, all of the signals due to the remaining aromatic protons shift upfield upon coordination to the triruthenium cluster. The bridging hydride signal of the quinoline complex, a singlet, occurs at −14.01 ppm. This value is normal for hydrides bridging an edge of a triruthenium cluster, e.g., $Ru_3(\mu\text{-}H)(\mu\text{-}O{=}C(Me))(CO)_{10}$ at −13.88 ppm[6] and $NEt_4Ru_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}$ at −12.76 ppm.[7]

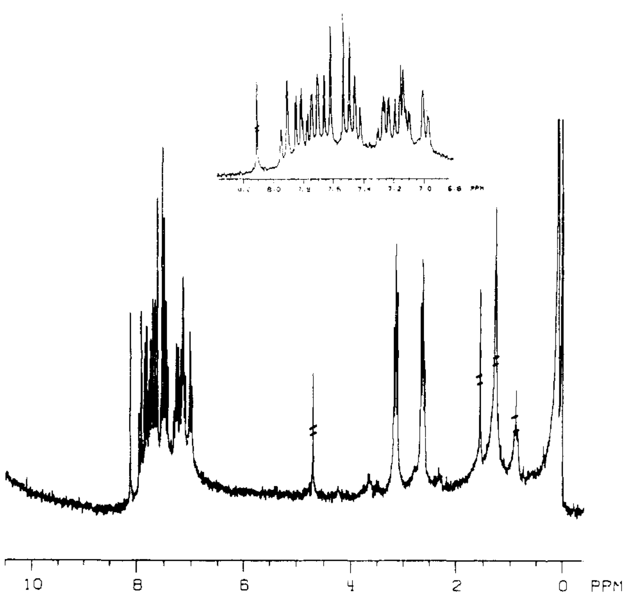
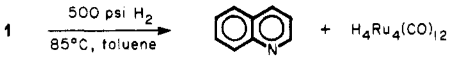


Figure 2. 200-MHz ^1H NMR spectrum of complex 2.

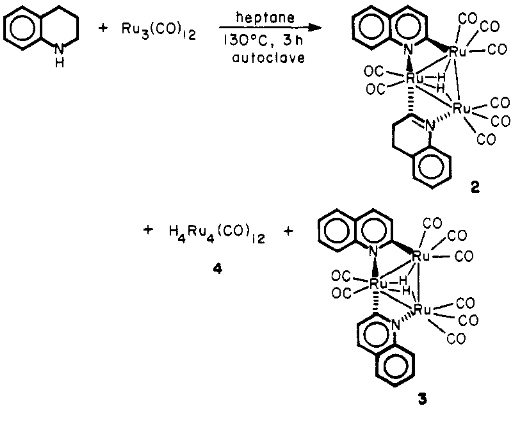
The Reaction of 1 with Hydrogen Gas. In order to determine the utility of the dimetallaazacyclobutenes as potential model intermediates in catalytic hydrogenation reactions, we studied the reaction of complex 1 with hydrogen gas (500 psi at 85 °C in toluene) and found that quinoline was formed along with $H_4Ru_4(CO)_{12}$ (eq 2). Apparently, the ligand is released as the cluster reacts with H_2 to form $H_4Ru_4(CO)_{12}$, a catalyst we studied in the hydrogenation of polynuclear heteroaromatic nitrogen compounds including quinoline.[1a,c]



(2)

The Reaction of Complex 1 with Hydride Reagents. Complex 1 was treated with both $LiAlH_4$ and $LiBEt_3H$; however, 1 does not appear to react even under forcing conditions, i.e., 60 °C for several hours in THF. Apparently, the carbon–nitrogen double bond is not reduced in the complex, while in the free ligand it is readily reduced.[8a,b] We can infer from these results that the nitrogen ligand is not the site of reaction with hydride or H_2 reactants (vide supra) for reasons that are not apparent as yet.

The Reaction of 1,2,3,4-Tetrahydroquinoline with $Ru_3(CO)_{12}$. $Ru_3(CO)_{12}$ reacts with 1,2,3,4-tetrahydroquinoline, under similar conditions as described above in the synthesis of the quinoline derivative, to form several different species. The major product 2 (33%) was a novel triruthenium cluster containing one molecule of quinoline and one of 3,4-dihydroquinoline. The proposed structure (eq 3) is based on ^1H and ^{13}C NMR, infrared, and mass spectroscopic evidence.



(3)

In the 200-MHz ^1H NMR spectrum, the region from 7.4 to 8.0 ppm strongly resembles that of the monosubstituted

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(6) Boag, N. M.; Kampe, C. E.; Lin, Y. C.; Kaesz, H. D. *Inorg. Chem.* **1982**, *21*, 1704.

(7) Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Suss, G. *J. Chem. Soc., Dalton Trans* **1979**, 1356.

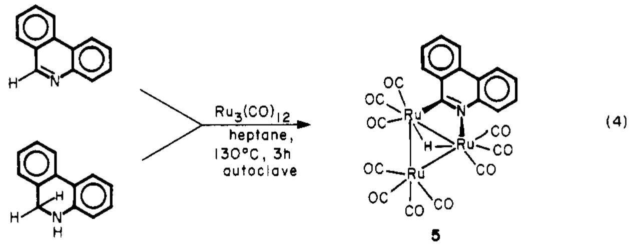
(8) (a) Braude, E. A.; Hannah, J.; Linstead, R. P. *J. Chem. Soc.* **1960**, 3249. (b) Wooten, W. C.; McKee, R. L. *J. Am. Chem. Soc.* **1949**, *71*, 2946.

quinoline derivative, complex 1. The 6.9–7.3 ppm region of the same NMR spectrum can therefore be interpreted as signals due to the 3,4-dihydroquinoline aromatic protons. Two triplets due to the methylene protons are located at 3.18 and 2.62 ppm (Figure 2). Signals for the two bridging hydrides were found at −14.01 and −17.64 ppm. The electron-impact mass spectrum (EIMS) had prominent fragment ions at *m/e* 687 ($M^{\bullet+}$ − Ru), 658 ($M^{\bullet+}$ − quinoline), and 657 ($M^{\bullet+}$ − 3,4-dihydroquinoline) and a sequence of ions that show a loss of CO from the *m/e* 658 and 657 ions to give eventually the ions at *m/e* 433 and 432 ($M^{\bullet+}$ − 8CO − quinoline or 3,4-dihydroquinoline). Additionally, the solution IR spectrum shows 12 CO stretches from 2104 to 1970 cm^{-1}. The osmium analogue of complex 2 was formed in minor amounts in the $Os_3(CO)_{12}$ reaction with THQ.[3]

The other minor products in the THQ reaction with $Ru_3(CO)_{12}$ are the bis(quinoline) complex 3[3] (<1%) and $H_4Ru_4(CO)_{12}$, 4 (15%). Complex 2 appears to disproportionate readily in cold (−30 °C) acetone over several days to afford $H_4Ru_4(CO)_{12}$ and quinoline. In an experiment to determine whether we could form complex 2 from complex 1, we reacted 1 with THQ but found only starting material and $H_4Ru_4(CO)_{12}$, 2 was not detected.

The formation of substantial amounts (15%) of $H_4Ru_4(CO)_{12}$ in the THQ reaction clearly indicates the production of hydrogen via a dehydrogenation mechanism occurring in the saturated nitrogen rings. While a mechanism has been proposed for the THQ–triosmium reaction pathway that also shows a tendency for these compounds to form dehydrogenated complexes,[3] our present results do not rule out $Ru_3(CO)_{12}$ as the dehydrogenating agent in a more complicated pathway leading to $H_4Ru_4(CO)_{12}$. The corresponding THQ studies with $Os_3(CO)_{12}$ did not report any osmium hydride products such as $Os_3H_2(CO)_{10}$ and $Os_4H_4(CO)_{12}$,[9] but their presence cannot be ruled out.[3]

The Reaction of Phenanthridine and Dihydrophenanthridine with $Ru_3(CO)_{12}$. The reaction of either phenanthridine or 9,10-dihydrophenanthridine with $Ru_3(CO)_{12}$ provided the same compound, 5 (eq 4). The NMR spectrum was consistent with the proposed structure of 5 with the absence of the C-9 proton at ca. 9.3 ppm, while the other signals were found between 8.4 and 7.61 ppm in the correct ratios and the bridging hydride was found at −13.73 ppm. The solution IR showed eight CO stretches between 2106 and 1991 cm^{-1}, while the EIMS had prominent ions at *m/e* 706 ($M^{\bullet+}$ − 2CO), 594 ($M^{\bullet+}$ − 6CO), and 482 ($M^{\bullet+}$ − 10CO).



(4)

In previous homogeneous catalytic hydrogenation studies with mononuclear ruthenium complexes, we showed, using deuterium gas in place of hydrogen gas, that reversibility, i.e., dehydrogenation, in the reduction of the nitrogen ring was a predominant reaction that led to placing two deuteriums on the carbon atom α to nitrogen.[1a,d] The present results confirm that the dehydrogenation pathway is prevalent in the synthesis of dimetallaazacyclobutenes. Clearly, the mechanism of dehydrogenation in these dimetallaazacyclobutenes complexes of ruthenium needs to be elucidated in a more systematic manner.

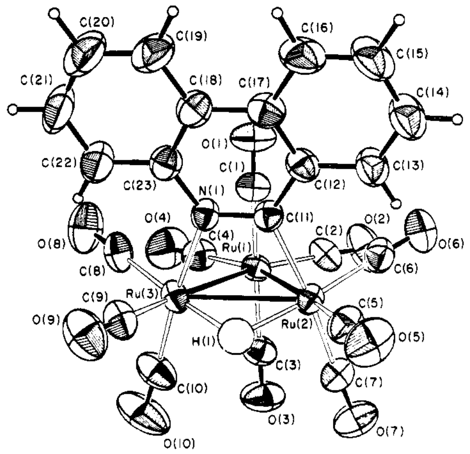


Figure 3. ORTEP diagram of $Ru_3(\mu\text{-}H)(\mu\text{-}C_{13}H_8N)(CO)_{10}$ (5) showing 50% probability ellipsoids.

Table I. Crystal Data for $Ru_3(\mu\text{-}H)(\mu\text{-}C_{13}H_8N)(CO)_{10}$ (25 °C)

space group	$P2_1/c$(monoclinic)
a, Å	11.805 (6)
b, Å	7.584 (6)
c, Å	27.747 (6)
β, °	91.13 (3)
V, $Å^3$	2483
Z	4
formula mass, amu	762.5
ρ(calcd), g/cm^3	2.04
ρ(obsd) g/cm^3	2.03
μ(Mo Kα), cm^{-1}	18.2
total data	3709
unique data	3050
unique data with $\lvert F_o\rvert^2 > 3\sigma\lvert F_o\rvert^2$	2876
final no. of variables	339
R(*F*), %	1.84
$R_w(F)$, %	2.94
GOF (e^2)	1.53
diffractometer	Enraf-Nonius CAD-4
monochromator	highly oriented graphite
radiation (Mo Kα)	0.71073 Å
scan range, type	$3 < 2\theta < 45$, ω
scan speed	0.63–6.7° min^{-1}
scan width, det	$\Delta\theta = (0.50 + 0.347 \tan\theta)$

The Reaction of Complex 5 with Hydrogen Gas and Hydride Reagents. The hydrogenation of complex 5, under longer reaction times than studied with complex 1, again provided the free ligand and $H_4Ru_4(CO)_{12}$ (4) as well as some of the reduced ligand 9,10-dihydrophenanthridine. This result is not too surprising, since the hydride 4 was active as a catalyst in the hydrogenation of polynuclear heteroaromatic nitrogen compounds.[1a,c] As with complex 1, complex 5 was unreactive in the presence of $LiAlH_4$ or $LiBEt_3H$. Again this is in contrast to the free ligand, which is readily reduced by $LiAlH_4$.[8a,b] It is conceivable that steric effects could prevent close proximity of the hydride reagents to the coordinated C–N double bond. Surprisingly, the hydride reagent does not attack the ruthenium cluster in contrast to the hydrogenation reaction.

The X-ray Crystal Structure of $Ru_3(\mu\text{-}H)(\mu\text{-}C_{13}H_8N)(CO)_{10}$ (5). In order to define more clearly the structure of 5 and compare the results to the recently reported X-ray crystal data of the quinoline–triosmium complex,[3] we performed a single-crystal X-ray analysis of 5; an ORTEP representation of the molecule is shown in Figure 3. The crystal data are presented in Table I. The molecule contains an isosceles triangle of ruthenium atoms

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(9) Knox, S. A. R.; Koepke, J. W.; Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3942.

Table II. Selected Bond Distances (Å) and Angles (deg) in $Ru_3(\mu\text{-}H)(\mu\text{-}C_{13}H_8N)(CO)_{10}$

Bond Distances			
Ru(1)-Ru(2)	2.851 (1)	Ru(3)-N(1)	2.133 (1)
Ru(2)-Ru(3)	2.866 (1)	Ru(3)-C(8)	1.894 (3)
Ru(3)-Ru(1)	2.844 (1)	Ru(3)-C(9)	1.920 (3)
Ru(1)-C(1)	1.931 (3)	Ru(3)-C(10)	1.918 (3)
Ru(1)-C(2)	1.906 (3)	Ru(3)-H(1)	1.76 (3)
Ru(1)-C(3)	1.930 (3)	N(1)-C(11)	1.312 (0)
Ru(1)-C(4)	1.920 (3)	C(18)-C(19)	1.397 (4)
Ru(2)-C(11)	2.133 (1)	C(18)-C(23)	1.401 (4)
Ru(2)-C(5)	1.912 (3)	C(19)-C(20)	1.373 (5)
Ru(2)-C(6)	1.905 (3)	C(20)-C(21)	1.363 (5)
Ru(2)-C(7)	1.915 (3)	C(21)-C(22)	1.367 (4)
Ru(2)-H(1)	1.81 (3)	C(22)-C(23)	1.419 (4)
		C(23)-N(1)	1.424 (3)
Bond Angles			
Ru(1)-Ru(2)-Ru(3)	59.66 (1)	C(7)-Ru(2)-Ru(1)	88.21 (9)
Ru(2)-Ru(3)-Ru(1)	59.92 (1)	C(7)-Ru(2)-Ru(3)	106.17 (9)
Ru(3)-Ru(1)-Ru(2)	60.42 (1)	C(7)-Ru(2)-C(5)	91.91 (12)
Ru(2)-H(1)-Ru(3)	106.9 (16)	C(7)-Ru(2)-C(6)	91.14 (12)
H(1)-Ru(3)-Ru(2)	37.1 (9)	C(7)-Ru(2)-C(11)	173.89 (11)
H(1)-Ru(2)-Ru(3)	36.0 (9)	C(7)-Ru(2)-H(1)	91.6 (8)
C(1)-Ru(1)-Ru(2)	85.20 (8)	C(10)-Ru(3)-Ru(1)	87.80 (9)
C(1)-Ru(1)-Ru(3)	85.02 (8)	C(10)-Ru(3)-Ru(2)	106.00 (11)
C(1)-Ru(1)-C(2)	93.42 (12)	C(10)-Ru(3)-N(1)	174.26 (13)
C(1)-Ru(1)-C(3)	173.07 (12)	C(10)-Ru(3)-C(8)	90.99 (14)
C(1)-Ru(1)-C(4)	94.55 (12)	C(10)-Ru(3)-C(9)	92.94 (13)
		C(10)-Ru(3)-H(1)	91.1 (8)

with a hydride atom and the phenanthridine ligand bridging one edge. The Ru(2)-Ru(3) bond (2.866 (1) Å), spanned by the two bridging ligands, is significantly longer than the other two Ru-Ru bonds (2.851 (1), 2.844 (1) Å) (Table II). In fact, this bond is longer than the average Ru-Ru bond length in $Ru_3(CO)_{12}$ (2.854 (7) Å).[10] It has been noted previously, by Churchill, DeBoer, and Rotella, that a hydride bridging two or more metal atoms unaccompanied by other bridging groups causes a lengthening of the metal-metal bond.[11] However, those metal-metal bonds bridged by a hydride and another ligand are generally shortened relative to the metal-metal bond in the unsubstituted compound. Bruce has suggested that the metal-metal bond length is a measure of the donor and π-acceptor capacity of the bridging ligand.[12] For example, if the bridging group is a good π-acceptor, a counter-balancing shortening effect on the metal-metal bond is noted: e.g., $HRu_3(CO)_{10}(COCH_3)$, 2.803 Å;[13] $HRu_3(CO)_{10}(C_2\text{-}t\text{-}Bu)$, 2.792 Å.[14] In this case, because the bond is lengthened, we conclude that the phenanthridine is only weakly bound to the cluster and does not seem to be involved in any delocalized back-bonding with the metals.

The phenanthridine ligand is nearly planar, the maximum deviations being those of atoms C(14) and C(22), 0.024 and −0.043 Å, respectively, from the best-weighted least-squares plane. The heterocyclic ligand is nearly perpendicular to the triangle of ruthenium atoms with a dihedral angle of 106.7° between the two planes. The angle between the plane of metal atoms and the plane consisting of Ru(2), Ru(3), and H(1) is 32.5°. The dihedral angle between the plane of the phenanthridine ligand and the Ru(2)-Ru(3)-H(1) plane is 74.2°, probably due to the steric congestion of the carbonyl ligands and the bulk of the phenanthridine. In comparison with the bond parameters of free phenanthridine, the C(11)-N bond is lengthened upon coordination by 0.021 Å (1.312 vs. 1.291 Å).[15] This effect has been noted previously in the case of coordination of alkenes and alkynes to Pt(II) and Pt(0) where the C-C bond lengthens by 0.015-0.02 Å.[16] The length of the C(11)-N bond of this study is somewhat shorter than those reported for similar osmium clusters with coordinated heterocycles, e.g., $Os_3(\mu\text{-}H)(\mu\text{-}C_9H_6N)(CO)_{10}$, 1.329 (35) Å, $Os_3(\mu\text{-}H)_2(\mu\text{-}C_9H_6N)_2(CO)_8$, 1.367-1.383 Å[3]. Other osmium clusters with bridging C-N bonds have bond lengths in the range 1.21-1.403 Å.[17a-c] Nubel, Wilson, and Brown have reported a dinuclear bridged pyridine complex, $Re_2(\mu\text{-}H)(\mu\text{-}C_5H_4N)(CO)_8$, with a C-N bond length of 1.372 (9) Å.[18]

Conclusions

The results we report in this study clearly point out that the dimetallaazacyclobutenes may be potential models for catalytic hydrogenation intermediates but are not good models[3] for the study of carbon-nitrogen bond cleavage reactions with nucleophilic reagents. It appears that the ruthenium cluster rather than the complexed nitrogen ligands is the site of reaction with hydrogen gas and electrophiles.[19] We plan to synthesize the three-member-ring mononuclear compounds, the metallaazacyclopropanes, with rhodium and iridium, to see if these are more appropriate models to study C-N bond cleavage reactions.

Experimental Section

All experiments were conducted under an atmosphere of nitrogen or argon using standard Schlenk techniques unless otherwise noted. $Ru_3(CO)_{12}$ was obtained from Strem Chemical Co. and was used as received. Quinoline and 1,2,3,4-tetrahydroquinoline were vacuum distilled and stored in the glovebox prior to use. Phenanthridine was purchased from Aldrich and was sublimed at 50 °C and 10^{-3} torr while dihydrophenanthridine was prepared by catalytic hydrogenation of phenanthridine.[1b] Heptane, toluene, and tetrahydrofuran (THF) were distilled under nitrogen from sodium benzophenone ketyl. Methylene chloride was distilled from CaH_2. $LiBEt_3H$ was supplied by Alfa as a 1.26 M solution in THF.

^1H and ^{13}C NMR spectra were recorded as $CDCl_3$ solutions using a 200-MHz high-field instrument assembled by Mr. Rudi Nunlist (UCB). All chemical shifts are reported relative to tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer 598 grating spectrophotometer using NaCl solution cells. Column chromatography was performed on silica gel (Davisil, grade 62, 60-200 mesh; purchased from Aldrich) under an atmosphere of argon. The reactor used for the closed-system high-temperature reactions has been described elsewhere.[1b]

$Ru_3(\mu\text{-}H)(\mu\text{-}C_9H_6N)(CO)_{10}$ (1). To the 45-mL glass liner of the reactor was added 0.2 g of $Ru_3(CO)_{12}$ (0.313 mmol) 0.21 mL of quinoline, and 10 mL of heptane. The mixture was degassed with argon and the reactor sealed. The entire reactor was then purged with argon and lowered into an oil bath. The reaction

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(10) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655.

(11) Churchill, M. R.; DeBoer, B. G.; Rotella, F. J. *Inorg. Chem.* **1976**, *15*, 1843.

(12) Bruce, M. I. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 4, Chapter 32.5.

(13) Johnson, B. F. G.; Lewis, J.; Orpen, A. G.; Raithby, P. R.; Suss, G. *J. Organomet. Chem.* **1979**, *173*, 187.

(14) Catti, M.; Gervasio, G.; Mason, S. A. *J. Chem. Soc., Dalton Trans.* **1977**, 2260.

(15) Roychowdhury, P. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *29B*, 1362.

(16) Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33.

(17) (a) Adams, R. D.; Dawoodi, Z.; Foust, D. F.; Segmuller, B. E. *J. Am. Chem. Soc.* **1983**, *105*, 831. (b) Adams, R. D.; Dawoodi, Z. *J. Am. Chem. Soc.* **1981**, *103*, 6510. (c) Dawoodi, Z.; Mays, M. J.; Raithby, P. R. *J Organomet. Chem.* **1981**, *219*, 103.

(18) Nubel, P. O.; Wilson, S. R.; Brown, T. L. *Organometallics* **1983**, *2*, 515.

(19) Reactions with an electrophilic reagent, trifluoroacetic acid, also appear to attack the ruthenium cluster to give H_2 and CO gas and a compound which we could not identify unequivocally (unpublished results of J.W. Dupon).

mixture was stirred and held at 130 °C for 3 h. At this time, the reactor was cooled to room temperature, vented, and opened in air. The resulting red solution was concentrated and chromatographed on silica gel, eluting with hexane, to give 0.1544 g of $Ru_3(\mu\text{-}H)(\mu\text{-}C_9H_6N)(CO)_{10}$ (**1**: 0.21 mmol, 69%) as well as 0.02 g of recovered $Ru_3(CO)_{12}$. **1** was crystallized from hexane as orange-red prisms, mp 122–124 °C. IR (cyclohexane): ν_{CO} 2107 vs, 2082 sh, 2067 vs, 2059 vs, 2032 vs, 2021 vs, 2008 vs, 1993 vs, 1984 vs, 1974 sh, 1954 sh cm^{-1}. ^1H NMR: δ 7.93 (b d, 1 H), 7.79 (t, 1 H), 7.69 (d, 1 H), 7.68–7.48 (q, 2 H), 7.43 (t, 1 H), −14.01 (s, 1 H). $^{13}C\{^1H\}$ NMR: δ 207.5, 204.2, 201.0, 200.8, 195.8, 191.6, 190.8, 190.4, 187.2, 186.8. Anal. Calcd for $C_{19}H_7NO_{10}Ru_3$: C, 32.30; H, 0.98; N, 1.97. Found: C, 32.01; H, 0.92; N, 1.97.

$Ru_3(\mu\text{-}H)_2(\mu\text{-}C_9H_6N)(\mu\text{-}C_9H_8N)(CO)_8$ (2). $Ru_3(CO)_{12}$ (0.205 g, 0.32 mmol), 10 mL of heptane, and 0.16 mL of 1,2,3,4-tetrahydroquinoline (1.3 mmol, 4× excess) were combined in the reactor cup of the Parr autoclave and degassed with argon. The reactor was sealed, and the mixture was stirred at 130 °C for 3 h. After being cooled to room temperature and vented, the reactor was opened in air and the contents were filtered through a glass frit. Thin-layer chromatography on preparative scale silica gel plates revealed four bands (eluted with 10:1 hexane/diethyl ether): 0.001 g of $Ru_3(CO)_{12}$: 0.084 g (33%) of $Ru_3(\mu\text{-}H)_2(\mu\text{-}C_9H_6N)(\mu\text{-}C_9H_8N)(CO)_8$ (**2**); 0.001 g (<1%) of $Ru_3\ (\mu\text{-}H)_2(\mu\text{-}C_9H_6N)_2(CO)_8$ (**3**); 0.0355 g (15%) of $Ru_4H_4(CO)_{12}$ (**4**). IR (cyclohexane): ν_{CO} 2104 sh, 2099 m, 2085 m, 2072 vs, 2059 s, 2047 vs, 2029 vs, 2013 s, 2007 sh, 1994 s, 1976 m, 1970 m cm^{-1}. ^1H NMR: δ 7.94 (b d, 1 H), 7.82 (t, 1 H), 7.73 (d, 1 H), 7.65–7.48 (q, 2 H), 7.44 (t, 1 H), 7.25 (d, 1 H), 7.19–7.08 (overlapping t, 1 H), 6.98 (d, 2 H), 3.1 (t, 2 H), 2.62 (t, 2 H), −14.1 (s, 1 H), −17.64 (s, 1 H). EIMS (*m/e*): 687, 659, 574, 546, 519, 489, 461, 432, 129. It decomposes without melting at 130–150 °C.

Attempted Reaction of $Ru_3(\mu\text{-}H)(\mu\text{-}C_9H_6N)(CO)_{10}$ with 1,2,3,4-Tetrahydroquinoline. $Ru_3(\mu\text{-}H)(\mu\text{-}C_9H_6N)(CO)_{10}$ (0.13 g, 0.18 mmol), 20 mL of heptane, and 0.045 mL (0.36 mmol, 2× excess) 1,2,3,4-tetrahydroquinoline (THQ) were degassed with argon and sealed into the Parr reactor. The mixture was heated to 130 °C for 5 h. After the reactor was cooled and vented the solvent was evaporated into a liquid N_2 cooled trap. GC analysis of the volatiles showed that only free THQ was present; no evidence for free quinoline was observed. The remaining orange oily solid was chromatographed on a preparative scale silica plate (eluent hexane): band 1 was shown to be $Ru_3(\mu\text{-}H)(\mu\text{-}C_9H_6N)(CO)_{10}$ by IR and NMR spectroscopy and band 2 was $H_4Ru_4(CO)_{12}$.

Reaction of $Ru_3(\mu\text{-}H)(\mu\text{-}C_9H_6N)(CO)_{10}$ (1) with H_2 Gas. $Ru_3(\mu\text{-}H)(\mu\text{-}C_9H_6N)(CO)_{10}$ (0.05 g, 0.07 mmol) and 10 mL of toluene were sealed into the Parr reactor. The reactor was purged by filling with H_2 gas and then releasing the gas pressure several times. The apparatus was then charged with 500 psi of H_2 and lowered into a constant temperature bath held at 85 °C. After 2 h of stirring at this temperature, the reactor was opened in air and the contents were removed for analysis. GC analysis of the solvent showed the presence of free quinoline. The yellow residue was identified as $Ru_4H_4(CO)_{12}$ by comparison to the IR and ^1H NMR characterization of an authentic sample.[9]

$Ru_3(\mu\text{-}H)(\mu\text{-}C_{13}H_8N)(CO)_{10}$ (5). In a similar experiment, the autoclave reactor was charged with 0.1722 g of $Ru_3\ (CO)_{12}$ (0.27 mmol), 0.05 g of phenanthridine, and 10 mL of heptane. After being degassed with argon, the mixture was heated at 135 °C for 2.5 h. Chromatography (eluent, hexane) and subsequent recrystallization from cold acetone produced a yield of 0.1575 g (77%; mp 158–160 °C) of $Ru_3(\mu\text{-}H)(\mu\text{-}C_{13}H_8N)(CO)_{10}$ (**5**). IR (cyclohexane): ν_{CO} 2106 s, 2066 vs, 2059 vs, 2031 sh, 2026 vs, 2021 vs, 2004 s, 1991 s cm^{-1}. ^1H NMR: δ 8.64–8.52 (m, 3 H), 8.16 (d, 1 H), 7.92–7.78 (m, 3 H), 7.61 (d, 1 H), −13.73 (s, 1 H). Anal. Calcd for $C_{23}H_9NO_{10}Ru_3$: C, 36.21; H, 1.18; N, 1.84. Found: C, 36.20; H, 1.22; N, 1.88. The reaction of dihydrophenanthridine with $Ru_3(CO)_{12}$ also provided **5** under the same conditions reported above.

Reaction of $Ru_3(\mu\text{-}H)(\mu\text{-}C_{13}H_8N)(CO)_{10}$ (5) with Hydrogen Gas. $Ru_3(\mu\text{-}H)(\mu\text{-}C_{13}H_8N)(CO)_8$ (**3**; 0.0426 g, 0.056 mmol), 10 mL of toluene, and a small stir bar were sealed into a Parr autoclave reactor. The reactor was purged with H_2 gas and was then charged with 500 psi of H_2. It was then lowered into an oil bath held at 85 °C. After 40 h at 85 °C, the reactor was vented and opened, disclosing an orange precipitate and pale yellow solution. The precipitate was identified as $H_4Ru_4(CO)_{12}$ by IR (ν_{CO} 2086 m, 2069 s, 2022 s, 2000 m cm^{-1}) and NMR spectroscopy.[9] The remaining yellow solution was shown to contain both phenanthridine and dihydrophenanthridine by ^1H NMR.

Attempted Reaction of $Ru_3(\mu\text{-}H)(\mu\text{-}C_9H_6N)(CO)_{10}$ 1, with $LiBEt_3H$. $Ru_3(\mu\text{-}H)(\mu\text{-}C_9H_6N)(CO)_{10}$ (0.08 g, 0.112 mmol) was placed in a 50-mL Schlenk flask with a rubber septum and a small stir bar. Under argon flow, 10 mL of freshly distilled THF was added. The orange solution was then degassed by two freeze–pump–thaw cycles. $LiBEt_3H$ (0.4 mL, 1.26 M in THF, Alfa, 0.45 mmol, 4× excess) was added slowly to the solution after being cooled to −61 °C ($CHCl_3/N_2$ bath). The mixture was stirred at this temperature 1.5 h. Examination of the IR spectrum showed no change. The solution was warmed to room temperature and was stirred an additional 3 h. At this time, the solvent was removed and an IR spectrum of the yellow-orange residue indicated that only the starting cluster was present.

Attempted Reaction of $Ru_3(\mu\text{-}H)(\mu\text{-}C_9H_6N)(CO)_{10}$ (1) with $LiAlH_4$. $Ru(\mu\text{-}H)(\mu\text{-}C_9H_6N)(CO)_{10}$ (**1**; 0.05 g, 0.07 mmol) was placed in a 100-mL Schlenk flask and was dissolved in 10 mL of freshly distilled THF. The yellow solution was degassed by two freeze–pump–thaw cycles. $LiAlH_4$ (0.008 g, 0.211 mmol, 3× excess) was placed in an addition tube, evacuated, and backfilled with argon three times. The tube was then connected to the flask under argon flow, and the contents were slowly added to the solution. No immediate visible reaction occurred. After the mixture was stirred 3 h at room temperature, thin-layer chromatography and an IR spectrum showed no reaction. The solution was then heated to 60 °C for 2 h. Again, no reaction was apparent by TLC or IR. After any remaining $LiAlH_4$ was destroyed with ethyl acetate, a ^1H NMR spectrum of the residue showed only resonances due to starting cluster **1**.

Attempted Reaction of $Ru_3(\mu\text{-}H)(\mu\text{-}C_{13}H_8N)(CO)_{10}$ (5) with $LiAlH_4$ or $LiBEt_3H$. As shown with complex **1**, the reaction of **5** with either $LiAlH_4$ or $LiBEt_3H$ under the same reaction conditions gave a similar result, i.e., no reaction was apparent with either reducing agent.

The Single-Crystal X-ray Structure of $Ru_3(\mu\text{-}H)(\mu\text{-}C_{13}H_8N)(CO)_{10}$ (5). Orange-red needles of complex **5** were obtained by slow crystallization from cold (−30 °C) acetone. Crystals of an appropriate size were mounted on glass fibers in air. Precession photographs indicated that the material belonged to the monoclinic system, space group C_{2h}^5—$P2_1/c$, and yielded preliminary cell dimensions.

The crystal used for data collection was transferred to an Enraf-Nonius CAD-4 diffractometer[20] and centered in the beam. Automatic peak search and standard indexing procedures afforded the monoclinic primitive cell obtained from the photographic data. The final cell parameters and details of the data collection procedure are given in Table I.

The unique data were reduced to structure factor amplitudes and their estimated standard deviations (esd) by correction for background, scan speed, and Lorentz and polarization factors after removal of redundant data due to systematic absences.[21–23] The structure was solved by Patterson methods and was refined by standard least-squares and Fourier techniques. An empirical absorption correction was applied with no significant improvement in fit. In a difference Fourier map calculated following refinement

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(20) Instrumentation (University of California at Berkeley, Chemistry Department) for the X-Ray Crystallographic Facility (CHEXRAY) consists of two Enraf-Nonius CAD-4 diffractometers, one controlled by a DEC PDP 8/a with an RK05 disk and the other by a DEC PDP 8/e with an RL01 disk. Both use Enraf-Nonius software as described in the *CAD-4 Operation Manual*: Enraf-Nonius: Delft, Nov 1977, updated Jan 1980.

(21) All calculations were performed on a PDP 11/60 equipped with 128 kilowords of memory, twin RK07 28 Mbyte disk drives, Versatec printer/plotter, and TU10 tape drive using locally modified Nonius-SDP(3) software operating under RSX-11M.

(22) *Structure Determination Package User*'s *Guide*: B.A. Frenz and Associates: College Station, TX 77840, 1982.

(23) The data reduction formulas are $F_o^2 = (\omega/Lp)(c - 2B)$, $F_o = (F_0^2)^{1/2}$, $\sigma_o(F_o^2) = (\omega/Lp)(c + 4B)^{1/2}$, and $\sigma_o(F) = \sigma_o(F_o^2)/2F_o$ where c = total count of the scan, B = sum of two background counts, ω = scan speed (deg/min), and $1/Lp = \sin 2\theta(1 + \cos^2 2\theta_m)/1 + \cos^2 2\theta_m - \sin^2 2\theta$, the correction for Lorentz and polarization effects in a reflection with scattering angle 2θ and radiation monochromatized with a 50% perfect single-crystal monochromator with scattering angle $2\theta_m$.

of all non-hydrogen atoms with anisotropic thermal parameters, the positions of all of the hydrogen atoms were determined. All hydrogen atoms, except the unique hydride whose position was determined from a difference electron density map and was refined, were included in the structure factor calculation in their anticipated positions on the basis of bonding geometry. All hydrogen atoms were assigned isotropic thermal parameters 1–2 Å larger than the equivalent B(iso) of the atom to which they were bonded. The hydrogen atoms, except the unique hydride, were not varied in the final refinement. A secondary extinction coefficient[24] was refined in the final cycle of least squares.

At the end of the refinement, the thermal parameters for C(11) and N(1) atoms of the phenanthridine ligand indicated either that the identities of the atoms were reversed or that there was disorder in the ligand orientation. After refinement with the atomic identities reversed, the B(eq) values were equally compatible with the alternative assignment. Therefore, it was concluded that there was disorder at these positions due to the presence of a pseudomirror plane and each atom was assigned 50% occupancy at the two sites. The least-squares refinement was then run to convergence.

The final residuals[25] for 339 variables refined against the 2876 unique data for which $F_o^2 > 3\sigma(F_o)^2$ were $R = 1.84\%$, $R_W = 2.94\%$, and GOF = 1.53.

The quantity minimized in the least-squares program was $w(|F_o| - |F_c|)^2$, where w is the weight of a given observation. The p factor,[25] used to reduce the weight of intense reflections, was set to 0.03 in the last cycles of the refinement. The analytical forms of the scattering factor tables for the neutral atoms were used,[26] and all non-hydrogen scattering factors were corrected for both the real and imaginary components of anomalous dispersion.[27]

Inspection of the residuals ordered in ranges of $(\sin \theta)/\lambda$, $|F_o|$, and value of the individual indices showed no unusual features or trends. The final positional parameters of the non-hydrogen atoms are listed in Table IV. Table V[28] presents anisotropic thermal parameters for the non-hydrogen atoms. Table VI lists hydrogen atom positional parameters. The $10|F_o|$ and $10|F_c|$ values are tabulated in Table VII.[28]

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Registry No. **1**, 98105-25-0; **2**, 104240-15-5; **5**, 104240-16-6; $Ru_3(CO)_{12}$, 15243-33-1; $Ru_4H_4(CO)_{12}$, 34438-91-0; quinoline, 91-22-5; 1,2,3,4-tetrahydroquinoline, 635-46-1; phenanthridine, 229-87-8.

Supplementary Material Available: Tables of best-weighted least-squares plane of the phenanthridine ligand (Table III), positional parameters for non-hydrogen atoms (Table IV), anisotropic thermal parameters (Table V), and hydrogen atom positional parameters (Table VI) (5 pages); a listing of structure factor amplitudes, the values of $10|F_o|$ and $10|F_c|$ (Table VII) (18 pages). Ordering information is given on any current masthead page.

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[24] Zachariasen, W. H. *Acta Crystallogr.* **1963**, *16*, 1139.

[25] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $wR = \{\sum w(|F_o| - |F_c|)^2/\sum wF_o^2\}^{1/2}$, and GOF = $\{\sum w(|F_o| - |F_c|)^2/(n_o - n_v)\}^{1/2}$, where n_o = number of observations, n_v = number of variables, $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = \sigma_0^2(F_0^2) + (pF^2)^2$, and p is the factor used to lower the weight of intense reflections.

[26] Cromer, D. T.; Weber, J. T. In *International Tables for X-Ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

[27] Cromer, D. T.; Weber, J.T. In *International Tables* for *X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

[28] See paragraph at end of paper regarding supplementary material.