Reactions of Electron-Deficient Benzoheterocycle Triosmium Complexes with Lithium Isobutyronitrile

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The reactions of the electron-deficient benzoheterocycle triosmium complexes of general formula $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-Bz})(\mu\text{-H})$ (BzH = phenanthridine, **3**; 2-methylbenzimidazole, **4**; 2,3-dimethylbenzimidazole, **5**; quinoxaline, **6**; 2-methylquinoxaline, **7**; benzothiazole, **8**; 2-methylbenzothiazole, **9**) with lithium isobutyryl nitrile are reported. Nucleophilic addition at the carbocyclic rings of all the complexes is observed as for the previously reported $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-Bz})(\mu\text{-H})$ (BzH = quinoline, **1**; 5,6-benzoquinoline, **2**), thus extending the novel alteration in the regiochemistry of nucleophilic attack to this entire class of complexes. However, in some of the complexes spontaneous rearomatization of the addition product is observed on workup or on exposure to air after addition of the carbanion. The degree to which this occurs is controlled by the steric and electronic properties of the heterocycle, and by careful adjustment of the reactions conditions either the nucleophilic addition or substitution product can be observed. The solid state structures of two of the nucleophilic addition products are reported for comparison with the previously reported analogous quinoline complexes.

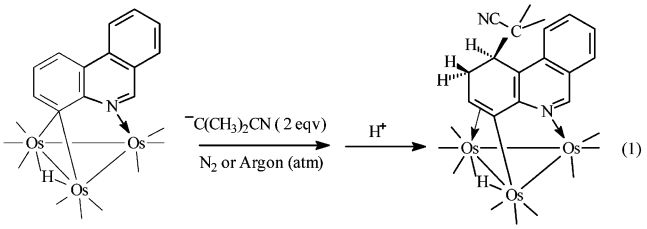
Introduction

The modification of the reactivity patterns of organic molecules by complexation to one or more metal atoms is certainly one of the more interesting and useful aspects of transition metal organometallic chemistry. We have previously reported the reactions of the electron-deficient quinoline triosmium complex $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-Bz})(\mu\text{-H})$ (HBz = quinoline, **1**, Figure 1) with hydride and carbanions where the normal site of nucleophilic attack at the 2-position (or the 4-position when the 2-positon is blocked) is changed to the 5-position as a result of the bonding mode of the heterocyclic ring with two metal atoms of the trimetallic cluster.[1−3] The origin of this change in regiochemistry is best understood in terms of the disposition of the LUMO on the complexes as indicated by DFT calculations and by the distribution of unpaired spin density in the corresponding radical anions.[4,5]

Extension of the novel regiochemistry to the complexes shown in Figure 1 would provide a convenient method for the modification of the carbocyclic ring not readily available by conventional routes. These modifications are of particular interest because the ring systems illustrated in Figure 1 form the basis for a class of pharmacologically important ring systems and because of the fact that the rearomatized ring-substituted heterocycles can be readily cleaved from the cluster with recovery of the starting osmium carbonyl.[3,6−10]

Results and Discussion

When compound **3** is reacted with a 2−3-fold excess of lithium isobutyronitrile at −78 °C, the dark green THF solution turned orange. After stirring and warming to 0 °C the solution was cooled to −78 °C and quenched with a slight excess (relative to the total carbanion added) of trifluoroacetic acid to give a light orange solution. After chromatographic purification, the nucleophilic addition product $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_{13}H_9(5\text{-}C(CH_3)_2CN)N)(\mu\text{-H})$ (**10**) was isolated in a 79% yield (eq 1). Compound **10** was characterized by IR, ^{1}H NMR, and elemental analysis and by comparison of its spectral properties with previously reported $\sigma-\pi$ vinyl complexes.[1−3]



(1)

The reaction of **4** with lithium isobutyronitrile gave both nucleophilic substitution and nucleophilic addition

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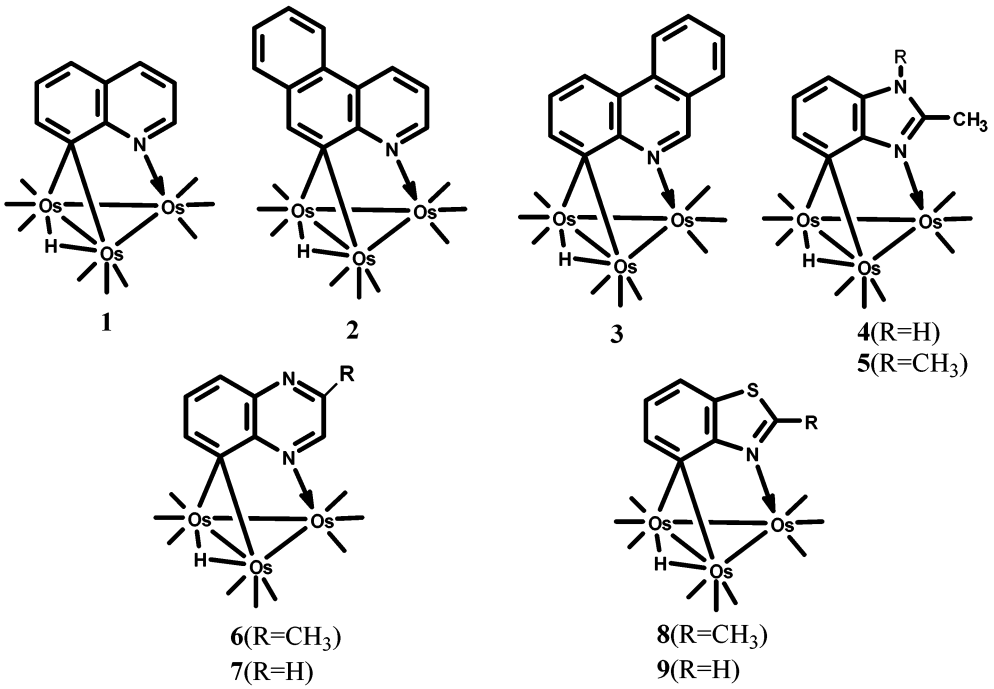
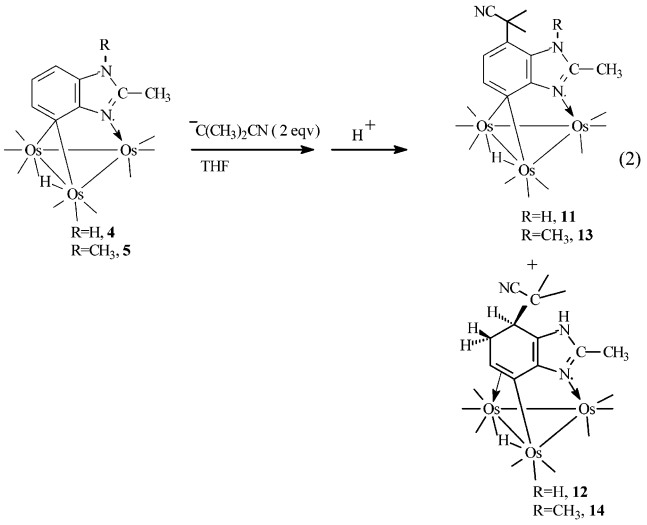


Figure 1. Structures of the electron-deficient benzoheterocycle complexes.

products, $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_7H_3(2\text{-}CH_3)(4\text{-}CCN(CH_3)_2)N_2)$ (**11**) and $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_7H_5(2\text{-}CH_3)(4\text{-}CCN(CH_3)_2)N_2)$ (**12**) (eq 2). Thus, when a 2-fold excess of carbanion was added to compound **4** at −78 °C, the bright green solution turned orange immediately. After quenching with an equivalent amount (relative to carbanion added) of trifluoroacetic acid the solution changed back to green to give the rearomatized nucleophilic addition product, **11**, as a major compound. This rearomatized green nucleophilic addition product, **11**, was purified by chromatographic separation and isolated in 72% yield. Compound **11** was characterized by IR, ^{1}H NMR, and elemental analysis.



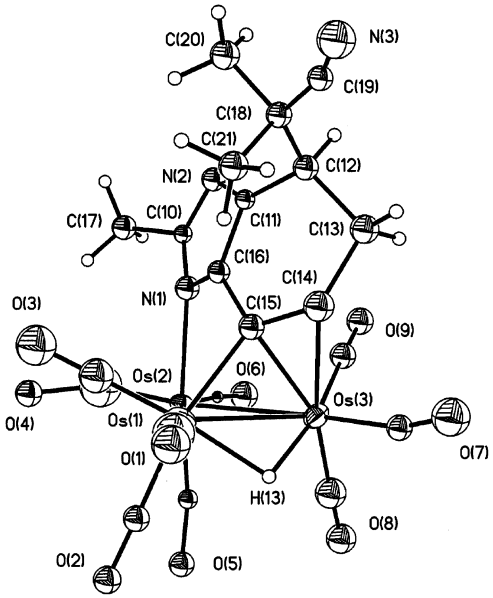


Figure 2. ORTEP drawing of the solid state structure of **12** showing the calculated position of the hydride and the 35% probability ellipsoids.

A second yellow band was also obtained from the thin layer chromatographic purification. Separation of this band provided the $\sigma-\pi$ vinyl nucleophilic addition product **12** as a minor product in 16% yield. Compound **12** was also characterized by IR, ^{1}H NMR, and elemental analysis, which are consistent with the formation of a $\sigma-\pi$ vinyl complex.

Complex **12** represents the first example of a $\sigma-\pi$ vinyl complex of the benzimidazole ring system, and so a solid state structural investigation was undertaken for this compound. The solid state structure is shown in Figure 2, crystal data are given in Table 1, and selected distances and bond angles are given in Table 2. The structure consists of an approximately equilateral triangle of Os atoms with three approximately equal

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Table 1. Crystal Data and Structure Refinement for Compounds 12 and 20

	12	20
empirical formula	$C_{21}H_{13}N_3O_9Os_3$	$C_{20}H_{11}N_2O_9Os_3S$
fw	1021.91	1025.97
temperature	100(2) K	100(2) K
wavelength	0.71073 Å	0.71073 Å
cryst syst	hexagonal	monoclinic
space group	*P*6(3)	*P*2/*n*
unit cell dimens	$a = 18.5450(18)$ Å, $\alpha = 90°$ $b = 18.5450(18)$ Å, $\beta = 90°$ $c = 12.621(2)$ Å, $\gamma = 120°$	$a = 15.0855$ Å, $\alpha = 90°$ $b = 9.9703(9)$ Å, $\beta = 112.684(2)°$ $c = 19.040116)$ Å, $\gamma = 90°$
volume	3759.1(9) Å^3	2642.2(2) Å^3
Z	6	4
density (calcd)	2.7114 g/cm^3	2.662 g/cm^3
absorp coeff	15.227 mm^{-1}	14.601 mm^{-1}
F(000)	2772	1908
cryst size	0.09 × 0.07 × 0.02 mm^3	0.19 × 0.17 × 0.04 mm^3
θ range for data collection	2.05−27.00°	1.48−32.96°
index ranges	$-23 \le h \le 23$ $-23 \le k \le 23$ $-16 \le l \le 16$	$-22 \le h \le 22$ $-15 \le k \le 15$ $-28 \le l \le 28$
no. of reflns collected	45 784	44 397
no. of indep reflns	5474 [*R*(int) = 0.2978]	9489 [*R*(int) = 0.0899]
completeness to θ	27.00°, 100%	32.96°, 95.4%
absorp corr	semiempirical from equivalents	semiempirical from equivalents
max. and min. transmn	1.000 and 0.345 848	1.000 and 0.543 807
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2
no. of data/restraints/params	5474/1/158	9489/0/346
goodness-of-fit on F^2	1.073	1.080
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0821$, $wR_2 = 0.1708$	$R_1 = 0.0483$, $wR_2 = 0.1090$
R indices (all data)	$R_1 = 0.1660$, $wR_2 = 0.2187$	$R_1 = 0.0733$, $wR_2 = 0.1180$
largest diff peak and hole	3.389 and −1.732 e Å^{-3}	3.695 and −2.901 e Å^{-3}

Table 2. Selected Bond Distances (Å) and Angles (deg) for 12[a]

Distances			
Os(1)−Os(2)	2.878(4)	C(14)−C(15)	1.36(5)
Os(1)−Os(3)	2.835(1)	C(13)−C(14)	1.62(6)
Os(2)−Os(3)	2.850(4)	C(12)−C(13)	1.56(5)
Os(2)−N(1)	2.22(2)	C(12)−C(11)	1.51(4)
Os(3)−C(14)	2.57(4)	C(16)−C(11)	1.42(4)
Os(1)−C(15)	2.07(4)	C(12)−C(18)	1.50(5)
Os(3)−C(15)	2.28(4)	C(10)−C(17)	1.53(4)
C(10)−N(1)	1.30(3)	C−O	1.16(5)[b]
C(10)−N(2)	1.36(3)	Os−CO[b]	1.92(4)
C(16)−N(1)	1.32(3)	C(11)−N(2)	1.36(3)
Angles			
Os(1)−Os(2)−Os(3)	59.32(4)	Os(1)−Os(2)−N(1)	83.8(10)
Os(1)−Os(3)−Os(2)	60.83(15)	C(13)−C(14)−C(15)	128.0(4)
Os(2)−Os(1)−Os(3)	59.85(15)	C(12)−C(13)−C(14)	108.0(3)
Os(1)−C(15)−C(14)	129.0(3)	C(11)−C(12)−C(18)	115.0(3)
Os(3)−C(15)−C(14)	86.0(3)	C(13)−C(12)−C(11)	112.0(3)
Os(3)−C(14)-C(15)	62.0(2)	C(10)−N(1)−C(16)	112.0(2)
Os−C−O	173.4(4)[b]		

[a] Numbers in parentheses are estimated standard deviations. [b] Average values.

metal−metal bonds (Os(1)−Os(2) = 2.878(4) Å, Os(1)−Os(3) = 2.835(1) Å, Os(2)−Os(3) = 2.850(4) Å). The hydride was located using the program WinGX.[11] The hydride is tucked below the plane of the metal triangle along the doubly bridged Os(1)−Os(3) edge. The N(1)−C(10) (1.30(3) Å), N(2)−C(10) (1.36(3) Å), and C(11)−C(16) (1.42(4) Å) bond lengths are all in the range of aromatic double bond (1.32−1.42 Å), suggesting that the reduction of the carbocyclic ring that results from the nucleophilic addition does not significantly perturb the aromaticity of the heterocyclic ring. The assignments of a σ interaction between Os(1)−C(15) (2.07(4) Å) and a π interaction between Os(3)−C(15) (2.28(4) Å) and Os(3)−C(14) (2.57(4) Å) are very similar to the bond lengths observed for the previously reported quinoline $\sigma-\pi$ vinyl complexes and for acyclic $\sigma-\pi$ vinyl complexes.[2,12]

That compound **11** is the major product from the alkylation of **4** suggests that perhaps deprotonation of the amine proton may be occurring after alkylation to give a dianion intermediate, which then drives the observed rearomatization by promoting hydride ejection from the carbocyclic ring. In fact, when compound **4** is reacted with H^-/H^+, only the starting **4** is isolated even though a transient anion consistent with initial attack at the 4-positon of the benzimidazole ring was observed by NMR. This was interpreted in terms of the dianionic intermediate referred to above.[13]

The complex $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_7H_3(2\text{-}CH_3)(3\text{-}CH_3)N_2)(\mu\text{-}H)$ (**5**), on the other hand, underwent nucleophilic reduction with H^-/H^+ across the C(4)−C(5) double bond to give a $\sigma-\pi$ vinyl complex.[13] On reaction with isobutyronitrile, complex **5** gives a mixture of both nucleophilic addition and nucleophilic substitution products, $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_7H_2(2\text{-}CH_3)(3\text{-}CH_3)(4\text{-}C(CH_3)_2CN)N_2)(\mu\text{-}H)$ (**13**) in 27% yield along and $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_7H_4(2\text{-}CH_3)(3\text{-}CH_3)(4\text{-}C(CH_3)_2CN)N_2)(\mu\text{-}H)$ (**14**) in 56% yield (eq 2).

During the course of reaction the addition of a 2-fold excess of carbanion to compound **5** at −78 °C changed the green color of the solution first to amber, then orange. Quenching of the solution with trifluoroacetic acid and subsequent warming to 0 °C turned the color to yellow, which then changed to green on standing in the air at room temperature. Thus it would appear from these color changes that the green substitution product forms from oxidation (dehydrogenation) of the addition product and not from the dianionic intermediate sug-

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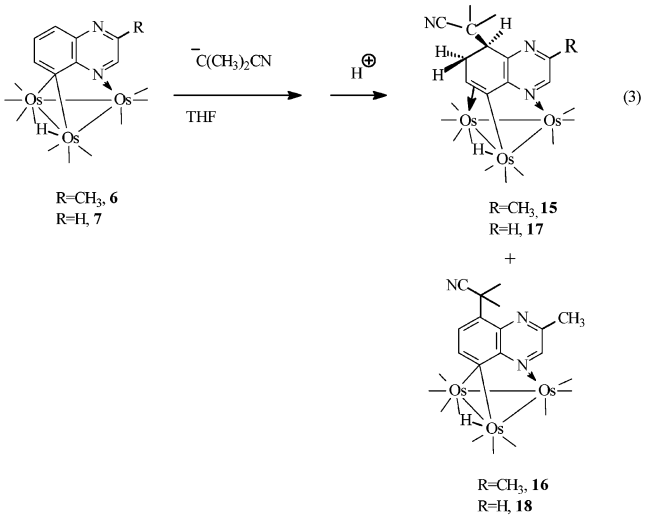
gested above. However, replacement of the proton on nitrogen with a methyl does result in almost complete inversion of the product distribution, although reasons for this are not apparent from this one example.

The reaction of the previously reported quinoxaline complex $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_8H_5N_2)(\mu\text{-}H)$ (**7**) with either H^-/H^+ or with carbanions leads to a complex mixture of products probably arising from competitive attack at the carbocyclic and heterocyclic rings in this more electron-poor heterocycle.[13] Using 2-methylquinoxaline as the ligand, we obtain $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_8H_4(3\text{-}CH_3)N_2)(\mu\text{-}H)$ (**6**), where the methyl group resides in the 3-position relative to the nitrogen that is coordinated to the cluster. Treatment of **6** with a 2−3-fold excess of lithium isobutyronitrile at −78 °C followed by neutralization with trifluoroacetic acid proceeded cleanly and provided a $\sigma-\pi$ vinyl nucleophilic addition product, $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_8H_5(3\text{-}CH_3)(5\text{-}C(CH_3)_2CN)N_2)(\mu\text{-}H)$ (**15**), in 62% yield. A trace amount of rearomatized product, $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_8H_3(3\text{-}CH_3)(5\text{-}C(CH_3)_2CN)N_2)(\mu\text{-}H)$ (**16**), was also obtained as a coproduct as indicated from its ^{1}H NMR spectrum. Compounds **15** and **16** were characterized by IR, ^{1}H NMR, and elemental analysis.

The relatively clean nucleophilic addition chemistry observed with **6** prompted us to attempt the reaction of the unsubstituted quinoxaline complex $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_8H_5N_2)(\mu\text{-}H)$ (**7**) with a bulky carbanion in order to understand whether the presence of the methyl group on the heterocyclic ring was the reason nucleophilic attack is redirected to the carbocyclic ring (compared with hydride) or whether the bulkiness of the carbanion alone is responsible for the observed chemistry. Reaction of **7** with lithium isobutyronitrile at −78 °C gave the rearomatized nucleophilic addition product $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_8H_4N_2)(5\text{-}C(CH_3)_2CN)(\mu\text{-}H)$ (**17**) in 23% yield along with a 6% yield of the $\sigma-\pi$ vinyl complex $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_8H_6N_2)(5\text{-}C(CH_3)_2CN)(\mu\text{-}H)$ (**18**) and were characterized on the basis of their ^{1}H NMR an IR spectra (eq 3).

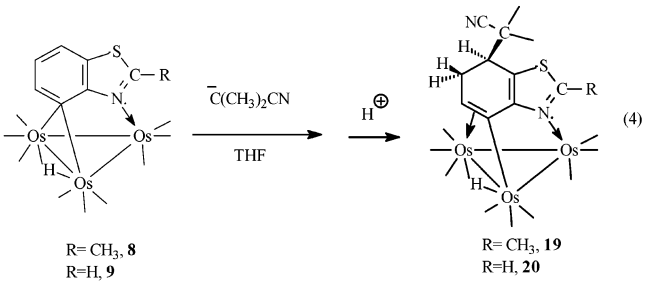


(3)

It should be noted that the overall yield of isolable products is much lower than for **6** and that considerable decomposition took place, as evidenced by the presence a dark streaky baseline during chromatographic purification. Because of the presence of minor impurities, it was not possible to obtain acceptable elemental analysis for **17** and **18**. Nonetheless, it is important to report these results, as they do indicate that to some significant extent the use of the bulky carbanion is a sufficient condition to redirect the site of nucleophilic attack. It is also interesting to note that the relative yields of nucleophilic addition versus nucleophilic substitution products are the reverse of that observed for **6**, indicating that the presence of the methyl group somehow stabilizes the addition product, **15**, toward dehydrogenation.

The results reported here so far indicate that nucleophilic attack at the carbocyclic ring observed in the previously reported quinoline systems can be generalized to the 5,6- and 6,6-fused ring heterocycles containing two nitrogen atoms with the distinct difference that facile rearomatization of the addition products to give the corresponding substitution products occurs to a significant extent. To investigate the impact of changing one heteroatom in these systems on the course of the nucleophilic attack, we have examined the reactions of the 2-methylbenzothiazole complex $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_7H_3(2\text{-}CH_3)NS)(\mu\text{-}H)$ (**8**) and the benzothiazole complex $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_7H_4NS)(\mu\text{-}H)$ (**9**) with lithium isobutyronitrile.

The reaction of **8** with a 2−3-fold excess of lithium isobutyronitrile followed by quenching with trifluoroacetic acid gave only a nucleophilic addition product, $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_7H_4(2\text{-}CH_3)(4\text{-}C(CH_3)_2CN)NS)(\mu\text{-}H)$ (**19**), in 74% yield, as characterized by IR, ^{1}H NMR, and elemental analysis, which exhibit spectral parameters typical for $\sigma-\pi$ vinyl complexes **9** (eq 4).[1−3]



(4)

When the benzothiazole complex **9** was treated with the less sterically demanding Et_3BH^-, the nucleophilic attack occurred at the C-2 position of the heterocyclic ring.[13] Subsequent neutralization of the resulting anionic complex by trifluoroacetic acid yielded a dihydride complex.[13] Reaction of **9** with lithium isobutyronitrile on the other hand results in nucleophilic attack at the 4-position of the carbocyclic ring. The C-2 atom of the heterocyclic ring is apparently not accessible for attack by the bulkier nucleophile. After chromatographic separation the nucleophilic addition product, $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_7H_5(4\text{-}C(CH_3)_2CN)NS)(\mu\text{-}H)$ (**20**), was isolated in 84% yield (eq 4). Thus by changing the heteroatom from nitrogen to sulfur the formation of rearomatized product is completely avoided. This is most likely due to the fact that the benzothiazole has less aromatic character than the benzimidazole ring system. Compound **20** was characterized by IR, ^{1}H NMR, and elemental analysis.

Given the different reactivities observed for **4** and **5** versus **8** and **9**, we thought it would be interesting to determine the solid state structural parameters that would elucidate these differences. The structure of **20**

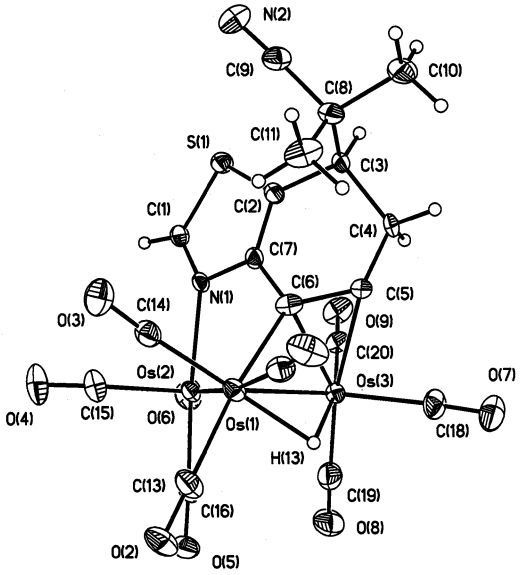


Figure 3. ORTEP drawing of the solid state structure of **20** showing the calculated position of the hydride and the 35% probability ellipsoids.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 20[a]

	Distances		
Os(1)−Os(2)	2.804(1)	C(5)−C(6)	1.40(1)
Os(1)−Os(3)	2.864(1)	C(4)−C(5)	1.52(1)
Os(2)−Os(3)	2.901(1)	C(3)−C(4)	1.56(1)
Os(2)−N(1)	2.16(6)	C(2)−C(3)	1.51(1)
Os(3)−C(5)	2.44(7)	C(2)−C(7)	1.36(1)
Os(1)−C(6)	2.10(8)	C(3)−C(8)	1.55(1)
Os(3)−C(6)	2.24(1)	C(6)−C(7)	1.46(1)
C(1)−N(1)	1.31(1)	C(7)−N(1)	1.38(1)
C(1)−S(1)	1.71(1)	Os−CO[b]	1.92(1)
C(2)−S(1)	1.72(1)	C−O	1.13(1)[b]
	Angles		
Os(1)−Os(2)−Os(3)	60.24(11)	Os(1)−Os(2)−N(1)	85.50(17)
Os(1)−Os(3)−Os(2)	58.20(11)	C(6)−C(5)−C(4)	120.5(7)
Os(2)−Os(1)−Os(3)	61.57(12)	C(3)−C(4)−C(5)	114.8(6)
Os(1)−C(6)−C(5)	124.8(6)	C(2)−C(3)−-C(8)	112.5(6)
Os(3)−C(6)−C(5)	80.3(5)	C(2)−C(3)−C(4)	105.6(6)
Os(3)−C(5)−C(6)	65.2(4)	C(1)−N(1)−C(7)	110.6(6)
Os−C−O	176.1(8)[b]	C(5)−C(6)−C(7)	113.0(7)

[a] Numbers in parentheses are estimated standard deviations. [b] Average values.

is shown in Figure 3, crystal data are given in Table 1, and selected distances and bond angles are given in Table 3. The structure consists of a triangle of Os atoms with metal−metal bonds (Os(1)−Os(2) (2.80(5) Å), Os(1)−Os(3) (2.86(4) Å), Os(2)−Os(3) (2.91(5) Å). The hydride was located using the program WinGX.[11] The hydride is tucked below the plane of the metal triangle along the doubly bridged Os(1)−Os(3) edge. The N(1)−C(1) (1.31(1) Å), C(5)−C(6) (1.40(1) Å), C(2)−C(7)(1.36(1) Å), and C(2)−C(3) (1.36(4) Å) bond lengths are in the range of double bonds, C(4)−C(5) (1.52(1) Å) and C(3)−C(4) (1.56(1) Å) are single bonds, while C(6)−C(7) (1.46(1) Å) can be considered as a slightly elongated double bond. The σ interaction between Os(1)−C(6) (2.10(8) Å) and a π interaction between Os(3)−C(6) (2.24(7) Å) and Os-(3)−C(5) (2.44(7) Å) are very similar to those in **12** and to other $\sigma-\pi$ interactions on triosmium clusters.[2,13] Thus changing a heteroatom from nitrogen to sulfur does not have a significant impact on the ground state structural features of these $\sigma-\pi$-vinyl complexes. However, it is interesting to note that the carbon−sulfur bond lengths in **20** (1.71(1) and 1.72(1) Å) are almost identical to the same bonds in **9** (1.75(1) Å), suggesting that there is little if any difference in aromaticity in the heterocyclic ring before and after nucleophilic addition, and the same is true for **4** versus **12**. Nonetheless, it is probably the greater intrinsic aromaticity of the benzimidazole system that drives the more facile rearomatization of **4** after alkylation.

Rearomatization of the Nucleophilic Addition Products. Reactions of **4** and **5** with $LiC(CH_3)_2CN$ gave green rearomatized complexes **11** and **12** in 72% and 27% yields. Rearomatized products were also noted in the reaction of **6** and **7** with $LiC(CH_3)_2CN$, while **3**, **8**, and **9** showed no rearomatized products. Rearomatization after alkylation was previously reported for an electron-deficient 6-methoxyquinoline complex.[3] Thus it appears that facile oxidation (dehydrogenation) of the intermediate nucleophilic addition occurs when there is either a second nitrogen atom with an available lone pair in the heterocycle or a strong π-electron-donating group, such as 6-methoxy, in the carbocyclic ring. Rearomatization of the nucleophilic addition products of some quinoline complexes was realized either by reaction of the intermediate anion with trityl cation or with dichloro, dicyano quinone (DDQ)/EtOH or by reaction of the $\sigma-\pi$ vinyl complex with diazabicyclononane (DBU) and DDQ/EtOH.[3]

In the cases reported here with π-donor substituents attached to the carbocyclic ring the rearomatization could be driven by more facile oxidation of the addition product brought about by additional π-electron density in the ring. It occurred to us that air oxidation of the intermediate anion prior to quenching with acid could result in rearomatization even in those cases where it was not observed to occur under inert atmosphere. Thus stirring the anions resulting from the addition of alkylating agent, $LiC(CH_3)_2CN$, to complexes **3**, **5**, and **7** for 1−2 h at 0 °C in the air before quenching with acid gave the rearomatized products $Os_3(CO)_9(\mu_3-\eta^2-C_{13}H_7(5-C(CH_3)_2CN)N)(\mu-H)$ (**21**) (eq 5), **13**, and **16** in 56%, 71%, and 42% yields, respectively. 2-Methylbenzothiazole complex **8** also gave rearomatized product $Os_3(CO)_9(\mu_3-\eta^2-C_7H_2(2-CH_3)(4-C(CH_3)_2CN)NS)(\mu-H)$ (**22**) (eq 6) in 30% yield by the same method but required relatively longer stirring (3−4 h). However, this method did not work for the benzothiazole complex **9**.

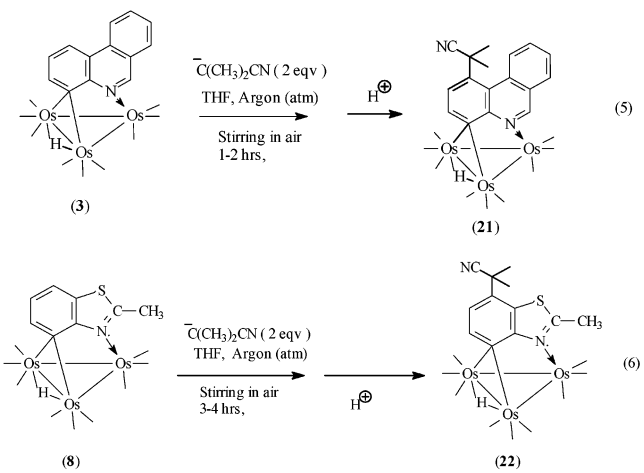


Table 4. Isolated Nucleophilic Addition Product Yields from the Reaction of Benzoheterocycle Complexes $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-L-H})(\mu\text{-H})$ with Isobutyronitrile Carbanion

L	σ,π-vinyl product (%)	rearomatized product (%)
phenanthridine[a]	79	
phenanthridine[b]		56
2-methylbenzimidazole[a]		82
2-methylbenzimidazole[c]	69	
2,3-dimethylbenzimidazole[a]	56	27
2,3-dimethylbenzimidazole[b]		71
2-methylquinoxaline[a]	62	4
2-methylquinoxaline[b]		42
2-methylbenzothiazole[a]	74	
2-methylbenzothiazole[b]		30
benzothiazole[a]	84	
quinoxaline[a]	6	23

[a] Anionic mixture was quenched with acid within 20 min. [b] Anionic mixture stirred in the air followed by acid quench. [c] Excess carbanion was added.

Thus, to some extent, one can control whether nucleophilic addition or nucleophilic substitution takes place simply by changing the order of exposure to air relative to the quenching of the reaction mixture with acid.

Conclusions

The reactions of electron-deficient benzoheterocycle complexes **3**−**9** with $LiC(CH_3)_2CN$ all undergo regioselective nucleophilic attack at the C-4 (for benzothiazole, benzimidazole) or C-5 (phenanthridine, quinoxaline) positions of the carbocyclic ring to give the nucleophilic addition products similar to those of the related quinoline complexes.[3] The yields of the reactions of these complexes with isobutyronitrile carbanion are summarized in Table 4. The yields obtained for these complexes are very similar to those obtained from the reactions of quinoline complexes with a wide range of carbanions.[1−3]

It is noteworthy that some of these complexes give rearomatized nucleophilic addition products by facile air oxidation (dehydrogenation) of the intermediate anion. This facile rearomatization has also been achieved with other benzoheterocycle complexes, thus, avoiding one extra step, the sequential reaction with DDQ and DBU leading to rearomatization.[3] The facility with which the rearomatization occurs appears to depend on the efficiency of the π-interaction with the heteroatom in the adjacent heterocyclic ring or substituents on the carbocyclic ring along with the overall degree of aromaticity of the rearomatized system. Thus **3**−**7** form rearomatized product, while **8** does only under forcing conditions and **9** not at all.

In order for this synthetic method to be developed as a useful tool for the synthesis of unusually substituted benzoheterocycles, cleavage of the functionalized heterocycles from the clusters must be demonstrated. Studies carried out in our laboratory have shown that quinoline, phenanthridine, and 5,6-benzoquinoline clusters undergo ligand cleavage at 70 °C in acetonitrile under carbon monoxide atmosphere. Benzothiazole, benzimidazole, and quinoxaline clusters require higher temperatures to undergo cleavage of the ligand.[2,14] We are also studying the reactions of **3**−**9** with a wider variety of more biomedically important carbanions. Applying this synthetic method it should be possible to obtain free rearomatized benzoheterocycles that are structurally novel and of interest for biomedical screening.

(14) Rokhsana, D.; Rosenberg, E., to be published.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of argon but were worked up in the air. Tetrahydrofuran was distilled from benzophenone ketyl. Methylene chloride and acetonitrile were distilled from calcium hydride. Infrared spectra were recorded on a Thermo-Nicolet 633 FT IR spectrometer, and ^1H and ^{13}C NMR were recorded on a Varian Unity Plus 400 MHz. Elemental analyses were done by Schwarzkopf Microanalytical Labs, Woodside, NY. Chemical shifts are reported downfield positive relative to tetramethylsilane.

Trifluoroacetic acid, diisopropylamine, and isobutyronitrile were purchased from Aldrich Chemical Co. The former compound was distilled from phosphorus pentoxide, and the last two were distilled calcium hydride before use.

Isobutyronitrile carbanion was generated by deprotonation of its neutral precursor with lithium diisopropyl amide, which was generated from diisopropylamine and Li ^{n}Bu according to published procedures.[15]

Preparation of $Os_3(CO)_9(\mu_3\text{-}\eta\text{-}C_{13}H_9(5\text{-}C(CH_3)_2CN)N)(\mu\text{-}H)$ (10). Dark green crystals of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_{13}H_8N)(\mu\text{-}H)$ (**3**) (100 mg, 0.10 mmol) were dissolved in 10 mL of THF in a 25 mL two-neck flask fitted with a gas inlet tube, evacuated and filled with argon. The solution was cooled to −78 °C, at which time a 2.5 molar excess (2 mL) of a freshly prepared lithium isobutyronitrile THF solution was added slowly by syringe. The color of the solution turned orange immediately. The reaction mixture was warmed to 0 °C, stirred for 20 min, cooled again to −78 °C, and quenched with trifluoroacetic acid (21 μL, 0.26 mmol), a slight excess of the amount of cluster used. At this stage, the solution changed to a light orange color as it warmed to room temperature. The solution was then rotary evaporated and purified by thin layer chromatography on 0.1 × 20 × 20 cm silica gel plates using CH_2Cl_2/hexane (1:3) as eluent. An orange band containing the nucleophilic addition product **10** was obtained, which moved just behind a green band of unconsumed starting material. Isolation of the orange band gave 85 mg of compound **10** (79%).

Analytical data for 10: Anal. Calcd for $C_{26}H_{16}N_2O_9Os_3$: C, 29.16; H, 1.50; N, 2.62. Found: C, 29.02; H, 1.39; N, 2.54. IR (ν CO) in CH_2Cl_2: 2080 m, 2049 s, 2027 s, 1992 s, br, 1967 w, br cm^{-1} and (ν CN): 2305 s, cm^{-1}. ^1H NMR at 400 MHz in $CDCl_3$: δ 9.42 (s, H(2)), 7.87 (dd, 2H(9 and 12)), 7.80 (d of t, H(10)), 7.57 (d of t, H(11)), 4.08 (q, H(7)), 3.38 (d, H(5)), 2.87 (m, H(6)), 2.29 (m, H(6)), 1.49 (s, $-CH_3$), 1.45 (s, $-CH_3$), and −17.14 (s, hydride).

Preparation of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_7H_3(2\text{-}CH_3)(4\text{-}C(CH_3)_2\text{-}CN)N_2)(\mu\text{-}H)$ (11) and $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_7H_5(2\text{-}CH_3)(4\text{-}C(CH_3)_2CN)N_2)(\mu\text{-}H)$ (12). Compound **4** (100 mg, 0.10 mmol) was dissolved in 10 mL of dry THF as above and cooled to −78 °C. A 2 molar excess (1.8 mL, 0.23 mmol) of a freshly prepared lithium isobutyronitrile solution in THF was added slowly by syringe. The color of the solution turned orange immediately. The reaction mixture was warmed to 0 °C, stirred for 20 min, cooled again to −78 °C, and quenched with 2.3 equiv (relative to carbanion added) of trifluoroacetic acid (18 μL). After acid addition the color of the solution turned back to green. The mixture was allowed to warm to room temperature, rotary evaporated, and purified by thin layer chroma-

(15) Semmelhack, M. F.; Clark, G. R.; Garcia, D. C.; Harrison, J. J.; Thebtarnonth, Y.; Wuff, W. A.; Yamashita, A. *Tetrahedron* **1981**, *37*, 3957.

tography on silica gel using CH_2Cl_2/hexane (2:3) as eluent. Two bands were obtained. The isolated major green band provided 74 mg of **11** (72%); the yellow orange band gave 16 mg of **12** (16%).

Analytical data for 11: Anal. Calcd for $C_{21}H_{13}N_3O_9Os_3$: C, 24.68; H, 1.27; N, 4.11. Found: C, 24.53; H, 1.34; N, 3.82. IR (ν CO) in CH_2Cl_2: 2074 m, 2047 s, 2015 s, 1988 s, br, 1944 w, br cm^{-1} and (ν CN): 2301 s, cm^{-1}. ^{1}H NMR at 400 MHz in $CDCl_3$: δ 9.68 (s, br, NH), 8.16 (d, H(6)), 6.82 (d, H(5)), 2.76 (s, $-CH_3$), 1.81 (s, 6H, C(CH_3)$_2$CN), −11.72 (s, hydride).

Analytical data for 12: Anal. Calcd for $C_{21}H_{15}N_3O_9Os_3$: C, 24.63; H, 1.47; N, 4.11. Found: C, 24.55; H, 1.38; N, 3.92. IR (ν CO) in CH_2Cl_2: 2078 m, 2054 s, 2044 s, 2020 s, 1992 m, br, 1967 w, br, 1942 w, br cm^{-1} and (ν CN): 2304 s, cm^{-1}. ^{1}H NMR at 400 MHz in $CDCl_3$: δ 8.48 (s, br, NH), 4.46 (m, H(6)), 2.82 (m, H(4)), 2.62−2.58 (m, 2H(5)), 2.39 (s, $-CH_3$), 1.35 (s, $-CH_3$ of C(CH_3)$_2$CN), 1.25 (s, $-CH_3$ of C(CH_3)$_2$CN), and −16.58 (s, hydride).

Preparation of $Os_3(CO)_9(\mu_3$-η^2-$C_7H_2(2\text{-}CH_3)(3\text{-}CH_3)(4\text{-}C(CH_3)_2CN)N_2)(\mu$-H) (13) and $Os_3(CO)_9(\mu_3$-η^3-$C_7H_4(2\text{-}CH_3)(3\text{-}CH_3(4\text{-}C(CH_3)_2CN)N_2)(\mu$-H) (14). Green crystals of **5** (100 mg, 0.10 mmol) were dissolved in 10 mL of THF in a 25 mL two-neck flask fitted with a gas inlet tube, evacuated and filled with argon. The solution was cooled to −78 °C, and a 2 molar excess of the freshly prepared isobutyronitrile carbanion (1.8 mL, 2.3 mmol) was added slowly. The color of the solution first turned amber, then orange after stirring for 15 min at −78 °C. The solution was quenched with trifluoroacetic acid (18 μL, equivalent amount of carbanion added) and stirred for 10 min before warming to 0 °C. The mixture was further stirred for 5 min at 0 °C, where a color change was observed from orange to yellow. The yellow solution then turned to green while standing in the air at room temperature. The reaction mixture was rotary evaporated and purified by thin layer chromatography on silica gel using CH_2Cl_2/hexane as eluent in 2:3 ratio. Two bands were separated. The major green band gave 58 mg of **13** (56%), while the slower moving minor yellow band provided 28 mg of **14** in 27% yields.

Analytical data for 13: Anal. Calcd for $C_{22}H_{15}N_3O_9Os_3$: C, 25.51; H, 1.45; N, 4.06. Found: C, 25.28; H, 1.31; N, 4.13. IR (ν CO) in CH_2Cl_2: 2072 m, 2045 s, 2018 s, 1985 s, 1942 w, br cm^{-1} and (ν CN): 2302 s, cm^{-1}. ^{1}H NMR 400 MHz in $CDCl_3$: δ 8.15 (d, H(6)), 6.90 (d, H(5)), 4.29 (s, N-CH_3), 2.77 (s, C-CH_3), 1.89 (s, 6H (C(CH_3)$_2$)CN), and −11.71 (s, hydride).

Compound 14: Anal. Calcd for $C_{22}H_{17}N_3O_9Os_3$: C, 25.46; H, 1.64; N, 4.05. Found: C, 25.27; H, 1.50; N, 3.96. IR (ν CO) in CH_2Cl_2: 2081 m, 2044 s, 2022 s, 1986 s, br, 1953 w, br cm^{-1} and (ν CN): 2305 s, cm^{-1}. ^{1}H NMR at 400 MHz in $CDCl_3$: δ 4.38 (dd, H(6)), 3.50 (s, N-CH_3), 2.73 (dd, H(4)), 2.68 (dd, H(5)), 2.55 (dd, H(5)), 2.36 (s, C-CH_3), 1.37 (s, CH_3 of (C(CH_3)$_2$)CN), 1.29 (s, CH_3 of C(CH_3)$_2$CN), and −16.65 (s, hydride).

Preparation of $Os_3(CO)_9(\mu_3$-η^3-$C_8H_5(3\text{-}CH_3)(5\text{-}C(CH_3)_2CN)N_2)(\mu$-H) (15). A solution of lithium isobutyronitrile (1.8 mL, 2.3 mmol) was added dropwise to a solution of **6** (100 mg, 0.104 mmol) in dry THF (10 mL) at −78 °C. A color change from green to dark brown was observed. The reaction solution was warmed to 0 °C, stirred for 20 min, cooled again to −78 °C, and quenched with trifluoroacetic acid (18 μL, 2.3 mmol). The reddish reaction mixture was warmed to room temperature, rotary evaporated, and purified by thin layer chromatography on silica gel using CH_2Cl_2/hexane (2:3) as eluent. The major orange band gave 64 mg (62%) of **15** in addition to ∼4 mg of a minor green band, which was identified as $Os_3(CO)_9$-(μ_3-η^3-C_8H_3(3-CH_3)(5-C(CH_3)$_2$CN)N_2)(μ-H) (**16**) on the basis of its ^{1}H NMR.

Analytical data for 15: Anal. Calcd for $C_{22}H_{15}N_3O_9Os_3$: C, 25.51; H, 1.45; N, 4.06. Found: C, 25.70; H, 1.36; N, 4.13. IR (ν CO) in CH_2Cl_2: 2079 m, 2045 s, 2026 s, 1992 s, 1965 w, br, 1941 w, br cm^{-1} and (ν CN): 2305 s, cm^{-1}. ^{1}H NMR at 400 MHz in $CDCl_3$: δ 8.34 (s, H(2)), 4.06 (m, H(7)), 2.74 (m, H(5)), 2.43 (m, H(6)), 2.41 (m, H(6)), 2.38 (s, CH_3), 1.44 (s, CH_3 of (C(CH_3)$_2$)CN), 1.41 (s, CH_3 of C(CH_3)$_2$CN), and −16.88 (s, hydride).

^{1}H NMR of **16** at 400 MHz in $CDCl_3$: δ 9.06 (s, H(2)), 8.56 (d, H(7)), 7.44 (d, H(6)), 2.77 (s, CH_3), 1.93 (s, 6H (C(CH_3)$_2$)-CN), and −12.32 (s, hydride).

Preparation of $Os_3(CO)_9(\mu_3$-η^2-$C_8H_4N_2)(5\text{-}C(CH_3)_2CN)(\mu$-H) (17) and $Os_3(CO)_9(\mu_3$-η^3-$C_8H_6N_2)(5\text{-}C(CH_3)_2CN)(\mu$-H) (18). Compounds **17** and **18** were synthesized by the same procedure as described for compound **15**. The color of the solution turned pinked when 1.8 mL of carbanion was added to 100 mg of **7** at −78 °C and again changed to purple after quenching with acid. Chromatographic separation on silica gel using CH_2Cl_2/hexane/THF (6:3:1) gave two bands. The green band provided rearomatized product **17** in 23% yield, while the orange band afforded $\sigma-\pi$ vinyl complex **18** in 6% yield.

^{1}H NMR of **17** at 400 MHz in $CDCl_3$: δ 9.21 (d, H(2)), 8.61 (d, H(3)), 8.55 (d, H(7)), 7.46 (d, H(6)), 1.92 (s, 6H (C(CH_3)$_2$)-CN), and −12.32 (s, hydride).

^{1}H NMR of **18** at 400 MHz in $CDCl_3$: δ 8.48 (d, H(2)), 8.21 (d, H(3)), 4.06 (m, H(7)), 4.03 (m, H(5)), 2.79 (m, H(6)), 2.45 (m, H(6)), 1.43 (s, CH_3 of (C(CH_3)$_2$)CN), 1.40 (s, CH_3 of C(CH_3)$_2$-CN), and −16.89 (s, hydride).

Preparation of $Os_3(CO)_9(\mu_3$-η^3-$C_7H_4(2\text{-}CH_3)(4\text{-}C(CH_3)_2CN)NS)(\mu$-H) (19) and $Os_3(CO)_9(\mu_3$-η^3-$C_7H_5(4\text{-}C(CH_3)_2CN)NS)(\mu$-H) (20). Compound **8** (100 mg, 0.102 mmol) or compound **9** (100 mg, 0.104 mmol) was dissolved in 10 mL of THF and cooled to −78 °C, at which time a 2.5 molar excess of the freshly prepared isobutyronitrile carbanion (2 mL) was added slowly. The solution turned deep orange after stirring for 5 min at −78 °C. The mixture was warmed to 0 °C, stirred for 15 min, cooled again to −78 °C, and quenched with trifluoroacetic acid (20 μL, 2.5 mmol). When the color of the solution for compound **9** changed to yellow after stirring for 15 min, the mixture was allowed to warm to room temperature and rotary evaporated. The color remained unchanged for complex **8**. Purification of the crude product by thin layer chromatography on silica gel using CH_2Cl_2/hexane (1:3) as eluent gave one major yellow band. Isolation of the band provided nucleophilic addition product **19** in a 74% yield. A crude mixture of **8** was purified by TLC using CH_2Cl_2/hexane in 1:1 ratio. Isolated product **20** was obtained in 84% yield.

Analytical data for 19: Anal. Calcd for $C_{21}H_{14}N_2O_9SOs_3$: C, 24.23; H, 1.35; N, 2.69. Found: C, 24.23; H, 0.97; N, 2.48. IR (ν CO) in CH_2Cl_2: 2081 m, 2057 s, 2026 s, 1990 s, 1968 w, br, cm^{-1} and (ν CN): 2306 s, cm^{-1}. ^{1}H NMR at 400 MHz in $CDCl_3$: δ 4.32 (m, H(6)), 2.83 (m, H(4)), 2.73 (m, H(5)), 2.50 (m, H(5)), 2.67 (s, CH_3), 1.36 (s, CH_3 of (C(CH_3)$_2$)CN), 1.34 (s, CH_3 of C(CH_3)$_2$CN), and −17.05 (s, hydride).

Analytical data for 20: Anal. Calcd. for $C_{20}H_{12}N_2O_9SOs_3$: C, 23.39; H, 1.17; N, 2.73. Found: C, 23.09; H, 0.85; N, 2.54. IR (ν CO) in CH_2Cl_2: 2080 m, 2050 s, 2027 s, 1987 s, br, 1968 w, br, cm^{-1} and (ν CN): 2305, s, cm^{-1}. ^{1}H NMR at 400 MHz in $CDCl_3$: δ 8.87 (s, H(2)), 4.45 (m, H(6)), 2.93 (m, H(4)), 2.83 (m, H(5)), 2.49 (m, H(5)), 1.37 (s, CH_3 of (C(CH_3)$_2$)CN), 1.36 (s, CH_3 of C(CH_3)$_2$CN), and −16.93 (s, hydride).

Rearomatization Experiments. The alkylation experiments were carried out exactly as described above except that before acid quenching the reaction mixtures were warmed to room temperature, the gas inlet tube removed, and the reaction mixture stirred for 1−4 h in the air. The reaction mixture was then quenched and worked up in the usual manner. The isolated yields obtained for the rearomatized products $Os_3(CO)_9(\mu_3$-η^2-$C_{13}H_7$(5-C(CH_3)$_2$CN)N)(μ-H) (**21**), **13**, and **16** were 56%, 71%, and 42%, respectively. The 2-methylbenzothiazole complex **8** also gave rearomatized product $Os_3(CO)_9(\mu_3$-η^2-$C_7H_2(2\text{-}CH_3)(4\text{-}C(CH_3)_2CN)NS)(\mu$-H), **22**.

Spectroscopic data for 21: IR (ν CO) in CH_2Cl_2: 2073 m, 2060 s, 2022 s, 1995 s, 1961 w, 1947 w, br, cm^{-1} and

(ν CN): 2302 s, cm^{-1}. ^1H NMR at 400 MHz in $CDCl_3$: δ 9.88 (d, H(7)), 9.67 (s, H(2)), 8.53 (d, H(6)), 7.88 (d, 2H(9 and 12)), 7.74 (dd, H(10)), 7.12 (d, H(11)), 1.75 (s, 2X-CH_3), and −12.35 (s, hydride).

Spectroscopic data for 22: IR (ν CO) in CH_2Cl_2: 2078 m, 2055 s, 2021 s, 1996 s, 1958 w, 1942 w, br, cm^{-1} and (ν CN): 2303, s, cm^{-1}. ^1H NMR at 400 MHz in $CDCl_3$: δ 8.60 (d, H(6)), 7.08 (d, H(5)), 3.07 (s, CH_3), 1.83 (s, 6H ($C(CH_3)_2$)CN)), and 12.0 (s, hydride).

X-ray Structure Analysis of 12 and 20. Suitable crystals of **12** and **20** were coated with paratone N oil, suspended in a small fiber loop, and placed in a cooled nitrogen gas stream at 100 K on a Bruker D8 SMART APEX CCD sealed tube diffractometer with graphite monochromated Mo Kα (0.71073 Å) radiation. A hemisphere of data was measured using a series of combinations of phi and omega scans with 10 s frame exposures and 0.3° frame widths. Data collection, indexing, and initial cell refinements were all carried out using SMART[16] software. Frame integration and final cell refinements were done using SAINT[17] software. The final cell parameters were determined from least-squares refinement on 4205 reflections. The SADABS[18] program was used to carry out absorption corrections.

The structure was solved using direct methods and difference Fourier techniques (SHELXTL, V6.12).[19] Hydrogen atoms were placed in their expected chemical positions using the HFIX command and were included in the final cycles of least squares with isotropic U_{ij}'s related to the atoms ridden on. The C−H distances were fixed at 0.93 Å (aromatic and amide), 0.98 Å (methine), 0.97 Å (methylene), or 0.96 Å (methyl). The hydride, H(13), was positioned by using the XHYDEX program in the WinGX suite of programs.[11] Only the osmium atoms were refined anisotropically. Scattering factors and anomalous dispersion corrections are taken from the *International Tables for X-ray Crystallography*.[20] Structure solution, refinement, graphics, and generation of publication materials were performed by using SHELXTL, V6.12 software. Additional details of data collection and structure refinement are given in Table 1.

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Supporting Information Available: Complete tables of bond lengths and angles, atomic coordinates, and thermal parameters are available as CIF files free of charge via the Internet at http://pubs.acs.org.

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