Functionalizing Heterocycles by Electron-Deficient Bonding to a Triosmium Cluster

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Abstract: A new synthetic methodology for adding carbon-based nucleophiles to the carbocyclic ring of quinolines has been developed, based on the electron-deficient bonding of the C(8) carbon and the protective coordination of the nitrogen atom to the metal core in the complexes $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_5(R)N)(\mu\text{-}H)$, **1a**−**1h**. These compounds react with a wide range of carbanions (e.g., R′Li) to give the nucleophilic addition products $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_9H_7(5\text{-}R')N)(\mu\text{-}H)$, **2a**−**2l**, and $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_9H_6(3\text{-}, 4\text{-}, \text{or } 6\text{-}R)(5\text{-}R')N)(\mu\text{-}H)$, **3b**−**3g**, after quenching with trifluoroacetic acid, in isolated yields of 25−86%. In the 6-substituted derivatives, this addition is stereoselective, forming only the cis-diastereomer. In the case the 6-chloro derivative, a second product is obtained, $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_5(6\text{-Cl})(5\text{-}C(CH_3)_2CN)N)(\mu\text{-}H)_2$, **4**, the result of protonation at the metal core and rearrangement of the carbocyclic ring. The trans-diastereomer of the 6-substituted derivatives can be obtained by quenching the intermediate anion of the unsubstituted complex with $(CH_3O)_2SO_2$ or acetic anhydride. Nucleophilic addition to the 5-chloro complex occurs across the 3,4-bond to give $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_6(5\text{-Cl})(4\text{-}C(CH_3)_2CN)N)(\mu\text{-}H)$, **5**. The addition products, types **2** and **3**, can be rearomatized by reaction with diazobicyclononane (DBU)/dichlorodicyanoquinone (DDQ) or by reaction of the intermediate anion with trityl cation or DDQ. The resulting rearomatized complexes can be cleanly cleaved from the cluster by heating in acetonitrile under a CO atmosphere, yielding the functionalized quinoline and $Os_3(CO)_{12}$ as the only two products. Solid structures of ***cis*-3e**, ***trans*-3e**, **4**, and **5** are reported.

Introduction

The transition metal-activated nucleophilic addition and substitution reactions of π-bound arenes have proven to be an extremely useful addition to the organic chemists' arsenal for functionalizing arenes, cyclizations, and asymmetric syntheses.[1−3] Recently, this methodology has been extended to include bicyclic arenes, heterocycles[4] and indoles.[3,5] Notably missing from this group of substrates for nucleophilic activation by transition metals is the quinoline family. Quinoline prefers η^1-N coordination over η^6 coordination to the carbocyclic ring, in sharp contrast to indoles, because of their greater basicity.[6] There are thus few $\pi\text{-}\eta^6$-arene complexes of quinoline, and nucleophilic addition and substitution have been studied only for the η^1-N transition metal complexes.[7] We recently reported the synthesis of a family of $\sigma\text{-}\mu_3\text{-}\eta^2$ complexes of quinoline that undergo regioselective nucleophilic addition of hydride at the 5-position (eqs 1 and 2).[8−10]

These initial results prompted us to try to extend to carbanions the regioselective nucleophilic attack observed with hydride. The site of nucleophilic attack in free quinolines or in η^1-N-coordinated quinolines is normally the 2-position (or the 4-position, if the former is blocked).[7,11] Successful addition of the carbanion would allow a novel method for derivatizing the quinoline family of heterocycles on the carbocyclic ring. We report here the results of these studies as well as some further characterization of the intermediate anion (eq 2) and discuss the reactivity of the nucleophilic addition products formed after quenching this anion with electrophiles. In light of the importance of the quinoline ring system in drug design and development,[12] as agonists or antagonists for neurotransmitter molecules,[12] and as intermediates in syntheses, of natural products[13] these results represent a potentially useful synthetic methodology not available via complexation by monometallic species.

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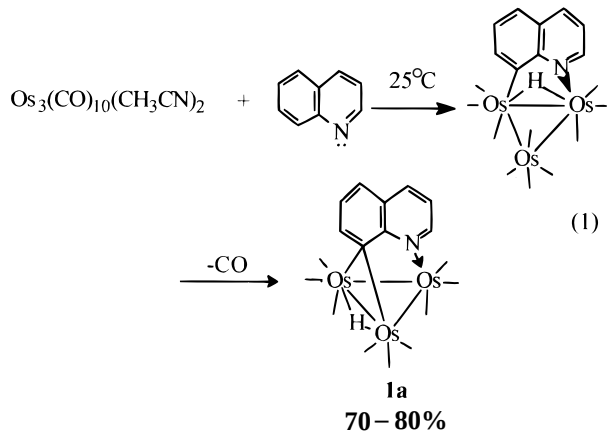
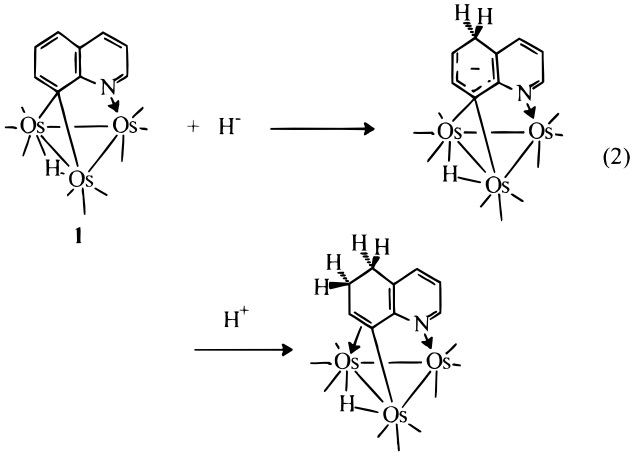
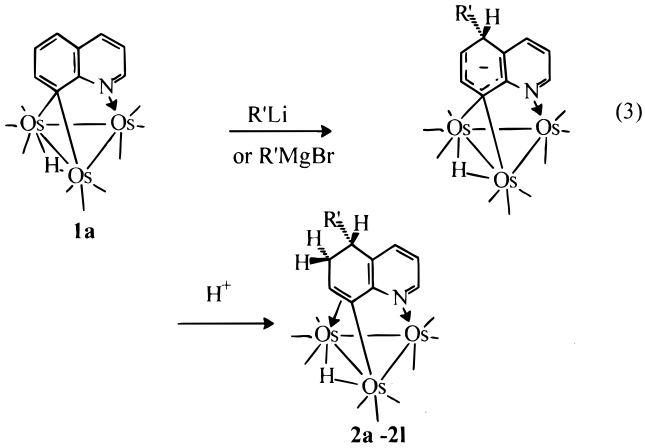




Results and Discussion

A. Reactions of Carbanions with the Parent Quinoline Complex 1a. When compound **1a** is reacted with a 2 to 3-fold excess of the carbanions listed in Table 1 at −78 °C, the deep green tetrahydrofuran (THF) solution turns dark orange or amber. After being stirred and warmed to 0 °C, the solution is cooled to −78 °C and quenched with a slight excess (relative to the total carbanion added) of trifluoroacetic acid to give an orange to red solution. After chromatographic purification, the nucleophilic addition products $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_9H_7(5\text{-}R')N)(\mu\text{-}H)$ (**2a**−**2l**) are isolated in the yields reported in Table 1 (eq 3). The only carbanion tried that did not result in nucleophilic

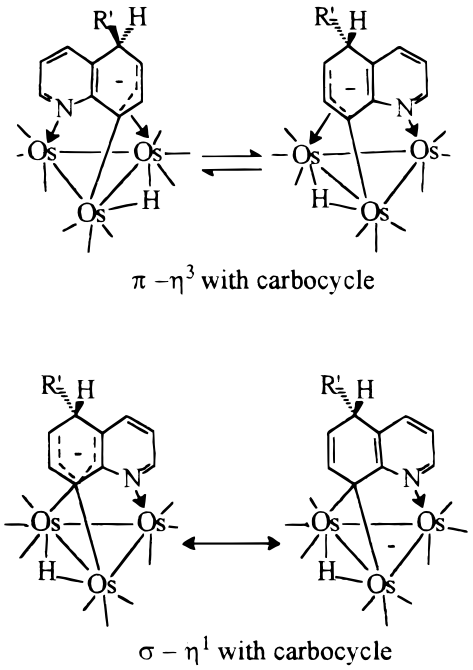


addition on the ring was sodium diethylmalonate, which apparently complexes with **1a** at the metal core, as evidenced by the reversible color change from green to yellow when this

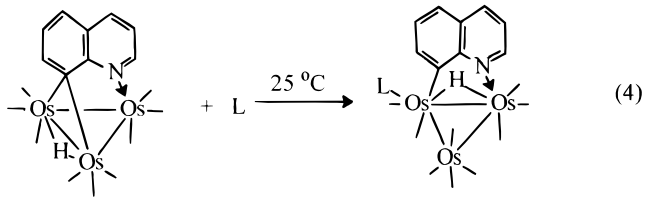
Table 1. Isolated Nucleophilic Addition Product Yields from the Reaction of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_6N)(\mu\text{-}H)$, **1a**, with Carbanions

compound	carbanion	yield, %
2a	LiMe	66
2b	Li^{n}Bu	45
2c	Li^{t}Bu	52
2d	LiBz	48
2e	LiPh	66
2f	$LiCH{=}CH_2$	51
2g	$LiC_2(CH_2)_3CH_3$	25
2h	$LiCH_2CN$	72
2i	$LiC(CH_3)_2CN$	69
2j	Li-$CHS(CH_2)_2S$-	72
2k	$LiCH_2CO_2{}^tBu$	86
2a	MeMgBr	43
2l	$CH_2{=}CHCH_2MgBr$	53

Scheme 1



reagent is added to **1a** at −78 °C and then warmed to room temperature. This behavior, and the associated color change, are similar to those observed for the reaction of **1a** with neutral 2-electron donors (eq 4).[8−10] Methoxide also failed to react with



1a. As seen from the yields listed in Table 1, the harder, more nucleophilic carbanions give somewhat lower yields than the softer nucleophiles, probably because of competing attack at the coordinated carbonyl groups by the former, leading to decomposition. Overall, **1a** reacts with a broader range of nucleophiles relative to the neutral monometallic π-arene complexes.[14] This is undoubtedly a result of localization of the electron deficiency at the 5-position induced by the electron-

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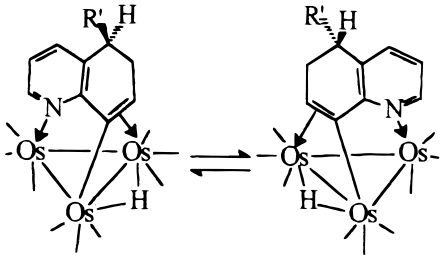
Scheme 2



deficient bonding to the cluster.[8−10] Thus lithium *tert*-butyl acetate reacts quite well with **1a**, whereas yields of (π-η^6-arene)-$Cr(CO)_3$ were quite low except in the presence of very polar solvents such as hexamethylphosphoramide or use of the corresponding potassium salt. Methyllithium and *n*-butyllithium will deprotonate (π-η^6-arene)$Cr(CO)_3$, whereas **1a** yields the usual nucleophilic addition products.[14] Indeed, we have attempted deprotonation of **1a** with lithium diisopropylamide, but observed no evidence for this mode of reaction.

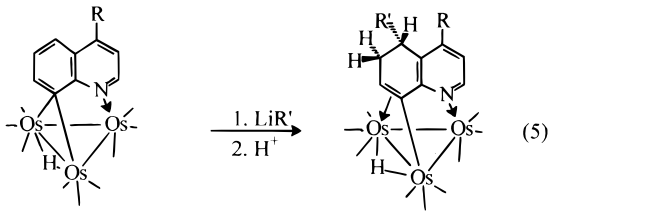
The structure of the intermediate anion produced after nucleophilic attack remained in question after our initial reports on the reactivity of **1a** and related compounds with hydride donors.[8−10] Two structural types are possible, according to the ^{1}H NMR data at room temperature: (1) a tilted μ_3-η^4-allyl, which is undergoing rapid $\sigma-\pi$-interchange; and (2) a μ_3-η^2-alkylidene, in which the quinoline remains perpendicular to the metal and is stabilized by electron delocalization to the metal core (Scheme 1). We have now examined the variable temperature (VT) ^{13}C NMR of a ^{13}CO-enriched sample of the anion that results from hydride attack on **1a**. At both 22 and −80 °C, five carbonyl resonances are observed, at 191.90, 186.76, 185.56, 183.43, and 181.11 ppm, in a relative intensity of 2:1:2:2:2. We think this result supports the perpendicular μ_3-η^2-structure since the $\sigma-\pi$-interchange process usually has a barrier of 40−50 kJ/mol in related systems and should be at least partially frozen out on the NMR time scale at −80 °C.[9]

Compound **2g** was isolated in rather poor yield along with an as-yet-unidentified coproduct that appears to involve some rearrangement of the carbocyclic ring. We are currently investigating the structure of this complex further.

The chiral center created at C(5) along with the overall chirality of these $\sigma-\pi$ vinyl complexes would be expected to lead to the isolation of diastereomers. However, the operative $\sigma-\pi$ vinyl interchange, which is apparently rapid on the NMR time scale in **2a**−**2l**, precludes the isolation of diastereomers (Scheme 2).[9]

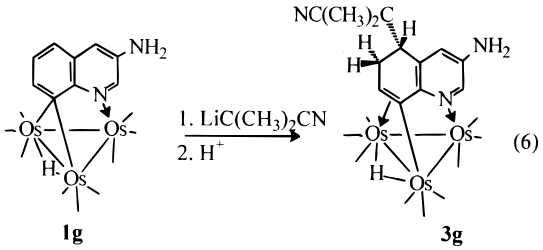
B. Reactions of Carbanions with Monosubstituted Quinolines. Substitution at both the carbocyclic and heterocyclic ring over a range of functional groups is well tolerated for the nucleophilic additions described above. Thus, reaction of **1b** with $LiC(CH_3)_2CN$ or $LiCH_2CO_2tBu$ gives the expected nucleophilic addition products $Os_3(CO)_9(\mu_3$-η^3-C_9H_6(4-R)(5-R′)N)-(μ-H) (R= Cl, R′= CH_2CO_2tBu, **3b**; R = Cl, R′= $C(CH_3)_2CN$, **3b′**) in reasonable yields (54 and 67%, respectively). Similarly, **1c** reacts with $LiCH_2CO_2tBu$ and **1g** reacts with $LiC(CH_3)_2CN$ in an analogous manner (eq 5 and 6).

The 6-substituted quinoline derivatives undergo nucleophilic addition as well, but with interesting differences. Complex **1d** reacts with $LiC(CH_3)_2CN$ to give two major products, the expected nucleophilic addition product, $Os_3(CO)_9(\mu_3$-η^3-C_9H_6-(6-Cl)(5-$C(CH_3)_2CN$)N)(μ-H), **3d**, and a dihydrido complex, $Os_3(CO)_9(\mu_3$-η^2-C_9H_5(6-Cl)(5-$C(CH_3)_2CN$)N)(μ-H)$_2$, **4**, apparently as a result of competitive protonation at the metal core



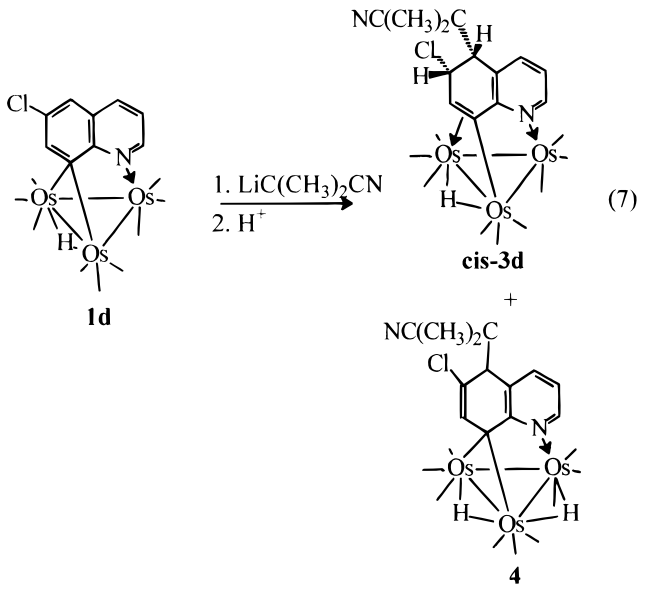
1b, R=Cl
1c, R=OCH_3

3b, R=Cl, R'=$C(CH_3)_2CN$
3b', R=Cl, R'=$CH_2CO_2{}^tBu$
3c, R=OCH_3, R'=$CH_2CO_2{}^tBu$



1g **3g**

(eq 7). From the NMR data alone, the bonding mode to the



1d **cis-3d** **4**

trimetallic core could not be assigned with certainty. A solid-state structural investigation was therefore undertaken.

The solid-state structure of **4** is shown in Figure 1, crystal data are given in Table 2, and selected distances and bond angles are shown in Table 3. The structure consists of an Os_3 triangle with two approximately equal metal−metal bonds (Os(1)−Os-(3) and Os(2)−Os(3) at 2.814(1) and 2.786(1) Å) and one slightly elongated metal−metal bond (Os(1)−Os(2), 2.962(1) Å). The two hydride ligands were located by determining the potential energy minimum with the program Hydex.[15] As expected, the elongated metal−metal bond has the hydride ligand located in-plane, whereas the doubly bridged Os(1)−Os(3) edge has the hydride ligand tucked well below the Os_3 plane.[9] Compound **4** is bound to the cluster by an electron-precise sp^3-μ-alkylidene linkage with C(8). The bonding is slightly asymmetric (Os(1)−C(8) = 2.19(1) and Os(3)−C(8) = 2.21(1) Å). These electron-precise bonds are considerably shorter than the related electron-deficient bonds in **1a** (2.28(1) and 2.32(1) Å). The Os(2)−N bond length in **4**, on the other

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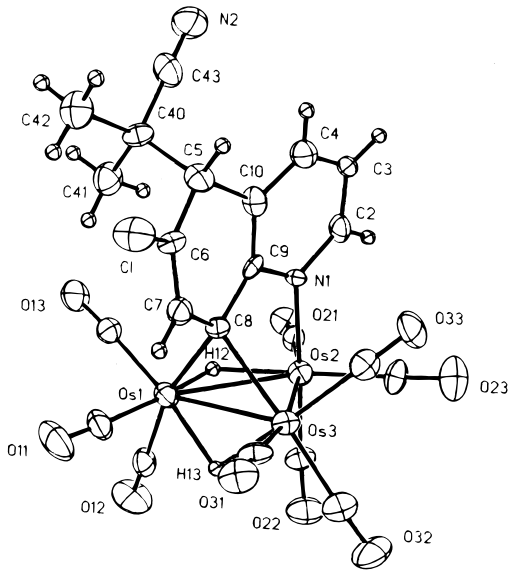

Figure 1. Solid-state structure of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_5(6\text{-}Cl)(5\text{-}C(CH_3)_2CN)N)(\mu\text{-}H)_2$, **4**, showing the calculated positions of the hydrides.

hand, is exactly the same as in **1a** (2.13(1) Å). The C(5)−C(6), C(6)−C(7), and C(7)−C(8) bonds can be considered as single, double, and single bonds, respectively, on the basis of the observed distances (1.46(2), 1.36(2), and 1.47(2) Å). In the solid state, only one of two geometric isomers of **4** is observed, with the hydride bridging the Os(1)−Os(2) edge *syn* to the isobutyronitrile group. In solution, a minor isomer can be observed (∼10% of the major) by ^{1}H NMR.

The formation of **4** from **1d** can be rationalized by the electron-withdrawing effect of the chloride, making protonation at the 6-position less favorable and resulting in competitive protonation at the metal core.[10] To some extent, the relative amounts of **3d** and **4** can be controlled. When a 10-fold excess of acid is used to quench the nucleophilic addition, **3d** and **4** are formed in a 3:2 ratio, when 1 equivalent of acid is used, the ratio is 5:1. This reflects the greater statistical probability for protonation at the Os_3 core relative to the C(6) position of the ring. Attempts to convert **4** to **3d** by heating at 80 °C in C_6D_6 for several hours failed. In metal cluster chemistry, it is not uncommon to observe the formation of two isomeric products that do not interconvert at temperatures below the decomposition temperature of the compounds.[16] The formation of **4** lends credence to our proposed structure for the intermediate anion because it is identical in structure to one of the resonance forms proposed (Scheme 1).

The reaction of **1d** with $LiC(CH_3)_2CN$ gave only one of the two possible diastereomers of **3d** (eq 7). The observed coupling constant between the C(5) and C(6) protons (5.77 Hz) gave no firm indication of the stereochemistry across the C(5)−C(6) bond since this value is right on the borderline between the values for cis and trans orientations around the C(3)−C(4) bonds in cyclohexenes.[17] In addition, the metal-ligand bonding framework for structural types **2** and **3** imparts an unusual puckered geometry to the carbocyclic ring,[9] which makes inferring stereochemistry from coupling constants ambiguous. Unfortunately, we were unable to obtain X-ray-quality crystals for **3d**.

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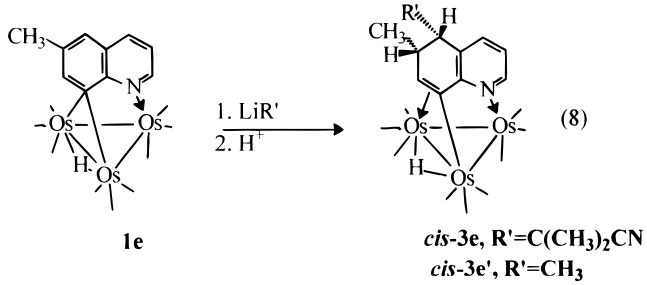
(17) Bovey, F. A. *NMR Data Tables for Organic Chemists*; Wiley-Interscience: New York 1967.

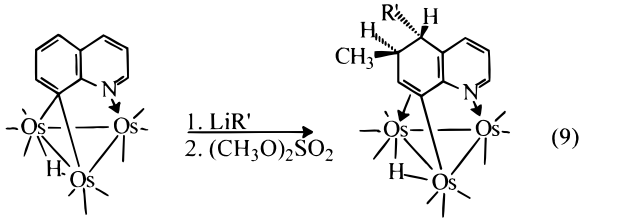
The reaction of **1e** with $LiC(CH_3)_2CN$ gave one major product in 71% yield, $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_9H_6(6\text{-}CH_3)(5\text{-}C(CH_3)_2\text{-}CN)N)(\mu\text{-}H)$, **3e**. This compound was also isolated as one diastereomer and showed a vicinal coupling constant for the C(5)−C(6) protons of 5.95 Hz, very similar to that observed in **3d** (eq 8). Examination of the crude reaction mixture by ^{1}H



1e ***cis*-3e, R'=C(CH$_3$)$_2$CN** ***cis*-3e', R'=CH$_3$**

NMR prior to chromatographic purification showed the presence of only one diastereomer of **3e** in addition to starting material. Thus, the single diastereomer appears to be the kinetic product and is not the result of equilibration on the silica gel used for purification. Suitable crystals of **3e** for X-ray analysis were obtained, which allowed us to firmly establish the stereochemistry across the C(5)−C(6) bond.

The solid-state structure of **3e** is shown in Figure 2, crystal data are given in Table 2, and selected distances and bond angles are listed in Table 4. The cis-configuration around the C(5)−C(6) double bond is obvious from the solid-state structure of *cis*-**3e**, as is the anticipated puckered-boat configuration of the carbocyclic ring. The overall structure is very similar to the previously reported $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_9H_8N)(\mu\text{-}H)$.[9] The $\sigma-\pi$-vinyl bonding mode is most likely undergoing a $\sigma-\pi$-interchange in solution, as observed for related compounds,[9] but we could not ascertain if this process was operative because of the asymmetry in **3e**. The cis-stereochemistry can be rationalized by exclusive trans-protonation of an essentially planar anionic intermediate (Scheme 1), where the bulky nucleophile blocks one face of the carbocyclic ring at C(6). Such is not the case for deuteride as a nucleophile, however, for both cis and trans isomers are observed in similar amounts when **1e** is treated with D^-/H^+.[9] When **1e** is reacted with $LiCH_3$, one major stereoisomer is obtained in 67% yield, $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_9H_6(5,6\text{-}CH_3)_2N)(\mu\text{-}H)$, **3e′**, which we can identify as the cis-diastereomer from ^{1}H NMR decoupling experiments in which a vicinal $^3J(^1H-^1H)$ of 4.5 Hz is revealed across the C(5)−C(6) bond. A trace amount of a second diastereomer is observed as companion peaks in the ^{1}H NMR of **3e′**. Thus, even a relatively small alkyl group on C(5) is sufficient to induce almost exclusive trans-protonation. If our hypothesis about trans-protonation is correct, then we should be able to obtain *trans*-**3e** by treating **1a** with $LiC(CH_3)_2CN$ followed by reaction with $(CH_3O)_2SO_2$. This is indeed the case (eq 9), although complete



1a ***trans*-3e, R'=C(CH$_3$)$_2$CN** ***trans*-3e', R'=CH$_3$**

Table 2. Crystal data and structure refinement for 4, *cis*-**3e**, *trans*-**3e**, and **6**[a]

	4	*cis*-**3e**	*trans*-**3e**	**6**
empirical formula	$C_{22}H_{13}ClN_2O_9Os_3$	$C_{23}H_{16}N_2O_9Os_3$	$C_{23}H_{16}N_2O_9Os_3$	$C_{22}H_{13}ClN_2O_9Os_3$
formula weight	1055.39	1034.98	1034.98	1055.39
temperature, K	293(2)	293(2)	293(2)	293(2)
wavelength, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	C_2/c (#15)	P-1	P-1	$P2_1/n$
Unit cell dimensions	$a = 32.976(7)$ Å $\alpha = 90°$ $b = 9.972(2)$ Å $\beta = 103.30(3)°$ $c = 15.980(3)$ Å $\gamma = 90°$	$a = 10.086(4)$ Å $\alpha = 91.65(5)°$ $b = 11.158(7)$ Å $\beta = 111.17(5)°$ $c = 12.569(9)$ Å $\gamma = 90.73(4)°$	$a = 9.203(3)$ Å $\alpha = 90.49(3)°$ b=9.730(3) Å $\beta = 98.35(3)°$ $c = 16.012(7)$ Å $\gamma = 107.06(2)°$	$a = 8.872(2)$ Å $\alpha = 90°$ $b = 20.838(4)$ Å $\beta = 95.87(3)°$ $c = 14.224(3)$ Å $\gamma = 90°$
volume, Z	5114(2) Å^3, 8	1318(1) Å^3, 2	1354.2(8) Å^3, 2	2615.9(10) Å^3, 4
density (calculated), mg/m^3	2.742	2.608	2.747	2.680
ϵ, mm^{-1}	15.029	14.476	14.293	14.690
F(000)	3808	936	1020	1904
crystal size, mm	0.18 × 0.13 × 0.08	0.20 × 0.18 × 0.13	0.38 × 0.30 × 0.20	0.25 × 0.13 × 0.08
θ range for data collection, deg	1.27−21.97	1.74−18.99	1.29−24.97	1.74−24.99
limiting indices	$-34 \le h \le 34, 0 \le k \le 10, -11 \le l \le 16$	$-9 \le h \le 9, -10 \le k \le 10, -10 \le l \le 11$	$-10 \le h \le 10, -11 \le k \le 9, -19 \le l \le 19$	$-10 \le h \le 10, 0 \le k \le 24, -16 \le l \le 16$
reflections collected	12 131	4222	7883	9179
independent reflections	3133 ($R_{int} = 0.022$)	2111 ($R_{int} = 0.103$)	4762 ($R_{int} = 0.0344$)	4593 ($R_{int} = 0.0543$)
max, min. transmission	0.9998, 0.5899	0.9983, 0.7745	1.000, 0.305	0.9992, 0.7989
data/restraints/parameters	3131/0/329	2111/0/164	4759/0/344	4593/0/334
goodness-of-fit on F^2	1.120	1.020	1.272	0.996
final R indices [I > 2σ(I)]	R1 = 0.0367, wR2 = 0.0661	R1 = 0.0690, wR2 = 0.1515	R1 = 0.0634, wR2 = 0.1633	R1 = 0.0400, wR2 = 0.0674
R indices (all data)	R1 = 0.0542, wR2 = 0.0780	R1 = 0.0897, wR2 = 0.1658	R1 = 0.0799, wR2 = 0.1761	R1 = 0.0704, wR2 = 0.0766
largest diff. peak and hole, eÅ^{-3}	0.713 and −0.879	2.038 and −2.394	2.784 and −6.194	0.820 and −0.801

[a] Absorption correction Ψ and refinement method of full-matrix least-squares on F^2 used for all four compounds.

Table 3. Selected Distances (Å) and Angles (Deg) for **4**[a]

distances			
Os(1)−Os(2)	2.962(1)	C(8)−C(9)	1.46(2)
Os(1)−Os(3)	2.814(1)	C(7)−(8)	1.47(2)
Os(2)−Os(3)	2.786(1)	C(6)−C(7)	1.36(2)
Os(1)−C(8)	2.19(1)	C(6)−C(5)	1.46(2)
Os(3)−C(8)	2.21(1)	C(6)−C(1)	1.75(1)
Os(2)−N(1)	2.13(1)	C(5)−C(40)	1.59(2)
Os−CO[b]	1.89(2)	C−O[b]	1.13(2)

angles			
Os(1)−Os(2)−Os(3)	58.53(2)	C(6)−C(7)−C(8)	125.(1)
Os(1)−Os(3)−Os(2)	63.86(2)	C(5)−C(6)−C(7)	124.(1)
Os(2)−Os(1)−Os(3)	57.61(2)	C(6)−C(5)−C(10)	109.(1)
Os(1)−C(8)−Os(3)	79.6(4)	C(10)−C(5)−C(40)	110.(1)
Os(3)−Os(2)−N(1)	81.9(3)	C(2)−N(1)−C(9)	117.(1)
Os−C−O[b]	177.(1)		

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

conversion to *trans*-**3e** is not realized because significant amounts (∼40%) of **2i** are formed. Presumably this occurs by incomplete alkylation of the anion intermediate, followed by protonation on workup with silica gel. It was not possible to separate *trans*-**3e** from **2i** by thin-layer chromatography (TLC) but we did obtain analytically pure samples by reversed-phase high pressure liquid chromatography (HPLC). Although it was immediately obvious that *trans*-**3e** was a different stereoisomer from *cis*-**3e**, the vicinal coupling constant across the C(5)−C(6) bond was observed to be <1 Hz. Because seemed very unusual for a trans-isomer, we decided to do a solid-state structure determination of trans-**3e**.

The solid-state structure of *trans*-**3e** is shown in Figure 3, crystal data are given in Table 2, and selected distances and bond angles are listed in Table 5. The geometry across the

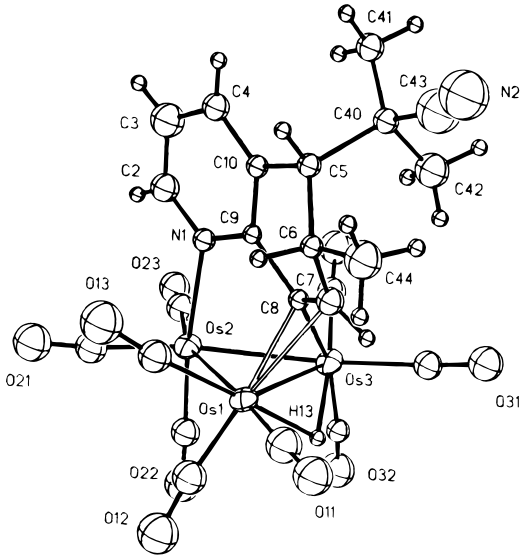


Figure 2. Solid-state structure of $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_9H_6(6\text{-}CH_3)(5\text{-}C(CH_3)_2CN)N)(\mu\text{-}H)$, *cis*-**3e**, showing the calculated position of the hydride.

C(5)−C(6) bond is trans and the conformation of the carbocyclic is such that the dihedral between the alkyl groups is 154°, whereas that between the calculated positions of the C(5) and C(6) hydrogen atoms is 80°. This explains the small coupling constant across this bond and suggests that the detailed conformation of the carbocyclic ring is controlled by steric interactions of the alkyl group across the C(5)−C(6) bond as well as the bonding mode to the metal core. The related dihedral angles in *cis*-**3e** are 52° and 51°, respectively. The other features of the structure are virtually identical with *cis*-**3e**.

Table 4. Selected Distances (Å) and Angles (Deg) for *cis*-**3e**[a]

	distances		
Os(1)−Os(2)	2.886(2)	C(7)−C(8)	1.35(3)
Os(1)−Os(3)	2.851(2)	C(5)−C(6)	1.52(3)
Os(2)−Os(3)	2.776(2)	C(6)−C(7)	1.54(3)
Os(1)−C(8)	2.16(3)	C(5)−C(10)	1.58(3)
Os(1)−C(7)	2.43(3)	C(5)−C(40)	1.65(4)
Os(3)−C(8)	2.09(2)	C(6)−C(44)	1.42(3)
Os(2)−N(1)	2.18(2)	C(9)−N(1)	1.33(3)
Os−CO[b]	1.86(3)	C(9)−C(10)	1.40(3)
		C−O[b]	1.16 (2)
	angles		
Os(1)−Os(2)−Os(3)	60.44(5)	C(6)−C(7)−C(8)	127(2)
Os(1)−Os(3)−Os(2)	61.68(5)	C(5)−C(6)−C(7)	107(2)
Os(2)−Os(1)−Os(3)	57.88(5)	C(6)−C(5)−C(10)	110(2)
Os(1)−C(7)−C(8)	62(2)	C(10)−C(5)−C(40)	106(2)
Os(1)−C(8)−C(7)	84(2)	C(2)−N(1)−C(9)	126(2)
Os(3)−C(8)−C(7)	126(2)		
Os(3)−Os(2)−N(1)	84.5(5)		
Os−C−O[b]	173(3)		

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

Table 5. Selected Distances (Å) and Bond Angles (Deg) for *trans*-**3e**[a]

	distances		
Os(1)−Os(2)	2.789(1)	C(7)−C(8)	1.37(2)
Os(1)−Os(3)	2.840(1)	C(6)−C(7)	1.55(2)
Os(2)−Os(3)	2.880(1)	C(5)−C(6)	1.55(2)
Os(1)−C(8)	2.11(1)	C(5)−C(10)	1.52(2)
Os(3)−C(8)	2.26(1)	C(5)−C(40)	1.56(3)
Os(3)−C(7)	2.45(2)	C(6)−C(44)	1.54(3)
Os(2)−N(1)	2.18(1)	C(9)−N(1)	1.30(3)
Os−CO[b]	1.91(2)	C−O[b]	1.14(2)
	angles		
Os(1)−Os(2)−Os(3)	60.09(3)	C(6)−C(7)−C(8)	124(1)
Os(1)−Os(3)−Os(2)	58.37(3)	C(5)−C(6)−C(7)	109(1)
Os(2)−Os(1)−Os(3)	61.54(3)	C(6)−C(5)−C(10)	109(1)
Os(1)−C(8)−C(7)	123(1)	C(10)−C(5)−C(40)	112(1)
Os(3)−C(8)−C(7)	80(1)	C(2)−N(1)−C(9)	120(1)
Os(3)−C(7)−C(8)	65(1)		
Os(1)−Os(2)−N(1)	84.2(4)		
Os−C−O[b]	177(1)		

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

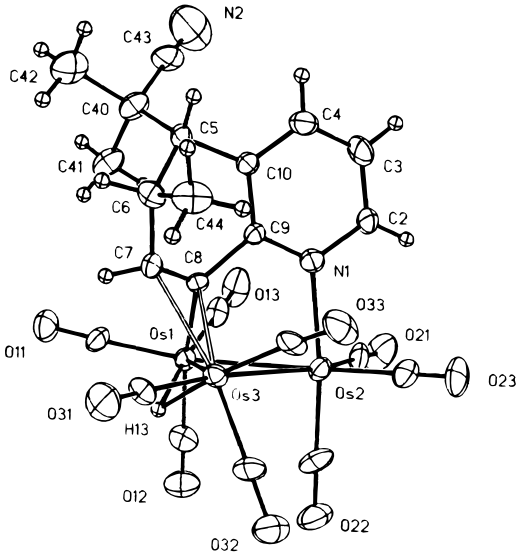
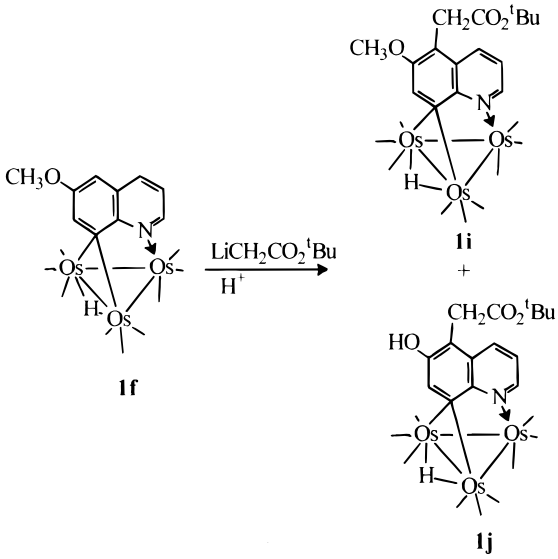


Figure 3. Solid-state structure of $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_9H_6(6\text{-}CH_3)(5\text{-}C(CH_3)_2CN)N)(\mu\text{-}H)$, *trans*-**3e**, showing the calculated position of the hydride.

The same reaction sequence with **1a**, but using LiMe and $(CH_3O)_2SO_2$, yielded *trans*-**3e′** (eq 9). In this case, alkylation was also incomplete and **2a** was isolated as a coproduct. The vicinal coupling constant in the case of *trans*-**3e** is 11.98 Hz, indicating that with the smaller methyl group, the carbocycle can adopt a conformation in which the hydrogens are approximately trans-diaxial.[17]

The anion generated from the treatment of **1a** with $LiCH_3$ can also be quenched with acetic anhydride to give *trans*-$Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_9H_6(5\text{-}CH_3)(6\text{-}CH_3CO)N)(\mu\text{-}H)$, **5**. The vicinal coupling constant across the C(5)−C(6) bond is 12.1 Hz. As might be expected, the more sterically compact sp^2 carbon of the acetyl group allows the substituents on C(5) and C(6) to adopt a diequatorial conformation, resulting in a trans-diaxial relationship for the hydrogens on these carbons as for *trans*-**3e′**.

The reaction of **1f** with $LiCH_2CO_2tBu$ gives the green aromatized complex $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_4(6\text{-}OCH_3)(5\text{-}CH_2CO_2\text{-}tBu)N)(\mu\text{-}H)$ (**1i**, eq 10) in 54% yield. In addition, 35% of the corresponding phenol, $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_4(6\text{-}OH)(5\text{-}CH_2CO_2\text{-}tBu)N)(\mu\text{-}H)$, **1j**, is also isolated, probably as a result of hydrolysis by trace moisture during the acid quench or the workup on silica gel. The facile oxidation (dehydrogenation) of the intermediate nucleophilic addition product is a result of the presence of the strongly π-electron-donating 6-methoxyl group and the alkyl substituent in the 5-position. Small amounts of rearomatized products were also noted in the reactions of **1e** with $LiCH_3$ and $LiC(CH_3)_2CN$.



(10)

The highly regioselective nature of the nucleophilic additions observed for structural type **1**, regardless of the nature or location of the substituents on the quinoline ring, poses the question as to what would occur if the 5-position were substituted with a reasonable leaving group. In the case of halide-substituted $\pi\text{-}\eta^6$-arene complexes, nucleophilic substitution competes with nucleophilic addition.[14] The reaction of **1h** with $LiC(CH_3)_2CN$ results in nucleophilic addition across the 3,4-bond of the quinoline ring to yield $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_6(5\text{-}Cl)(4\text{-}C(CH_3)_2\text{-}CN)N)(\mu\text{-}H)$, **6**, (eq 11). The ^1H−COSY NMR of **6** clearly shows the coupling of the most-downfield aromatic resonance (i.e., the C(2)−H) to the most-upfield aliphatic resonance and two separately coupled aromatic resonances. These data are consistent with the structure shown in eq 11. However, as with **4**, the mode of bonding of the ligand to the metal core was not evident from these data alone and so a solid-state structure of **6** was undertaken.

The solid-state structure of **6** is shown in Figure 4, crystal data are given in Table 2, and selected distances and bond angles

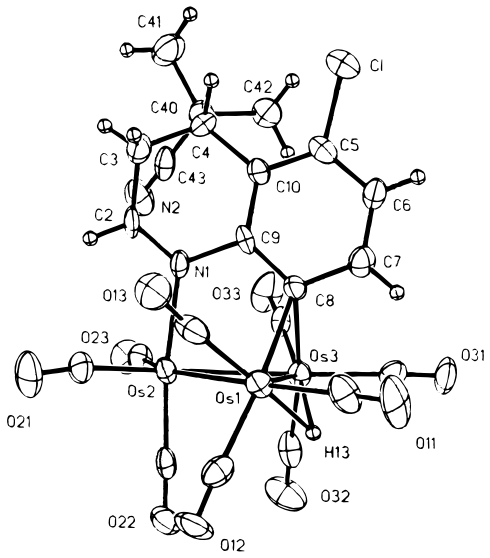
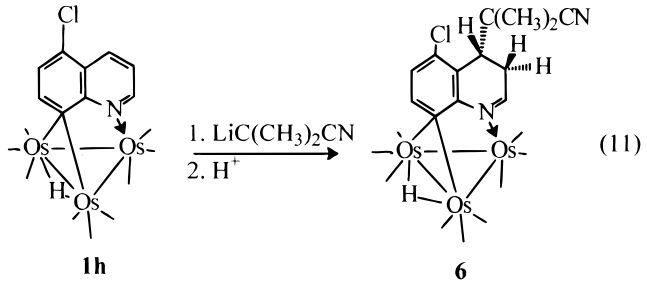


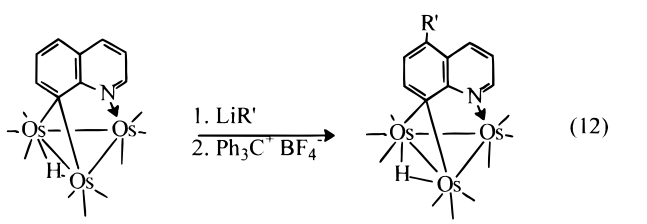
Figure 4. Solid-state structure of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_6(5\text{-Cl})(4\text{-}C(CH_3)_2CN)N)(\mu\text{-H})$, **6**, showing the calculated position of the hydride.



(11)

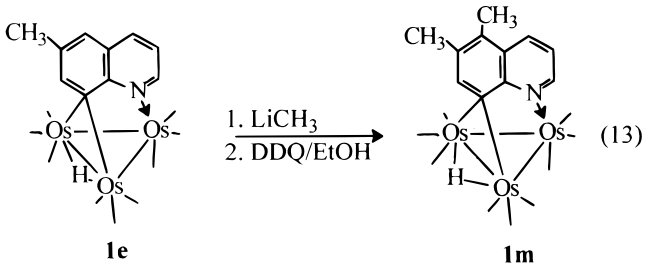
are listed in Table 6. The solid-state structure of **6** is that proposed from the ^{1}H NMR data. The core consists of an essentially equilateral triangle with a hydride bridging the Os(1)−Os(3) edge. The electron-deficient bonds between C(8), Os(1), and Os(3) are slightly asymmetric, and the bond vectors are about the same as in **1a**; 2.31(1) and 2.26(1) Å in **6** and 2.32(1) and 2.28(1) Å in **1a**. The Os(2)−N(1) bond is slightly elongated in **6** with respect to **1a** (2.17(1) and 2.13(1) Å, respectively), as was observed in *cis*- and *trans*-**3e**. The N(1)−C(2) bond, at 1.30(1) Å, is typical of a C−N double bond, and the remaining bond lengths are unremarkable.

C. Rearomatization of the Nucleophilic Addition Products. The facile rearomatization of the nucleophilic addition product derived from the addition of $LiCH_2CO_2tBu$ to **1f** (eq 11) prompted us to attempt to reproduce this process in a deliberate manner. Several methods proved adequate for this. The addition of trityl cation to the anion that resulted from the addition of alkylating agents RLi (R = n-Bu, CH_2CO_2tBu) to **1a** gave the rearomatized products $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_5(5\text{-R})N)(\mu\text{-H})$ (**1k**, R= ^{n}Bu; **1l**, R = CH_2CO_2tBu; eq 12) in yields of 53% and



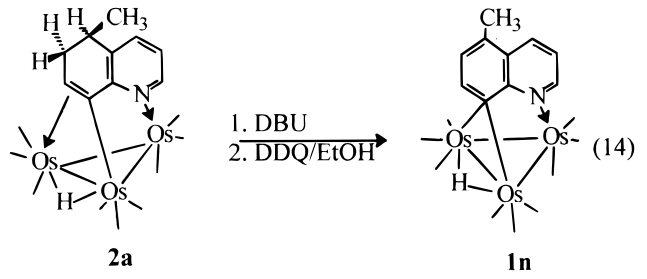
(12)

83%, respectively. In some other cases, we found the coproduct triphenyl methane difficult to separate from the products. An alternative route is the addition of dichlorodicyanoquinone (DDQ), followed by an ethanol quench of the resulting hydroquinone anion and excess carbanion. Thus, treating **1a** with $LiCH_3$ and then DDQ/EtOH yields $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_4(5,6\text{-}CH_3)_2N)(\mu\text{-H})$, **1m**, eq 13). Finally, one can add a deprotonating



(13)

agent such as diazabicycloundecane (DBU) to the isolated nucleophilic addition products of type **2** or **3**, followed by DDQ/EtOH, as demonstrated with **2a,** which yielded $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_5(5\text{-}CH_3)N)(\mu\text{-H})$, **1n**, (eq 14). Attempts to react **2** or **3**



(14)

with DDQ directly failed. Which is the best route from among these methods remains uncertain at present except that DDQ seems to tolerate functionality somewhat better and its reaction products are easier to separate from the cluster reaction products. In cases where multiple products result (eq 7), isolation of the nucleophilic addition product followed by treatment with DBU/DDQ would be the method of choice.

D. Cleavage of the Functionalized Quinoline from the Cluster. For this synthetic methodology to be developed as a useful tool for synthesis of novel quinoline derivatives, a clean method for cleavage of the quinoline ligand from the cluster is required. For the rearomatized derivatives of structural type **1**, heating the quinoline cluster complex at 70 °C in acetonitrile under an atmosphere of carbon monoxide. This leads to isolation of the free quinoline and formation of $Os_3(CO)_{12}$. The $Os_3(CO)_{12}$

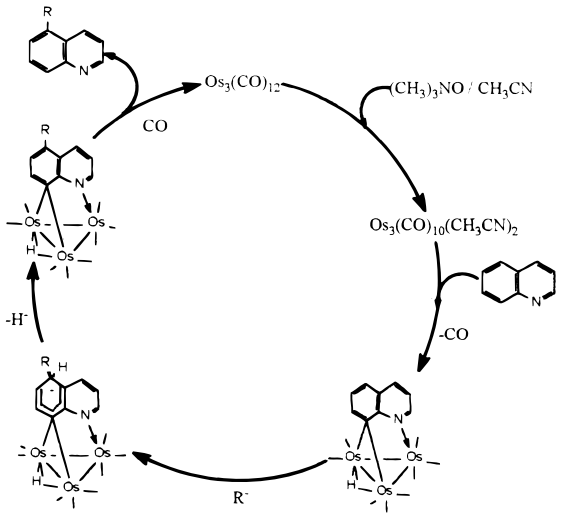
Table 6. Selected Distances (Å) and Bond Angles (Deg) for **6**

distances			
Os(1)−Os(2)	2.772(1)	N(1)−C(2)	1.30(1)
Os(1)−Os(3)	2.756(1)	C(2)−C(3)	1.50(1)
Os(2)−Os(3)	2.770(1)	C(3)−C(4)	1.51(2)
Os(1)−C(8)	2.26(1)	C(4)−C(10)	1.51(1)
Os(3)−C(8)	2.31(1)	C(4)−C(40)	1.59(2)
Os(2)−N(1)	2.17(1)	C(5)−Cl	1.73(1)
Os−CO[b]	1.92(2)	C(5)−C(6)	1.36(2)
		C−O[b]	1.13(2)

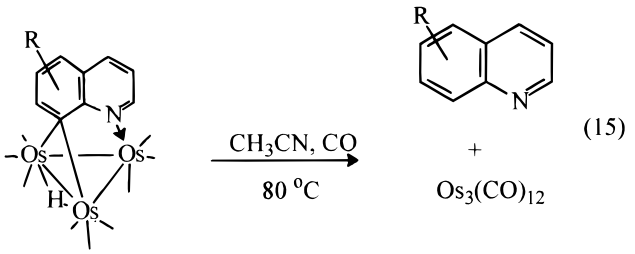
angles			
Os(1)−Os(2)−Os(3)	59.65(2)	N(1)−C(2)−C(3)	122(1)
Os(1)−Os(3)−Os(2)	60.22(2)	C(2)−C(3)−C(4)	112(1)
Os(2)−Os(1)−Os(3)	60.12(2)	C(3)−C(4)−C(10)	108(1)
Os(1)−C(8)−Os(3)	74.2(3)	C(3)−C(4)−C(40)	112(1)
Os(3)−Os(2)−N(1)	84.9(2)	C(10−C(5)−Cl	120(1)
Os(1)−Os(2)−N(1)	82.4(2)	C(7)−C(8)−C(9)	116(1)
Os−C−O[b]	176(1)		

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

Scheme 3



precipitates almost quantitatively from the cooled reaction solution, and the quinoline can be recovered by evaporation of solvent and filtration through silica if necessary (eq 15).



(15)

Including the aromatization procedures outlined above, successful cleavage by this method constitutes a stoichiometric cycle for selectively alkylating quinolines at the 5-position (Scheme 3). Unfortunately, this method does not extend to the nucleophilic addition products of structural type **2** or **3**. Although cleavage is observed at elevated pressures of carbon monoxide, the reaction is not clean but results in a mixture of products. Other approaches to the cleaving of these ligands are currently being explored.

Conclusions

The three-center, two-electron bonding of the C(8) carbon of the quinoline ring with two metal atoms of the Os_3 triangle imparts a significant electron deficiency to C(5) of the quinoline ring, making it subject to regiospecific attack by a wide range of carbanions. In sharp contrast to the π-η^6-chromium arenes, we do not observe lithiation with LiMe or Li^{n}Bu.[14] Substitution is not observed in the case of the 5-haloquinoline derivatives, whereas for the π-η^6-arene complex, substitution is competitive with nucleophilic addition for most nucleophiles with halogen-substituted arenes.[14] Substitution of halogen at the 5-position redirects nucleophilic attack to the 4-position, resulting in nucleophilic addition across the 3,4-double bond after acid quench.

These results suggest that the electron deficiency is concentrated at the 5-position (and presumably the 7-position, which is apparently sterically blocked). The failure to observe lithiation even with small, relatively hard carbanions probably reflects this concentration of the electron deficiency, whereas in the π-coordinated arenes, the electron-withdrawing effect of the metal is distributed among all 6 carbon atoms. The fact that substitution for halogens is a less-accessible pathway for these quinoline derivatives than for π-η^6-arenes is more difficult to rationalize but may result from the direction of the electron polarization being along the reaction coordinate for substitution in the case of the π-η^6-arenes, which is not the case for the μ_3-η^2-quinoline complexes.

These quinoline derivatives also react reasonably well with methyl and allyl Grignard reagents, whereas the π-η^6-arenes do not. This is probably also related to the concentration of the electron deficiency, as described above. In addition, the carbonyl ligands on the osmium cluster may be less subject to competitive nucleophilic attack than the carbonyls in the π-η^6-chromium arenes, given the higher average infrared stretching frequencies and/or force constants of the osmium cluster C−O carbonyl ligand bonds.[18]

The strictly trans addition of the electrophiles (H^+, CH_3^+,CH_3-CO^+) is a consequence of the planar structure of the intermediate anion (eq 2, Scheme 1). What is a bit surprising here is that, even with the relatively small methyl group, addition is >95% trans as detected by ^{1}H NMR, whereas with hydride as the nucleophile and proton as the electrophile, the stereoselectivity is completely lost, and both cis and trans addition take place to about the same extent.[9] These results indicate that the stereoselectivity is steric in origin rather than being directed by prior coordination of the electrophile to the metal core or the carbonyl ligands. That complex **4** does not convert to **3d** is consistent with this interpretation. In the case of π-η^6-arene complexes, quenching with electrophiles other than protons leads primarily to electrophilic alkylation of the carbanion, owing to the reversibility of the nucleophilic addition.[14] We see no evidence for reversible addition in the reaction of **1** with nucleophiles, although two to three fold excesses of the carbanions were sometimes necessary to drive the reaction to completion. Stereoselective *trans* acylation is observed for π-η^6-arenes with methyl iodide as the electrophile in the presence of carbon monoxide; in this case, interaction with the carbonyl ligands on chromium directs the trans addition.[14] Topside attack of both nucleophile and electrophile to give overall *cis* addition is observed in the nucleophilic additions across the 5,6-bond of π-η^6-dihydronaphthyl chromium tricarbonyls.[19]

Overall, there are distinct steric and electronic differences between the activation of quinolines by the μ_3-η^2-bonding mode to triosmium clusters and the well-known π-η^6-arene complexes. Of course, none of this chemistry would be possible without the presence of the third metal atom, which coordinates the nitrogen lone pair and apparently blocks attack at the 2-position, the normal site of nucleophilic attack in quinolines.[11] Indeed, this chemistry is extendable to a wide range of benzoheterocycles with pyridinyl nitrogens. Thus, the synthetic methodology outlined here is applicable to quinoxaline, benzothiazole 2-methyl benzimidazoles, benzotriazoles, and phenanthradines[20]—work that is currently underway in our laboratories.

Experimental Section

All reactions were carried out under an atmosphere of nitrogen but were worked up in air. THF was distilled from benzophenone ketyl, and methylene chloride and acetonitrile were distilled from calcium hydride.

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Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer and ^{1}H and ^{13}C NMR were recorded on a Varian Unity Plus 400. Elemental analyses were done by Schwarzkopf Microanalytical Labs (Woodside, NY). Chemical shifts are reported downfield positive relative to tetramethylsilane, and coupling constants are reported only for those resonances relevant to the stereochemistry; finally, only the multiplicities of resonances with standard couplings are reported.

Osmium carbonyl was purchased from Strem Chemical, used as received and converted to $Os_3(CO)_{10}(CH_3CN)_2$ by published procedures.[21] Quinoline was purchased from Aldrich Chemical and distilled from calcium hydride before use. The 3-amino, 4-chloro, 6-methoxy, 6-methyl, and 6-chloro quinolines were purchased from Aldrich Chemical and used as received. The 5-chloro[22] and 4-methoxy[23] quinolines were prepared according to literature procedures. DDQ and trityl tetrafluoroborate were purchased from Aldrich Chemical and used as received. Trifluoroacetic acid and diisopropylamine were purchased from Aldrich Chemical and distilled from phosphorus pentoxide and calcium hydride, respectively, before use. The carbanion reagents LiMe, Li^{n}Bu, Li^{t}BuL, MeMgBr, and allylMgBr were purchased from Aldrich and used as received. The carbanion reagents BzLi and PhLi were prepared in ether directly before use by reacting the corresponding diorganomercury compound (Strem) with lithium metal (Aesar). The other carbanions were generated by deprotonation of their corresponding neutral precursor with lithium diisopropyl amide, which was generated from diisopropylamine and Li^{n}Bu according to published procedures,[3] except for the carbanions resulting from 1,3-dithiane and vinyl bromide, which were generated by treatment with Li^{n}Bu and Li^{t}Bu, respectively, at −78 °C. Preparations of compounds **1a**, **1e**, and **1g** were previously reported.[8−10]

Preparation of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_5(R)N)(\mu\text{-}H)$ (R = 4-Cl, 1b; R = 4-OCH$_3$, 1c; R = 6-Cl, 1d; R = 6-OMe, 1f; R = 5-Cl, 1h). The following procedure was used for synthesizing all of the above-substituted quinoline triosmium complexes. $Os_3(CO)_{10}(CH_3CN)_2$ (0.250−0.500 g, 0.27−0.54 mmol) was dissolved in 150−300 mL of CH_2Cl_2 and a 2-fold molar excess of the appropriate quinoline was added. The reaction mixture was stirred for 12−20 h and then filtered through a short silica gel column to remove excess ligand. The yellow-green reaction solution was collected in a 500-mL quartz reaction vessel and irradiated in a Rayonet photoreaction chamber for 2−4 h until no further conversion was detected by analytical TLC. The dark green solution was then filtered through a short silica gel column, concentrated to 50−150 mL, and cooled at −20 °C to yield 200−300 mg of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_5(R)N)(\mu\text{-}H)$. The mother liquor was rotary evaporated and taken up in a minimum amount of CH_2Cl_2, and the solution was eluted on 0.1 × 20 × 40 cm silica gel TLC plates with CH_2Cl_2/hexane (20−40% CH_2Cl_2) as the eluent. Three bands were eluted. The faster-moving two yellow bands contained minor amounts of the decacarbonylquinoline triosmium complexes; the slower-moving dark green band contained an additional product that was crystallized from methylene chloride hexanes. The combined total yields (based on $Os_3(CO)_{12}$) of the products are listed below with the analytical and spectroscopic data.

Compound **1b**. Yield: 75.9%. Anal. Calcd for $C_{18}H_6ClNO_9Os_3$: C, 21.90; H, 0.61; N, 1.41. Found: C, 22.50; H, 0.70; N, 1.38. IR (ν CO) in hexane: 2077 (m), 2050 (s), 2021 (m), 1991 (br), 1969 (w) cm^{-1}. ^{1}H NMR in $CDCl_3$: δ 9.16 (dd, H(2)), 8.83 (dd, H(5)), 8.67 (d, H(7)), 7.29 (dd, H(6)) 7.18 (dd, H(3)), −12.06 (s, hydride).

Compound **1c**. Yield: 69.0%. Anal. Calcd for $C_{19}H_9NO_{10}Os_3$: C, 23.24; H, 0.91; N, 1.43. Found: C, 23.44; H, 0.93; N, 1.46. IR (ν CO) in hexane: 2075 (m), 2046 (s), 2018 (m), 1988 (br) cm^{-1}. ^{1}H NMR in $CDCl_3$: δ 9.03 (d, H(2)), 8.88 (dd, H(5)),8.65 (dd, H(7)), 7.14 (dd, H(6)), 6.42 (d, H(3), 4.08 (s, OCH_3) −12.01 (s, hydride).

Compound **1d**. Yield: 73.6%. Anal. Calcd for $C_{18}H_6ClNO_9Os_3$: C, 21.90; H, 0.61; N, 1.41. Found: C, 22.90; H, 1.01; N, 1.16. IR (ν CO) in hexane: 2060 (m), 2031 (s), 2027 (s), 1992 (w), 1983 (br) cm^{-1}. ^{1}H NMR in $CDCl_3$: δ 9.24 (dd, H(2)), 8.35 (dd overlap, H(5) & H(7)), 7.97 (dd, H(4)), 7.13 (dd, H(3)), −12.12 (s, hydride).

Compound **1f**. Yield: 56.1%. Anal. Calcd for $C_{19}H_9NO_{10}Os_3$: C, 23.21; H, 0.91; N, 1.43. Found: C, 22.58; H, 0.87; N, 1.15. IR (ν CO) in hexane: 2102 (m), 2077 (s), 2047 (s), 2019 (s), 1989 (br) cm^{-1}. ^{1}H NMR in $CDCl_3$: δ 9.04 (d, H(2)), 8.06 (d, H(7)), 7.92 (dd, H(4)), 7.53 (d, H(5)), 7.04 (dd, H(3)), 3.89 (s, OCH_3) −12.27 (s, hydride).

Compound **1h**. Yield: 69.7%. Anal. Calcd for $C_{18}H_6ClNO_9Os_3$: C, 21.90; H, 0.61; N, 1.41. Found: C, 22.66; H, 0.71; N, 1.37. IR (γ CO) in hexane: 2078 (m), 2049 (s), 2023 (s), 1990 (br) cm^{-1}. ^{1}H NMR at 400 MHz in $CDCl_3$: δ 9.33 (dd, H(2)), 8.52 (d, H(6)), 8.48 (dd, H(4)), 7.27 (d, H(7)) 7.20 (t, H(3)), −12.09 (s, hydride).

Preparation of $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_9H_7(5\text{-}R')N)(\mu\text{-}H)$ (2a−2l), $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_9H_6(R)(R')N)(\mu\text{-}H)$ (3b, 3b′, 3c, 3c′, 3d, *cis*-3d, *cis*-3e, *cis*-3e′, 3g, 1i, 1j, 4b, 6). The following procedure was used for the compounds listed above. $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_5(R)N)(\mu\text{-}H)$ (25−200 mg, 0.025−0.20 mmol) was dissolved in 5 mL of THF and cooled to −78 °C, at which time a 1.5−3 molar excess of the appropriate carbanion was added slowly by syringe. The amount of carbanion added was governed by an observable color change from deep green to dark amber or orange. The reaction mixture was warmed to 0 °C, stirred for 0.25−1 h, cooled again to −78 °C, and quenched with trifluoroacetic acid, 10% in excess of the amount of carbanion used. The solution generally turned orange-red as it warmed to room temperature. The clear orange-red solution was then rotary-evaporated, taken up in minimum CH_2Cl_2, filtered, and then purified by TLC on 0.1 × 20 × 20 cm or 0.1 × 20 × 40 cm silica gel plates with CH_2Cl_2/hexane (20−50% CH_2Cl_2) as eluent. In general, one major orange band containing the nucleophilic addition product was observed in addition to minor amounts of unconsumed starting material and $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C_9H_5(R)N)(\mu\text{-}H)$; in the case of **3d**, complex **4** was obtained as a yellow band that moved faster than the major product but slower than the starting material. Yields are given along with the analytical and spectroscopic data below.

Compound **2a**. Yield: 65.9% (46.7% when using MeMgBr). Anal. Calcd for $C_{19}H_{11}NO_9Os_3$: C, 23.58; H, 1.14; N, 1.45. Found: C, 23.86; H, 0.83; N, 1.38. IR (ν CO) in hexane: 2117 (m), 2078 (s), 2046 (s), 2024 (s), 1989 (br), 1968 (br) cm^{-1}. ^{1}H NMR $CDCl_3$: δ 8.41 (d, H(2)), 7.39 (d, H(4)), 6.84 (t, H(3)), 4.09 (t, H(7)) 2.84 (m, H(5)), 2.28 & 1.98 (m, H(6), 2H), 1.17 (d, CH_3), −16.99 (s, hydride).

Compound **2b**. Yield: 44.6%. Anal. Calcd for $C_{22}H_{17}NO_9Os_3$: C, 26.20; H, 1.69; N, 1.36. Found: C, 26.05; H, 1.67; N, 1.23. IR (ν CO) in hexane: 2079 (s), 2047 (s), 2024 (s), 1998 (w), 1991 (br), 1967 (w) cm^{-1}. ^{1}H NMR in $CDCl_3$: δ 8.42 (dd, H(2)), 7.36 (dd, H(4)), 6.82 (t, H(3)), 4.03 (t, H(7)), 2.52 (m, H(5)), 2.31 (m 2H, CH_2 on butyl), 1.50 m (H(6), 2H), 1.29 (m, CH_2,4H), 0.86 (t, CH_3) −16.99 (s, hydride).

Compound **2c**. Yield: 51.6%. Anal. Calcd for $C_{22}H_{17}NO_9Os_3$: C, 26.16; H, 1.68; N, 1.38. Found: C, 25.82; H, 1.70; N, 1.32. IR (ν CO) in hexane: 2102 (m), 2078 (m), 2057 (w), 2048 (s), 2023 (s), 2003 (w), 1989 (m), 1969 (br) cm^{-1}. ^{1}H NMR in $CDCl_3$: δ 8.49 (dd, H(2)), 7.36 (dd, H(4)), 6.82 (t, H(3)), 4.06 (t, H(7)), 2.70 & 2.16 (m, H(6), 2H), 2.28 (d, H(5)), 0.934 (s, 9H,CH_3 on ^{t}Bu) −16.95 (s, hydride).

Compound **2d**. Yield: 48.2%. Anal. Calcd for $C_{25}H_{15}NO_9Os_3$: C, 22.17; H, 1.36; N, 1.27. Found: C, 28.17; H, 1.33; N, 1.29. IR (ν CO) in hexane: 2079 (s), 2046 (s), 2024 (s), 1990 (s), 1967 (br) cm^{-1}. ^{1}H NMR in $CDCl_3$: δ 8.40 (dd, H(2)), 6.68 (t, H(3)), 6.97 (dd, H(4)), 2.70 (m, H(5)), 2.27 & 2.12 (m, H(6), 2H), 4.03 (t, H(7)), 7.22 (m, 4H), 6.95 (m, 1H), 2.86 (m, CH_2 of benzyl), −16.99 (s, hydride).

Compound **2e**. Yield: 66.1%. Anal. Calcd for $C_{24}H_{13}NO_9Os_3$: C, 27.96; H, 1.26; N, 1.25. Found: C, 27.55; H, 1.33; N, 1.25. IR (ν CO) in hexane: 2079 (s), 2047 (s), 2025 (s), 1991 (s), 1969 (br) cm^{-1}. ^{1}H NMR in $CDCl_3$: δ 8.46 (d, H(2)), 7.09−7.32 (m, 5H) 7.03 (d, H(4)), 6.77 (dd, H(3)), 4.02 (m, H(7)), 3.97 (m, H(5)), 2.48 (m, H(6), 2H), −16.99 (s, hydride).

Compound **2f**. Yield: 50.8%. Anal. Calcd for $C_{20}H_{11}NO_9Os_3$:C, 24.52; H, 1.12; N, 1.43. Found: C, 24.43; H, 1.07; N, 1.42. IR (ν CO) in hexane: 2101 (w), 2079 (s), 2047 (s), 2024 (s), 2001 (w), 1991 (br), 1969 (w) cm^{-1}. ^{1}H NMR in $CDCl_3$: δ 8.45 (dd, H(2)), 7.38 (dd, H(4)), 6.84 (t, H(3)), 5.69 (m, 1H), 5.25 & 5.04 (d, 2H), 4.02 (t, H(7)), 3.42 (m, H(5)), 2.25 (m, H(6), 2H), −17.00 (s, hydride).

Compound **2g**. Yield: 25.0%. Anal. Calcd for $C_{24}H_{17}NO_9Os_3$: C, 27.86; H, 1.65; N, 1.35. Found: C, 27.77; H, 1.81; N, 1.16. IR (ν CO) in hexane: 2102 (w), 2079 (s), 2046 (s), 2025 (s), 1990 (br), 1968 (w) cm^{-1}. ^{1}H NMR in $CDCl_3$: δ 8.42 (dd, H(2)), 7.35 (dd, H(4)), 6.82 (t,

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H(3)), 4.03 (t, H(7)), 2.58 (m, CH_2), 2.21 m (H(6), 2H), 1.72 (m, CH_2), 1.52 (m, H(5)), 1.28 (m, CH_2), 0.978 (t, CH_3), −17.00 (s, hydride).

Compound **2h**. Yield: 72.1%. Anal. Calcd for $C_{20}H_{10}N_2O_9Os_3$: C, 24.16; H, 1.01; N, 2.42. Found: C, 24.07; H, 1.22; N, 2.51. IR (ν CO) in hexane: 2057 (w), 2048 (s), 2023 (s), 2003 (w), 1991 (m), 1969 (br) cm^{-1}. ^1H NMR at 400 MHz in $CDCl_3$: δ 8.52 (dd, H(2)), 7.49 (dd, H(4)), 6.92 (t, H(3)), 3.90 (t, H(7)), 3.06 (m, H(5)), 2.39 (m, CH_2), 2.32 (m, H(6), 2H), −17.06 (s, hydride).

Compound **2i**. Yield: 69.1%. Anal. Calcd for $C_{22}H_{14}N_2O_9Os_3$: C, 25.90; H, 1.27; N, 2.74. Found: C, 26.04; H, 1.38; N, 2.50. IR (ν CO) in hexane: 2050 (s), 2025 (s), 2003 (w), 1991 (m), 1969 (br), 1957 (w) cm^{-1}. ^1H NMR $CDCl_3$: δ 8.58 (d, H(2)), 7.54 (d, H(4)), 6.91 (t, H(3)), 3.93 (m, H(7)), 2.81 & 2.64 (dd, H(6), 2H), 2.25 (d, H(5)), 1.42 (s, CH_3), 1.35 (s, CH_3), −17.00 (s, hydride).

Compound **2j**. Yield: 72.4%. Anal. Calcd for $C_{22}H_{15}NO_9Os_3S_2$: C, 24.63; H, 1.40; N, 1.31. Found: C, 24.56; H, 1.34; N, 1.21. IR (ν CO) in hexane: 2102 (m), 2078 (m), 2057 (w), 2048 (s), 2023 (s), 2003 (w), 1989 (m), 1969 (br) cm^{-1}. ^1H NMR in $CDCl_3$: δ 8.45 (dd, H(2)), 7.48 (d, H(4)), 6.83 (t, H(3)), 4.04 (t, H(7)), 4.21 (d, 1H), 1.79 (m, H(5)), 2.82 (m, 2H), 2.17 (tt, H(6), 2H), 2.05 (m, 2H), −17.00 (s, hydride).

Compound **2k**. Yield: 85.8%. Anal. Calcd for $C_{24}H_{19}NO_{11}Os_3$: C, 26.98; H, 1.78; N, 1.31. Found: C, 27.38; H, 1.55; N, 1.27. IR (ν CO) in hexane: 2079 (s), 2047 (s), 2025 (s), 1991 (m), 1969 (br) cm^{-1}. ^1H NMR in $CDCl_3$: δ 8.43 (dd, H(2)), 7.45 (dd, H(4)), 6.82 (t, H(3)), 3.99 (t, H(7)), 3.14 (m, H(5)), 2.45 (dd, H(6), 2H), 2.22 (t, CH_2), 1.39 (s, CH_3, 9H), −17.04 (s, hydride).

Compound **2l**. Yield: 52.6%. Anal. Calcd for $C_{21}H_{13}NO_9Os_3$: C, 25.35; H, 1.31; N, 1.41. Found: C, 25.31; H, 1.36; N, 1.31. IR (ν CO) in hexane: 2079 (s), 2046 (s), 2024 (s), 1991 (m), 1969 (br) cm^{-1}. ^1H NMR in $CDCl_3$: δ 8.42 (dd, H(2)), 7.33 (dd, H(4)), 6.81 (t, H(3)), 5.64 (m, 1H), 5.05 (m, 2H) 4.01 (t, H(7)), 2.65 (m, H(5)), 2.23 (m, H(6), 2H), 2.25 (m, CH_2), −17.00 (s, hydride).

Compound **3b**. Yield: 53.6%. Anal. Calcd for $C_{24}H_{18}ClNO_{11}Os_3$: C, 26.08; H, 1.81; N, 1.27. Found: C, 26.12; H, 1.93; N, 1.16. IR (ν CO) in hexane: 2081 (m), 2050 (s), 2028 (s), 2002 (m), 1975 (w), 1968 (w), 1955 (w) cm^{-1}. ^1H NMR $CDCl_3$: δ 8.31 (d, H(2)), 6.85 (d, H(3)), 3.90 (t, H(7)), 3.45 (m, H(5)), 2.46 (m, CH_2), 2.05 (m, H(6), 2H), 1.44 (s, CH_3, 9H), −17.05 (s, hydride).

Compound **3b′**. Yield: 67.1%. Anal. Calcd for $C_{22}H_{13}ClN_2O_9Os_3$: C, 25.02; H, 1.23; N, 2.65. Found: C, 24.96; H, 1.15; N, 2.31. IR (ν CO) in hexane: 2081 (s), 2050 (s), 2027 (s), 1992 (br), 1972 (w), 1958 (w) cm^{-1}. ^1H NMR at 400 MHz in $CDCl_3$: δ 8.46 (d, H(2)), 6.94 (d, H(3)), 3.92 (dd, H(7)), 3.17 (m, H(5)), 2.19 (m, H(6), 2H), 1.47 (s, CH_3), 1.43 (s, CH_3), −17.02 (s, hydride).

Compound **3c**. Yield: 64.0%. Anal. Calcd for $C_{25}H_{21}NO_{12}Os_3$: C, 27.32; H, 2.01; N, 1.27. Found: C, 27.81; H, 2.20; N, 1.06. IR (γ CO) in hexane: 2104 (m), 2080 (s), 2048 (s), 2027 (s), 1991 (br) cm^{-1}. ^1H NMR in $CDCl_3$: δ 8.30 (d, H(2)), 6.32 (d, H(3)), 3.91 (dd, H(7)), 3.82 (s, OCH_3), 3.43 (m, H(5)), 2.02 (dt, H(6), 2H), 2.76 m & 2.35 (dd, CH_2 of tBuAc), 2.12 (s, CH_3, 9H), −17.06 (s, hydride).

Compound **3c′**. Yield: 72.0%. Anal. Calcd for $C_{23}H_{16}N_2O_{10}Os_3$: C, 26.28; H, 1.42; N, 2.61. Found: C, 26.60; H, 1.22; N, 2.54. IR (ν CO) in hexane: 2104 (m), 2088 (s), 2048 (s), 2028 (s), 1990 (br) cm^{-1}. ^1H NMR in $CDCl_3$: δ 8.43 (d, H(2)), 6.41 (d, H(3)), 4.00 (dd, H(7)), 3.84 (s, OCH_3), 3.10 (d, H(5)), 2.73 & −2.18 (m, (H(6), 2H), 1.37 (s, CH_3), 1.35 (s, CH_3), −17.06 (s, hydride).

Compound **3g**. Yield: 60.1%. Anal. Calcd for $C_{22}H_{15}N_3O_9Os_3$: C, 25.51; H, 1.54; N, 4.05. Found: C, 27.12; H, 1.87; N, 3.75. IR (ν CO) in hexane: 2080 (m), 2049 (s), 2027 (s), 2004 (m), 1992 (s), 1969 (w), 1964 (w),1952 (w) cm^{-1}. ^1H NMR in $CDCl_3$: δ 8.06 (d, H(2)), 7.29 (br, NH_2), 6.73 (s, H(4)), 3.95 (dd, H(7)), 2.71 & 2.25 (m, H(6), 2H), 2.54 (d, H(5)), 1.40 (s, CH_3), 1.33 (s, CH_3), −17.01 (s, hydride).

Compound *cis*-**3d**. Yield (1 equiv of acid used ≈ 10% of **4** obtained): 63.0%. Anal. Calcd for $C_{22}H_{13}ClN_2O_9Os_3$: C, 25.02; H, 1.23; N, 2.65. Found: C, 25.46; H, 1.28; N, 2.19. IR (ν CO) in hexane: 2102 (m), 2083 (m), 2076 (m), 2051 (s), 2030 (m), 2018 (w), 1995 (br) cm^{-1}. ^1H NMR in $CDCl_3$: δ 8.58 (d, H(2)), 7.51 (d, H(4)), 6.96 (t, H(3)), 4.47 (t, H(6), J(H(5)−H(6)) = 5.77 Hz)), 3.74 (d, H(7)), 3.02 (d, H(5)), 1.64 (s, CH_3), 1.50 (s, CH_3), −17.26 (s, hydride).

Compound **4**. Yield (10 equiv of acid used ≈ 50% of **3d** obtained): 36.1%. Anal. Calcd for $C_{22}H_{13}ClN_2O_9Os_3$: C, 25.02; H, 1.25; N, 2.65. Found: C, 25.41; H, 1.31; N, 2.32. IR (ν CO) in hexane: 2101 (s), 2076 (s), 2046 (s), 2015 (s), 1999 (br), 1969 (br) cm^{-1}. ^1H NMR at 400 MHz in $CDCl_3$: δ 7.49 (d, H(2)), 7.04 (d, H(4)), 6.69 (s, H(7)), 5.79 (t, H(3)), 3.52 (s, H(5)), 1.18 (s, CH_3), 0.88 (s, CH_3), −13.51 (d, hydride, J(hydride−hydride) = 1.6 Hz), −14.52 (d, hydride).

Compound *cis*-**3e**. Yield: 71.3%. Anal. Calcd for $C_{23}H_{16}N_2O_9Os_3$: C, 26.60; H, 1.54; N, 2.70. Found: C, 26.56; H, 1.53; N, 2.69. IR (ν CO) in hexane: 2080 (s), 2050 (s), 2026 (s), 1999 (m), 1990 (br), 1969 (w), 1958 (w) cm^{-1}. ^1H NMR in $CDCl_3$: δ 8.55 (d, H(2)), 7.42 (d, H(4)), 6.88 (t, H(3)), 3.64 (d, H(7)), 2.72 (d, H(5), J(H(5)−H(6)) = 4.80 Hz), 2.59 (m, (H(6), 2H, J(H(6)−H(7)) = 5.95 Hz), 1.64 (d, CH_3, on C(6)), 1.40 (s, CH_3), 1.32 (s,CH_3), −17.03 (s, hydride).

Compound *cis*-**3e′**. Yield: 67.1%. Anal. Calcd for $C_{20}H_{13}NO_9Os_3$: C, 24.49; H, 1.32; N, 1.43. Found: C, 24.42; H, 1.07; N, 1.43. IR (ν CO) in hexane: 2078 (s), 2047 (s), 2024 (s), 1990 (m), 1968 (br) cm^{-1}. ^1H NMR in $CDCl_3$: δ 8.39 (dd, H(2)), 7.33 (dd, H(4)), 6.78 (tt, H(3)), 3.52 (d, H(7)), 2.53 (m, H(5) J(H(5)−H(6)) = 4.50 Hz), 2.37 (m, H(6), J(H(6)−H(7)) = 4.0 Hz), 1.25 (d, CH_3 on C(6)), 1.04 (d, CH_3 on C(5)), −17.02 (s, hydride).

Compound **1i**. Yield: 54.1%. Anal. Calcd for $C_{25}H_{19}NO_{12}Os_3$: C, 27.32; H, 1.73; N, 1.27. Found: C, 27.39; H, 1.75; N, 1.29. IR (ν CO) in hexane: 2075 (s), 2047 (s), 2019 (s), 1989 (br, m) cm^{-1}. ^1H NMR in $CDCl_3$: δ 9.15 (dd, H(2)), 8.36 (s, H(7)), 8.14 (dd, H(4)), 7.08 (tt, H(3)), 3.95 (s, OCH_3), 3.77 (s, CH_2), 1.3 (s,CH_3, 9H), −11.99 (s, hydride).

Compound **1j**. Yield 35.2%. Anal. Calcd for $C_{24}H_{17}NO_{12}Os_3$: C, 26.56; H, 1.57; N, 1.29. Found: C, 27.21; H, 1.45; N, 1.25. IR (ν CO) in hexane: 2075 (s), 2048 (s), 2019 (s), 1989 (br, m) cm^{-1}. ^1H NMR in $CDCl_3$: δ 9.16 (dd, H(2)), 8.24 (dd, H(4)), 8.22 (s, H(7)), 7.15 (t, H(3)), 7.81 (s, OH), 3.75 (s, CH_2), 1.406 (s, CH_3, 9H), −12.27 (s, hydride).

Compound **6**. Yield: 65.5%. Anal. Calcd $C_{22}H_{13}ClN_2O_9Os_3$. C, 25.02; H, 1.20; N 2.65. Found: C, 25.15; H, 1.09; N, 2.59. IR (ν CO) in hexane: 2077 (m), 2050 (s), 2023 (s), 1991 (s) cm^{-1}. ^1H NMR in $CDCl_3$: δ 8.78 (dd, H(2)), 8.22 (d, H(6)), 6.96 (d, H(7)), 3.68 (d, H(4)), 3.24 (dd, H(3), 2H), 1.47 (s, CH_3), 1.28 (s, CH_3), −12.78 (s, hydride).

Preparation of $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_9H_6(6\text{-}R)(5\text{-}R')N)(\mu\text{-}H)$: *trans*-3e, *trans*-3e′, *trans*-5. 1a (50−100 mg, 0.05−0.100 mmol) was dissolved in 5 mL of THF, cooled to −78 °C, and treated with a 2−3 molar excess of $LiC(CH_3)_2CN$ or $LiCH_3$. The reaction solution was warmed to 0 °C, the THF removed by trap distillation, and then 5 mL of CH_2Cl_2, with a 2-fold excess (based on the amount of carbanion used) of dimethyl sulfate or acetic anhydride, was slowly added by syringe. The reaction mixture was then warmed to room temperature, rotary-evaporated, taken up in minimum methylene chloride, filtered, and purified by TLC with CH_2Cl_2/hexane as eluent. It was not possible to separate *trans*-**3e** and *trans*-**3e′** from **2i** and **2a**, respectively, which were formed (40% of total yield by ^1H NMR) as a result of incomplete electrophilic alkylation of the intermediate anion. The two compounds were separated by preparative HPLC with a reversed-phase C_{18} column and 15% water:acetonitrile as eluent. In the case of **5**, the formation of **2a** was also observed (∼10%) but as a distinct orange band on the TLC plate. Isolated yields of *trans*-**3e**, *trans*-**3e′**, and **5** are given below with the spectroscopic and analytical data.

Compound *trans*-**3e**. Yield: 41.1%. Anal. Calcd for $C_{23}H_{16}N_2O_9Os_3$: C, 26.61; H, 1.54; N, 2.70. Found: C, 26.56; H, 1.53; N, 2.69. IR (ν CO) in hexane: 2080 (s), 2050 (s), 2026 (s), 1999 (m), 1990 (br), 1969 (w), 1958 (w) cm^{-1}. ^1H NMR in $CDCl_3$: δ 8.60 (dd, H(2)), 7.52 (d, H(4)), 6.90 (t, H(3)), 4.54 (d, H(7)), 2.74 (t, H(6), J(H(6)−H(7)) = 8.0 Hz), 2.42 (s, H(5), J(H(5)−H(6)) = <1 Hz), 1.05 (d, CH_3 on C(6)), 1.36 (s, CH_3), 1.30 (s, CH_3), −16.51 (s, hydride).

Compound *trans*-**3e′**. Yield: 30.1%. Anal. Calcd for $C_{20}H_{13}NO_9Os_3$: C, 24.49; H, 1.32; N, 1.43. Found: C, 24.41; H, 1.08; N, 1.41. IR (ν CO) in hexane: 2078 (s), 2024 (s), 1990 (m), 1967 (br) cm^{-1}. ^1H NMR in $CDCl_3$: δ 8.40 (dd, H(2)), 7.47 (dd, H(4)), 6.86 (t, H(3)), 3.74 (d, H(7)), 2.55 (m, H(5), J(H(5)−H(6)) = 11.98 Hz), 1.76 (m, H(6), J(H(6)−H(7)) = 4.0 Hz), 1.24 (t, CH_3 on C(6)), 1.15 (d, CH_3 on C(5)), −17.01 (s, hydride).

Compound *trans*-**5**. Yield: 56.7%. Anal. Calcd for $C_{21}H_{13}NO_{10}Os_3$: C, 24.95; H, 1.29; N, 1.39. Found: C, 25.31; H, 1.18; N, 1.27. IR (ν CO) in hexane: 2080 (s), 2049 (s), 2026 (s), 1991 (m), 1967 (w). ^{1}H NMR in $CDCl_3$: δ 8.42 (d, H(2)), 7.48 (d, H(4)), 6.92 (t, H(3)), 3.60 (d, H(7)), 3.18 (m, H(5), J(H(5)−H(6)) = 12.12 Hz), 2.73 (m, (H(6)), J(H(6)−H(7)) = 4.40 Hz), 2.36 (s, $COCH_3$), 1.12 (d, CH_3), −17.12 (s, hydride).

Preparation of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_5(5\text{-}R)N)(\mu\text{-}H)$ (R′ = nBu, 1k; CH_2CO_2tBu, 1l); Rearomatization of the Nucleophilic Addition Products with Ph_3CBF_4. 1a (50 mg, 0.025 mmol) in 5 mL of THF was treated with a 2-fold molar excess of LiR(R−n-Bu, CH_2CO_2tBu) at −78 °C. The reaction solution was warmed to 0 °C and the solvent removed by trap-to-trap distillation. Then 5 mL of CH_2Cl_2 was added, followed by 2.1 equivalents of $Ph_3C^+BF_4^-$ (based on **1a**) as a solid. The reaction mixture was stirred for 30 min, rotary-evaporated, and then purified by TLC with CH_2Cl_2/hexane (50% CH_2Cl_2) as eluent to yield one major band (30−35 mg, 55−60%) of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_5(R')N)(\mu\text{-}H)$ (R = nBu, **1k**; CH_2CO_2tBu, **1l**). Additional minor bands for products derived from the trityl cation were also present (Ph_3CH, Ph_3C−nBu or $Ph_3C-CH_2CO_2$tBu).

Compound **1k**. Yield: 53.2%. Anal. Calcd for $C_{22}H_{15}NO_9Os_3$: C, 26.21; H, 1.49; N, 1.39. Found: C, 26.05; H, 1.70; N, 1.27. IR (ν CO) in hexane: 2077 (s), 2047 (s), 2019 (m), 1990 (m) cm^{-1}. ^{1}H NMR in $CDCl_3$: δ 9.27 (dd, H(2)), 8.49 (d, H(6)), 8.27 (dd, H(4)), 7.13 (t, H(3)), 7.04 (d, H(7)), 2.78 (t, CH_2 on C(5)), 1.68−1.45 (m, CH_2, 4H), 0.957 (t, CH_3), −12.29 (s, hydride).

Compound **1l**. Yield: 83.4%. Anal. Calcd for $C_{24}H_{17}NO_{11}Os_3$: C, 26.64; H, 1.66; N, 1.29. Found: C, 27.64; H, 1.58; N, 1.23. IR (ν CO) in hexane: 2075 (m), 2047 (s), 2018 (m), 1990 (s), 1973 (br) cm^{-1}. ^{1}H NMR in $CDCl_3$: δ 9.29 (dd, H(2)), 8.53 (d, H(6)), 8.25 (dd, H(4)), 7.14 (t, H(3)), 7.08 (d, H(7)), 3.75 (s, CH_2), 1.32 (s, CH_3, 9H), −12.24 (s, hydride).

Preparation of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_4(5,6\text{-}CH_3)_2N)(\mu\text{-}H)$ (1m): Rearomatization with DDQ. 1e (50 mg, 0.025 mmol) in 5 mL of THF was treated with a 2-fold molar excess of $LiCH_3$ in THF/hexane at −78 °C. The reaction mixture was warmed to room temperature and the solvent removed by trap-to-trap distillation. To the reaction residue, 5 mL of absolute ethanol was added, followed by 1.1 equivalents of DDQ in 1.0 mL of absolute ethanol. The reaction mixture was stirred for 20 min, then rotary-evaporated, taken up in a minimum amount of CH_2Cl_2, filtered, and purified by TLC with 1:1 CH_2Cl_2:hexane as eluent. In addition to a minor amount of **1e**, one major green band for **1m** was isolated, 33 mg (58%).

Compound **1m**. Anal. Calcd for $C_{20}H_{11}NO_9Os_3$: C, 24.48; H, 1.12; N, 1.43. Found: C, 24.37; H, 0.97; N, 1.42. IR (ν CO) in hexane: 2075 (s), 2045 (s), 2017 (m), 1987 (br, m) cm^{-1}. ^{1}H NMR in $CDCl_3$: δ 9.19 (dd, H(2)), 8.34 (s, H(7)), 8.27 (dd, H(4)), 7.08 (t, H(3)), 2.54 (s, CH_3 on C(5)), 2.24 (s, CH_3 on C(6)), −12.29 (s, hydride).

Reaction of $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_9H_7(5\text{-}CH_3)N)$, 2a, with DBU/DDQ. To 50.0 mg (0.025 mmol) of **2a** in 5 mL of CH_2Cl_2 was added 1.1 equivalent DBU by syringe. The solution was stirred for 5 min and then 1.1 equivalent of DDQ in 1.0 mL of absolute ethanol was added by syringe. The reaction mixture turned dark green almost immediately; it was stirred for 1 h, rotary-evaporated, and then purified by TLC with 1:1 CH_2Cl_2:hexane as eluent. One major band of 36 mg was isolated, which was identified as $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_5(5\text{-}CH_3)N)(\mu\text{-}H)$, **1n**.

Compound **1n**. Yield: 67.3%. Anal. Calcd for $C_{19}H_9NO_9Os_3$: C, 23.62; H, 0.932; N, 1.45. Found: C, 23.94; H, 1.00; N, 1.45. IR (ν CO) in hexane: 2075 (s), 2046 (s), 2018 (m), 1990 (br, m) cm^{-1}. ^{1}H NMR in $CDCl_3$: δ, 8.25 (dd, H(2)), 8.19 (dd, H(4)), 7.97 (d, H(7)), 7.18 (d, H(6)), 7.06 (dd, H(3)), 3.15 (s, CH_3), −12.851 (s, hydride).

Cleavage of the Quinoline Ligand from $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_5(5\text{-}R)N)(\mu\text{-}H)$ (R = H, 1a; nBu, 1k; CH_2CO_2tBu, 1l). The following procedure, given here for **1a**, worked equally well for the other complexes of type **1**. **1a** (100 mg, 0.10 mmol) was dissolved in 15 mL of CH_3CN and degassed with CO. The initially deep green solution turned bright yellow and was stirred at 70 °C for 36 h under a CO atmosphere, during which time a precipitate of $Os_3(CO)_{12}$ began to form. The paler yellow solution was cooled to −20 °C to complete the precipitation of the carbonyl, filtered, rotary-evaporated, and extracted with hexane. The residue from the extraction was combined with the initial precipitate to yield 61 mg (75%) of pure (by IR) $Os_3(CO)_{12}$. Rotary evaporation of the hexane extract yielded 9.2 mg (80%) of quinoline, which was >95% pure by ^{1}H NMR.

X-ray Structure Determination of *cis*-3e, *trans*-3e, 4, and 6. Crystals of ***cis*-3e**, ***trans*-3e**, **4**, and **6** for X-ray examination were obtained from saturated solutions of each in hexane/dichloromethane solvent systems at −20 °C. Suitable crystals of each were mounted on glass fibers, placed in a goniometer head on the Enraf-Nonius CAD4 diffractometer, and centered optically. Unit cell parameters and an orientation matrix for data collection were obtained by using the centering program in the CAD4 system. Details of the crystal data are given in Table 2. For each crystal, the actual scan range was calculated by scan width = scan range + 0.35 tan θ, backgrounds were measured by using the moving-crystal moving-counter technique at the beginning and end of each scan. Two representative reflections were monitored every 2 h as a check on instrument and crystal stability. Lorentz, polarization, and decay corrections were applied, as was an empirical absorption correction based on a series of Ψ scans, for each crystal. The weighting scheme used during refinement was $1/\sigma^2$, based on counting statistics.

Each of the structures was solved by the Patterson method with use of SHELXS-86,[24] which revealed the positions of the metal atoms. All other nonhydrogen atoms were found by successive-difference Fourier syntheses. The expected hydride positions in each were calculated by using the program HYDEX;[15] hydrogen atoms were included in each structure and were placed in their expected chemical positions by using the HFIX command in SHELXL-93.[25] The hydrides were given fixed positions and U's; other hydrogen atoms were included as riding atoms in the final least squares refinements with thermal parameters that were related to the atoms ridden on. All other nonhydrogen atoms were refined anisotropically in *trans*-**3e**, **4**, and **6**; however, only the osmium atoms in *cis*-**3e** could be refined anistropically, given to the poor crystallinity of the sample. In addition, dichloromethane solvent was present in the lattice of *trans*-**3e**, which could not be modeled precisely.

Scattering factors and anomalous dispersion coefficients were taken from International Tables for X-ray Crystallography.[26] All data processing was carried out on a DEC 3000 AXP computer using the Open MolEN system of programs.[27] Structure solution, refinement, and preparation of figures and tables for publication were carried out on PCs using SHELXS-86,[24] SHELXL-93,[25] and SHELXTL/PC[28] programs.

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Supporting Information Available: Complete bond distances and angles, atomic coordinates, anisotropic thermal parameters and hydrogen coordinates for compounds *cis*- and *trans*-**3e**, **4**, and **6**, Tables 7−22. See any current masthead page for ordering information and Web access instructions.

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