Cleavage of Conjugated Alkenes by Cationic Osmium Nitrides: Scope of the Reaction and Dynamics of the Azaallenium Products

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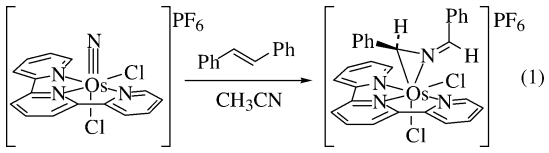
The cationic osmium(VI) nitride complex *cis*-[(terpy)$OsNCl_2$]PF_6 (**1**; terpy = 2,2′:6′,2″-terpyridine) reacts with a variety of aryl-substituted alkenes and acyclic and cyclic dienes to form the η^2-azaallenium complexes *cis*-[(terpy)$OsCl_2$(RR′C═N═CHR″)]PF_6 (**2**) by net nitrogen atom insertion into a C═C double bond. More electron-rich alkenes are more reactive, and electron-poor alkenes such as cinnamate esters do not react. Isomeric *trans*-[(terpy)$OsNCl_2$]PF_6 (**3**), as well as the tris(pyrazolyl)methane complex [(Tpm)$OsNCl_2$]PF_6 (**4**), give analogous products, although the scope of the reaction is restricted to dienes with these nitrides. The aryl-substituted azaallenium complexes *cis*-[(terpy)$OsCl_2$(η^2(*C*,*N*)-R[Ar]-*C*═*N*═CHR″)]PF_6 display hindered rotation about the C−C_{ipso} bond, because π-stacking interactions favor a close approach of the aryl group to the terpyridine ligand. The osmium migrates slowly between the two C═N bonds of the azaallenium ligands, leading to both regio- and stereoisomerizations. These two processes can be observed separately in the case of *cis*-[(terpy)$OsCl_2$([*p*-$Me_2NC_6H_4$]CH═N═CHCH_3)]PF_6, with regioisomerization preceding stereoisomerization. The isomerizations appear to take place by an "allene-roll" mechanism, as judged by the similar rates observed for cyclic and acyclic azaallenium complexes.

Introduction

Reactions of alkenes with metal−ligand multiple bonds represent an important method of functionalizing carbon−carbon double bonds. Prominent examples include reactions of metal oxo complexes with alkenes to give epoxides[1] or 1,2-diols[2] and reactions of metal carbene species to give cyclopropanes[3] or the products of olefin metathesis.[4] Reactions of compounds with metal−nitrogen multiple bonds are less common, though imido complexes are clearly involved in manganese-mediated aziridinations[5] and probably involved in copper-catalyzed aziridinations[6] and metal nitrido complexes have been reported to undergo [1,4]-additions with dienes.[7]

Several years ago, one of us reported a very unusual reaction of *cis*-[(terpy)$OsNCl_2$]PF_6[8] (terpy = 2,2′:6′,2″-terpyridine) with aryl-substituted alkenes in which the nitrogen atom inserts between the two carbons of the alkene, cleaving the alkene to form η^2-azaallenium complexes (e.g., eq 1).[9] While highly energetic reagents



such as ozone are known to cleave carbon−carbon double bonds with concomitant formation of carbon−heteroatom bonds, the ability of a stable metal nitride to cleave such a strong, nonpolar bond is noteworthy, and the formation of carbon−nitrogen bonds in this manner has potential synthetic utility. Thus, we were motivated to explore the scope and limitations of this transformation. Here we report the extension of this chemistry to a wide variety of conjugated alkenes, including mono-, di-, and trisubstituted olefins, and to cyclic and acyclic dienes as well as aryl-substituted alkenes. Analogous reactions of the cationic osmium nitride complexes *trans*-[(terpy)$OsNCl_2$]PF_6[8] and [(Tpm)-$OsNCl_2$]PF_6 (Tpm = tris(1-pyrazolyl)methane)[10] with dienes are also described, as are fluxional processes and regio- and stereoisomerizations of the η^2-azaallenium complexes *cis*-[(terpy)$OsCl_2$(RR′C═N═CHR″)]PF_6.

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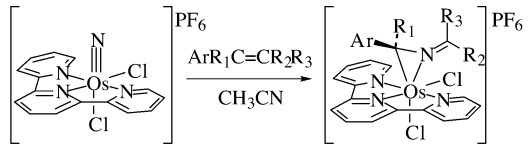
Scheme 1. Reactions of *cis*-[(terpy)OsNCl$_2$]PF$_6$ (1) with Arylalkenes To Give the Azaallenium Complexes *cis*-[(terpy)OsCl$_2$(η^2(*C*,*N*)-ArR$_1$*C*=*N*=CR$_2$R$_3$)]PF$_6$ (2a−p)



1 **2**

	Ar[a]	R_1	R_2	R_3[a]	Conditions, Isolated Yield
2a[b]	Ph	H	H	Ph	65°, 15 h, 66%
2b[c]	Ph	H	H	MeC_6H_4	65°, 42 h, 75%
2c[c]	Ph	H	H	$MeOC_6H_4$	65°, 24 h, 71%
2d[c]	Ph	H	H	HOC_6H_4	RT, 36 h, 71%
2e	Ph	H	H	$Me_2NC_6H_4$	RT, 9 h, 82%
2f	$MeOC_6H_4$	H	H	$MeOC_6H_4$	65°, 18 h, 85%
2g	Ph	H	H	CH=CHPh	65°, 18 h, 79%
2h	Ph	H	H	$(CHCH)_2$Ph	65°, 18 h, 61%
2i	Ph	H	H	CH_3	RT, 24 h, 81%
2j	MeC_6H_4	H	H	CH_3	RT, 36 h, 78%
2k	$MeOC_6H_4$	H	H	CH_3	RT, 4 h, 90%
2l[c]	$Me_2NC_6H_4$	H	H	CH_3	RT, 0.25 h, 90%
2m	Ph	H	CH_3	CH_3	RT, 48 h, 72%
2n	$MeOC_6H_4$	H	CH_3	CH_3	RT, 48 h, 71%
2o	$Me_2NC_6H_4$	H	CH_3	CH_3	RT, 1 h, 86%
2p	Ph	CH_3	H	CH_3	RT, 72 h, 76%

[a] Aryl substituents are in the *para* position. [b] Prepared using *cis*-stilbene; reaction with *trans*-stilbene requires 72 h. [c] Isolated as a mixture of regioisomers; the major isomer is shown here.

Results

Reaction of *cis*-[(terpy)OsNCl$_2$]PF$_6$ with Arylalkenes. The pale orange osmium(VI) nitrido complex *cis*-[(terpy)OsNCl$_2$]PF$_6$ (**1**) reacts with a variety of aryl-substituted alkenes in acetonitrile solution to give the azaallenium complexes *cis*-[(terpy)OsCl$_2$(η^2(*C*,*N*)-ArR$_1$-*C*=*N*=CR$_2$R$_3$)]PF$_6$ (**2**) (Scheme 1). The reactions are carried out without precautions to exclude air or moisture, and the blood red azaallenium complexes can be isolated in good yield as analytically pure microcrystals after recrystallization from acetonitrile−ether. Reactions of β-methylstyrenes and even trisubstituted β,β- or α,β-dimethylstyrenes proceed readily at room temperature in the presence of a moderate excess of alkene, while reactions of stilbenes and styrylalkenes (with the exception of the very electron-rich *p*-hydroxy- and *p*-(dimethylamino)stilbenes) are rather slow and require mild heating to proceed to completion in a reasonable time. The compounds are air-stable indefinitely as solids and at least for several weeks in solution. The complexes are very soluble in acetone and acetonitrile, moderately soluble in methylene chloride, and insoluble in ether or hydrocarbons.

The product of the reaction of **1** with 1,6-diphenyl-1,3,5-hexatriene, **2h**, has been characterized by X-ray crystallography (Table 1). The geometry of the complex (Figure 1, Table 2) is best viewed as octahedral, with the initial cis orientation of the chlorides retained in the product and with the sixth site occupied by a C=N double bond of an azaallenium fragment. The terpyridine ligand shows deviations from regular octahedral geometry (the bond to the central nitrogen is shorter by 0.12 Å than the bonds to the outer nitrogens, and the trans N11−Os−N31 angle of 153.4(2)° is rather acute) that are typical of metal−terpyridine complexes.[11]

The bonding in the azaallenium complex can be regarded as a resonance hybrid between two canonical structures, an Os(II) azaallenium complex and an Os(IV) azametallacyclopropane. The metrical data of the organic fragment (C1−N1 = 1.374 Å, C1−N1−C2 = 137.5°) lie between these two extreme forms, with substantial bending and lengthening of the bound C=N bond compared to what would be expected for the

Table 1. Crystallographic Data for *cis*-[(terpy)OsCl$_2$(η^2(*C*,*N*)-(PhCH-*N*=CHCH=CHCH=CHPh)]PF$_6$·(CD$_3$)$_2$CO (2h·(CD$_3$)$_2$CO)

empirical formula	$C_{36}H_{27}D_6Cl_2F_6N_4OOsP$
fw	949.73
temp (K)	293
λ	0.710 73 Å (Mo Kα)
space group	$P\bar{1}$
total no. of data collected	6341
no. of indep rflns	6341
a (Å)	11.7391(12)
b (Å)	13.2219(10)
c (Å)	14.1111(12)
α (deg)	94.154(6)
β (deg)	113.610(7)
γ (deg)	111.576(7)
V (Å^3)	1803.2(3)
Z	2
calcd ρ (g/cm^3)	1.749
cryst size (mm)	0.22 × 0.10 × 0.05
μ (mm^{-1})	3.796
R indices ($I > 2\sigma(I)$)[a]	R1 = 0.0342, wR2 = 0.0715
R indices (all data)[a]	R1 = 0.0490, wR2 = 0.0774
goodness of fit on F^2	1.045

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2)^{1/2}$.

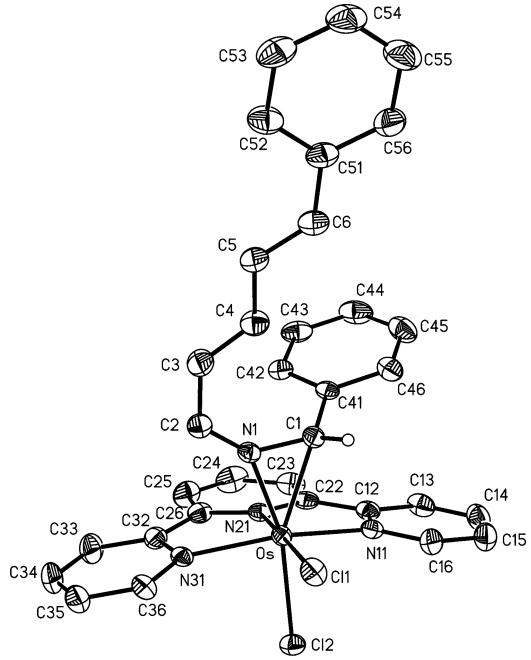


Figure 1. Thermal ellipsoid plot (30% ellipsoids) of the cation of *cis*-[(terpy)OsCl$_2$(η^2(*C*,*N*)-(PhCHN=CHCH=CH-CH=CHPh)]PF$_6$·(CD$_3$)$_2$CO (**2h**·(CD$_3$)$_2$CO).

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for *cis*-[(terpy)OsCl$_2$(η^2-*C,N*)-(Ph*CH*=*N*=CHCH=CHCH=CHPh)]PF$_6$·(CD$_3$)$_2$CO (2h·(CD$_3$)$_2$CO)

Os−C1	2.182(5)	C1−N1	1.374(7)
Os−N1	2.006(4)	N1−C2	1.293(7)
Os−N11	2.082(4)	C2−C3	1.423(8)
Os−N21	1.967(4)	C3−C4	1.334(9)
Os−N31	2.087(4)	C4−C5	1.424(8)
Os−Cl1	2.4197(14)	C5−C6	1.339(9)
Os−Cl2	2.3715(14)		
C1−Os−N1	38.0(2)	C1−N1−C2	137.3(5)
N11−Os−N21	79.2(2)	Os−N1−C1	77.9(3)
N21−Os−N31	78.5(2)	Os−N1−C2	143.8(4)
N11−Os−N31	153.4(2)	Os−C1−N1	64.0(3)
N21−Os−Cl1	177.49(13)	Os−C1−C41	120.5(4)
N21−Os−Cl2	89.26(12)	N1−C1−C41	120.6(5)
Cl1−Os−Cl2	88.34(5)	N1−C2−C3	126.5(3)
C1−Os−N11	77.7(2)		
N1−Os−N31	81.9(2)		

free organic ligand. For comparison, 1,3-ditolyl-2-azaallenium triflate has C=N bond lengths of 1.258 Å,[12] close to the 1.293(7) Å length of the uncoordinated C=N bond in **2h**. In contrast, the one previously structurally characterized azaallenium complex, CpMo(CO)$_2$(η^2-Tol$_2$C=N=CTol$_2$), clearly lies far toward the azametallacyclopropane canonical form (C−N = 1.43 Å, C−N−C = 128.3°).[13] This is consistent with stronger back-bonding by Mo(0) than by Os(II). The twisting between the two C=N planes characteristic of cumulenes is clearly evident in the structure of **2h**.

Several features of the orientation of the azaallenium ligand in **2h** are noteworthy. First, the C1−N1 bond eclipses the terpyridine N11−Os and N31−Os bonds. Presumably this orientation is adopted for electronic reasons, as it maximizes back-bonding by allowing separate Os dπ orbitals to back-bond to the central pyridine of the terpy ligand (which is the strongest π-acceptor due to its short Os−N distance) and to the π^* orbital of the azaallenium ligand. Second, the phenyl group bound to C1 lies over the terpyridine ring, with the phenyl carbons C41−C46 only 3−4 Å from the mean plane of the terpyridine. This cannot be a sterically favorable position, and rotation of the azaallenium fragment by 180° about the vector between the osmium and the midpoint of the coordinated C−N bond would give an electronically equivalent position that would place the phenyl group between Cl1 and N31, a less congested region of the molecule. Possibly the complex adopts the observed orientation because the π-stacking interaction between the electron-rich aryl group bound to C1 and the electron-poor terpyridine is a favorable one. Finally, the polyene chain in **2h** adopts an s-cis conformation between C2 and C3. However, this appears to be an artifact of crystal packing, since a large vicinal coupling constant (J_{H2-H3} = 10 Hz) is observed in solution, indicative of an s-trans conformation. (The double bonds between C3−C4 and C5−C6 are trans both in the crystal and in solution.)

Spectral data indicate that all of the compounds **2a**−**p** adopt structures in solution similar to that adopted by **2h** in the solid state. In particular, very distinct environments are apparent for the CH groups bound to osmium and doubly bonded to nitrogen in the ^{1}H (δ 6.62 for H$_\alpha$, δ 8.21 for the iminium hydrogen in **2a**) and the ^{13}C{^{1}H} NMR spectra (δ 44.75 for C$_\alpha$, δ 163.12 for the iminium carbon in **2a**) of the azaallenium complexes. The fact that these resonances are sharp indicates that these environments do not exchange on the NMR time scale. As in free allenes,[14] long-range coupling is observed, with $^4J_{HH}$ in Os(RC*H*N=C*H*R′) being about 2 Hz. In addition, the methyl hydrogens in complexes **2i**−**o** derived from β-methylstyrenes consistently show a detectable five-bond coupling to H$_\alpha$ of 1.5−2 Hz as well. The terpyridine ligand in each azaallenium complex **2** gives rise to 11 resonances in the ^{1}H NMR and 15 in the ^{13}C{^{1}H} NMR spectra, consistent with an unsymmetrical structure due to the asymmetry of C$_\alpha$.

Each of the compounds **2a**−**p** has one aryl group which shows hindered rotation about the aryl−C$_{ipso}$ bond, giving rise to inequivalent ortho and meta resonances in the ^{1}H NMR (δ 5.48, 6.72 (ortho) and 6.49, 7.02 (meta) in **2a**). Both the observed barrier to rotation and the upfield shifts strongly suggest that the orientation observed in the crystal of **2h**, with the phenyl group on C1 lying over the terpyridine ligand, is retained in solution. The proximity to the terpyridine explains both the barrier to rotation (due to steric difficulties in rotating past the terpyridine) and the upfield shifts (due to placement of protons in the shielding region of the terpy). The pattern of aryl shifts, with one side of the aryl group (both ortho and meta) more shifted than the other side, and the para hydrogen not significantly shifted, is consistent with a through-space effect, but not with a through-bond effect that would be expected if the upfield shift were due to electron donation by the osmium−carbon bond.

While rotation of the aryl group bound to C$_\alpha$ is always hindered, the barrier to rotation does vary, depending on the steric and electronic features of the azaallenium group. Sterically, larger substituents on the iminium carbon impede rotation of the aryl group on C$_\alpha$. Thus, while stilbene-derived compounds **2a**−**f**, with aryl groups on the iminium carbon, show sharp signals for the α-aryl resonances (k_{rot} < 3 s^{-1} at room temperature), complexes **2g**,**h**, with alkenyl groups on the iminium carbon, show broadening ($k_{rot} \approx 18$ s^{-1}) and the resonances for methyl-substituted compound **2i** are broader still ($k_{rot} \approx 23$ s^{-1}). The complexes with *gem*-dimethyl substitution on the iminium carbon (**2m**−**o**) show stopped rotation on the NMR time scale at room temperature, suggesting that the *syn*-methyl group increases the steric profile of the *anti*-methyl group via a buttressing effect. Electronically, more electron-donating substituents on the aryl group on C$_\alpha$ result in slower rotation. For example, the phenyl group in **2i** shows substantially broadened resonances, the *p*-tolyl group in **2j** shows moderate broadening, the *p*-anisyl group in **2k** shows only slight broadening, and no detectable broadening is seen in the *p*-(dimethylamino)phenyl group in the room-temperature NMR spectrum of **2l**.

The presence of a slowly rotating aryl group with upfield shifts in the ^{1}H NMR can be used to assign the regiochemistry of the azaallenium adducts **2**. This establishes, for example, that the products derived from

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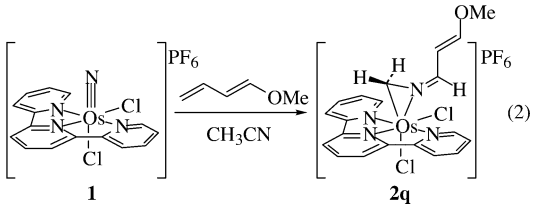
β-alkyl- or β-alkenylstyrenes (**2g**−**p**) adopt structures with the aryl group, rather than alkyl or vinyl groups, on C_α. Remarkably, this is true even for the α-substituted compound derived from 2-phenyl-2-butene, **2p**, whose aryl resonances (δ 5.60, 6.65 (ortho), 6.73, 6.95 (meta), 7.25 (para)) clearly indicate that the aryl group is bound to C_α, even though this forms what is effectively a tertiary metal−carbon bond. The methyl group on C_α is shifted upfield (δ 0.94), with the CH_3 group on the iminium carbon resonating at a chemical shift (δ 2.40) typical of that seen in other products derived from β-methylstyrenes (**2i**−**l**, δ 2.31−2.48).

The one exception to the ubiquity of aryl substitution on C_α occurs in the reaction of *p*-(dimethylamino)-β-methylstyrene with **1** to form **2l** as a 5:1 mixture of isomers **2l-i** and **2l-ii**. The major isomer, **2l-i**, does have the *p*-(dimethylamino)phenyl group on C_α (δ 5.29, 6.27 (ortho), 5.93, 6.37 (meta)), but the minor isomer does not (δ 7.26 (2H, ortho), 6.67 (2H, meta)). This pattern, coupled with the upfield shift of the CH_3 group (δ 0.80), indicates that **2l-ii** is the regioisomer of **2l-i**, with the methyl group on C_α and the aryl group on the iminium carbon. Regioisomers are also observed in the reactions of unsymmetrical stilbenes to give complexes **2b**−**d**. In each case the major regioisomer is the one with the unsubstituted phenyl group bound to C_α (2:1 for **2b**, 4:1 for **2c**, and 5:1 for **2d**; **2e** exists as a single isomer by NMR).

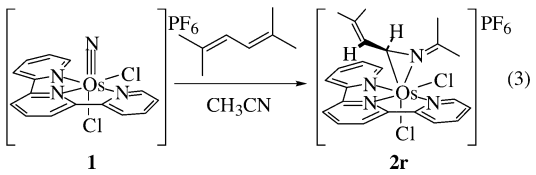
In contrast to the occasionally observed regioisomerism, in no case do any of the isolated complexes show evidence of stereoisomerism about the C=N bond. Thus, all compounds with a single substituent on the iminium carbon are assigned the *E* configuration about the C=N bond, by analogy with crystallographically characterized **2h** and consistent with expectations from steric effects. Complexes **2m**−**o** (where no stereoisomerism is possible) show two methyl resonances in the ^{1}H NMR, one at δ 2.40−2.43, assigned to the anti CH_3 group by analogy to **2i**−**l**, and another at δ 1.72−1.77, assigned to the syn CH_3 group. Both resonances show long-range coupling to H_α. All of the products derived from trisubstituted alkenes also show one proton due to the terpy 6,6″-hydrogens that resonates downfield of 9.50 ppm; in contrast, all protons in **2a**−**l** are upfield of 9.25 ppm. This downfield shift may be caused by a steric interaction between the terpy and azaallenium groups.

Unsubstituted styrenes such as styrene or 4-methoxystyrene react with *cis*-[(terpy)OsNCl$_2$]PF$_6$ (**1**), but the products formed are relatively unstable and no azaallenium complex has been isolated from these reactions. Similarly, while β-methylstyrenes with electron-donating substituents are excellent substrates for alkene cleavage, more electron-poor *p*-cyano-, *p*-chloro-, or *p*-fluoro-β-methylstyrenes react more slowly and do not yield isolable products. The very electron-deficient methyl cinnamate is inert to **1**.

Cleavage of 1,3-Dienes by *cis*-[(terpy)OsNCl$_2$]-PF$_6$. Sufficiently electron-rich conjugated dienes also undergo the alkene cleavage reaction exhibited by stilbenes and substituted styrenes. Thus, while 1,3-butadiene and 2,3-dimethyl-1,3-butadiene are rather unreactive toward the osmium nitride complex **1**, 1-methoxy-1,3-butadiene reacts rapidly to give the insertion product **2q** in 88% isolated yield (eq 2). The reaction, like the reaction of diphenylhexatriene to give **2h**, is completely regioselective, with only cleavage of the terminal double bond. Presumably this site is preferred for electronic rather than steric reasons, as this is the less hindered site in methoxybutadiene but the more hindered site in diphenylhexatriene. ^{1}H and ^{13}C NMR spectra of **2q** establish that the azaallenium group binds with the CH_2 group attached to osmium, with both the equivalence of the two CH_2 protons (δ 4.35, d, 2 Hz) and the observation of equivalent 6,6″-terpyridine protons (δ 9.10) indicating that the molecule has a time-averaged mirror plane. The methoxyvinyl group is contained in that mirror plane and retains a trans geometry and an s-trans conformation about the single bond to the iminium carbon. Presumably the molecule adopts the same binding orientation as seen in the crystal of **2h**, with the bound C−N bond eclipsing the trans nitrogens of the terpyridine ligand, but rotation of the group about the axis connecting osmium to the midpoint of the C−N bond is rapid, as judged by the retention of apparent C_s symmetry in acetone solution even at −90 °C.



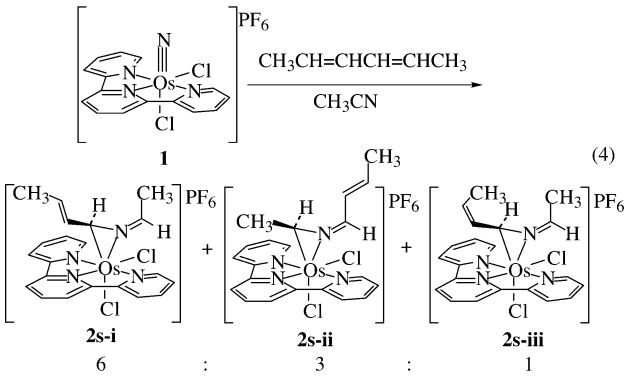
Reaction with 2,5-dimethyl-2,4-hexadiene, which takes place at a rate comparable to reaction with 1-methoxy-1,3-butadiene, gives an azaallenium complex (**2r**) of opposite regioselectivity (eq 3). In this case, the presence



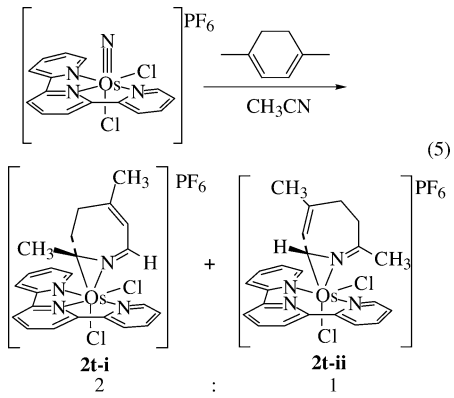
of the dimethylvinyl group on the carbon bound to osmium is established by the lack of a mirror plane (e.g., 6,6″-H resonances at δ 9.28, 9.26) and by the inequivalence of all four methyl groups (δ 2.47, 1.73, 1.40, 0.94 in the ^{1}H NMR). The ^{13}C NMR spectra of both **2q** and **2r** show the upfield shifts of the osmium-bound carbons (δ 31.73 and 45.40, respectively) and downfield shifts of the iminium-like carbons (δ 167.38, 183.21) characteristic of the η^2-azaallenium moiety.

The less electron-rich 2,4-hexadiene reacts rather sluggishly with the nitride complex **1** to give a mixture of three isomeric azaallenium complexes **2s**, which are isolated in 45% overall yield (eq 4). While the isomers could not be separated from each other, they could be identified by their distinctive coupling patterns in the ^{1}H NMR. Ninety percent of the material consists of the two possible regioisomers produced by cleavage of one of the equivalent double bonds of the *trans*,*trans*-diene, with the major isomer (**2s-i**) having the methyl group bound to the iminium carbon (N=C*H*CH$_3$, δ 7.35, qd, 5.5, 2.5 Hz) and the minor isomer (**2s-ii**) having the methyl group bound to C_α (OsCHCH_3, δ 0.79, d, 5 Hz). There is also 10% of an isomer (**2s-iii**) with the same

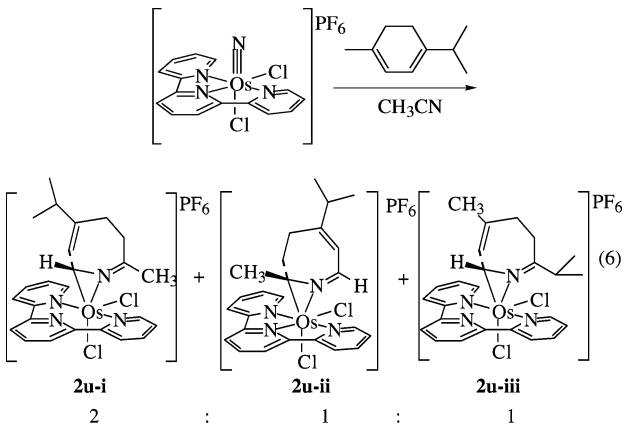
regiochemistry as **2s-i**, but with a *cis*-propenyl group ($^3J_{HH}$ = 12 Hz in **2s-iii**) rather than a *trans*-propenyl group ($^3J_{HH}$ = 16 Hz in **2s-i**) bound to C_α. Presumably **2s-iii** arises from attack on the *cis*,*trans*-diene present in the commercial technical grade 2,4-hexadiene.



As previously described,[7] *cis*-[(terpy)$OsNCl_2$]PF_6 (**1**) reacts with the cyclic dienes 1,3-cyclohexadiene and 1-methoxy-1,3-cyclohexadiene by net [4 + 1] cycloaddition to give azanorbornene complexes of osmium(IV). However, 1,4-dialkylcyclohexadienes do undergo alkene cleavage to give cyclic azaallenium complexes in their reactions with **1**. For example, 1,4-dimethyl-1,3-cyclohexadiene reacts rapidly with **1** to give a 2:1 mixture of two regioisomeric azaallenium complexes **2t** in overall 87% yield (eq 5). In this case, osmium is bound preferentially to the more substituted C═N bond of the cyclic azaallenium ion, as indicated by the appearance of the characteristically downfield iminium hydrogen in the ^{1}H NMR of **2t-i** (δ 7.72, d, 4 Hz), with the minor isomer **2t-ii** displaying instead an upfield shift (δ 4.21) due to H_α. Note that the lack of a mirror plane in either isomer excludes the possibility that this substrate has undergone [4 + 1] cycloaddition.



α-Terpinene (1-isopropyl-4-methyl-1,3-cyclohexadiene) also reacts with **1** to form a mixture of isomeric azaallenium complexes **2u** (eq 6). Both of the inequivalent carbon−carbon double bonds in α-terpinene are attacked, with a 3:1 preference for cleavage of the less hindered methyl-substituted bond. The major, methyl-substituted azaallenium ion again forms two regioisomeric complexes differing in the site of binding to osmium, though in this case the binding selectivity is reversed, favoring the less substituted C═N bond by a 2:1 ratio. Only the less substituted C═N bond is observed to be bound to osmium in **2u-iii**; no complex is observed with the isopropyl group on the carbon directly bonded to osmium. Unlike the acyclic compounds **2a**−**s**, these cyclic azaallenium complexes are somewhat unstable, decomposing in solution over the course of a few days at room temperature. This may reflect a modest amount of strain in these seven-membered cyclic allenes. Free 1,2-cycloheptadiene is estimated to be strained by about 20 kcal/mol,[15] though complexation to osmium is expected to substantially reduce that strain (note that 1,2-cycloheptadiene is not isolable, while a number of its metal complexes are[16]).



Reactions of Other Osmium(VI) Nitrides with 1,3-Dienes. The cationic osmium(VI) nitrides *trans*-[(terpy)$OsNCl_2$]PF_6 (**3**) and [(Tpm)$OsNCl_2$]PF_6 (**4**; Tpm = tris(1-pyrazolyl)methane) have been reported to react similarly to *cis*-[(terpy)$OsNCl_2$]PF_6 with a number of reagents.[17] However, **3** and **4** react much more slowly with arylalkenes than does **1**, and in no cases have azaallenium complexes been isolated from these reactions. For example, the tris(pyrazolyl)methane complex **4** reacts very slowly with *trans*-*β*-methylstyrene, with only 57% consumption of **4** in 4 days at room temperature (under conditions where **1** would be completely consumed in 24 h). No azaallenium complex derived from **4** could be identified by NMR in this reaction mixture (maximum concentration <10% of total osmium), although the formation of significant amounts of both acetaldehyde and benzaldehyde (31% and 22% yield based on Os, respectively) on heating the reaction mixture (in the presence of air and moisture) does suggest that at least some alkene cleavage, probably through an unstable azaallenium complex, is taking place.

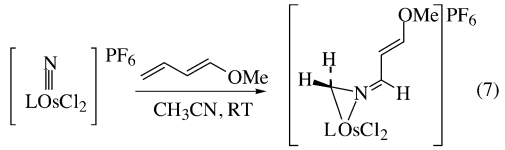
The accessibility of alkene cleavage to the nitride complexes **3** and **4** is demonstrated by their reactions with certain 1,3-dienes, where stable azaallenium complexes can be isolated. For example, both **3** and **4** react with 1-methoxy-1,3-butadiene to give azaallenium complexes **5q** and **6q**, respectively (eq 7). The resonances

(15) Early calculations[15a] estimated the strain energy in this allene at 15 kcal/mol, while more recent calculations[15b,c] put the energy of the cyclic cumulene 23 kcal/mol higher than that for unstrained 1,3-cycloheptadiene:[15d] (a) Gasteiger, J.; Dammer, O. *Tetrahedron* **1978**, *34*, 2939−2945. (b) Angus, R. O., Jr.; Schmidt, M. W.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 532−537. (c) Bettinger, H. F.; Schleyer, P. v. R.; Schreiner, P. R.; Schaefer, H. F., III. *J. Org. Chem.* **1997**, *62*, 9267−9275. (d) Roth, W. R.; Adamczak, O.; Breuckmann, R.; Lennartz, H. W.; Boese, R. *Chem. Ber.* **1991**, *124*, 2499−2521.

(16) Jones, W. M.; Klosin, J. *Adv. Organomet. Chem.* **1998**, *42*, 147−221.

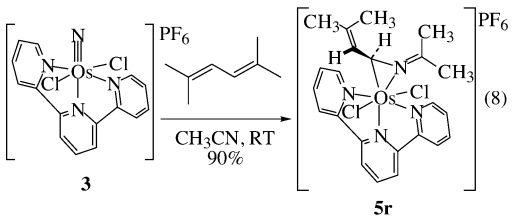
(17) Meyer, T. J.; Huynh, M. H. V. *Inorg. Chem.* **2003**, *42*, 8140−8160.

due to the azaallenium moiety in these complexes are very similar to those in the *cis*-terpy complex **2q**, and as in **2q**, the complexes consist of a single regioisomer



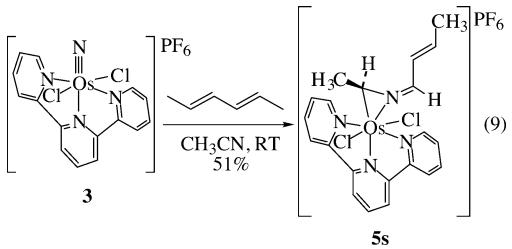
L = *trans*-terpy, **3** L = *trans*-terpy, **5q** (47%)
L = Tpm, **4** L = Tpm, **6q** (92%)

with attack taking place exclusively on the less substituted bond of the diene and the osmium bound to the less substituted bond of the azaallenium ligand. However, the trans complex **5q** is spectroscopically distinct from the cis isomer **2q**. This is to be contrasted with the reactions of the trans nitride **3** with slow-reacting alkenes such as stilbenes, where the azaallenium products formed have exclusively the cis geometry around osmium (i.e., **2a** forms in the reaction of **3** with *cis*- or *trans*-stilbene). The fact that azaallenium formation with reactive substrates such as methoxybutadiene takes place with retention of the stereochemistry around osmium strongly suggests that formation of cis products from **3** with stilbenes takes place by initial trans → cis isomerization of the starting nitride, followed by stereospecific (at Os) formation of the cis azaallenium adducts **2**. Stereospecific insertion is also seen in the reaction of **3** with 2,5-dimethyl-2,4-hexadiene to give the trans complex **5r**, with no sign of the cis isomer **2r** (eq 8). The regiochemistry of binding is the same as in the



3 **5r**

cis isomer, as confirmed by the observation of four separate methyl resonances (δ 3.06, 2.52, 2.22, 1.92), but the terpyridine shows time-averaged symmetry in the ^{1}H NMR due to rapid rotation of the azaallenium group about the vector connecting the Os to the midpoint of the bound C−N bond. 2,4-Hexadiene also reacts with **3**, to give the trans complex **5s** as a single regio- and stereoisomer (eq 9). In this case, only binding of

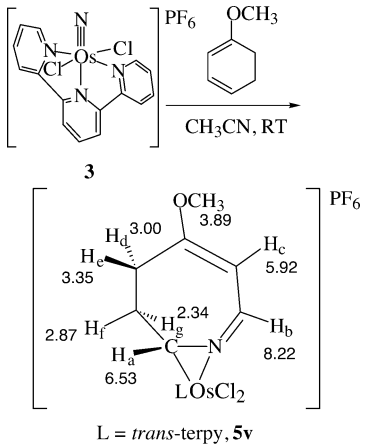


3 **5s**

the osmium to the methyl-substituted carbon is observed, as indicated by coupling of the iminium hydrogen (δ 8.33) to the alkene hydrogen at δ 7.17 with ^3J = 10 Hz.

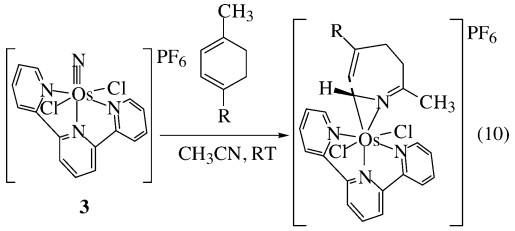
Both 1,3-cyclohexadiene and 1-methoxy-1,3-cyclohexadiene were previously reported to react with *trans*-[(terpy)OsNCl$_2$]PF$_6$ by [4 + 1] cycloaddition to give azanorbornene complexes.[7] However, a careful reanalysis of the ^{1}H NMR spectrum of the latter product indicates that this formulation is incorrect and that 1-methoxy-1,3-cyclohexadiene in fact reacts with **3** at room temperature to give the azaallenium complex **5v** (Scheme 2). An authentic [4 + 1] cycloadduct can be observed at low temperature but readily dissociates diene.[18] Several key features of the spectrum of **5v** are incompatible with an azanorbornene structure but consistent with an azaallenium structure. First, the 9 Hz coupling between H$_a$ and H$_g$ is inconsistent with H$_a$ occupying a bridgehead position. This coupling establishes that the H$_a$−C$_1$−C$_7$−H$_g$ dihedral angle is about 140° (consistent with the ~80° H$_a$−C$_1$−C$_7$−H$_f$ dihedral suggested by J_{af} = 2 Hz).[19] Second, the coupling pattern exhibited by the methylene hydrogens, with only one large vicinal coupling (J_{ge} = 13 Hz, with J_{dg} and J_{df} both about 4 Hz), is typical of a gauche conformation of the CH$_2$CH$_2$ moiety, rather than the eclipsed conformation imposed by the bicyclo[2.2.1] skeleton of the [4 + 1] cycloadducts. The geminal coupling J_{de} of 20 Hz is also anomalously large for a norbornane skeleton and indicates that the plane of the vinyl ether double bond roughly bisects the allylic CH$_2$ group.[20] Finally, the chemical shift of H$_b$ (δ 8.22) is downfield of what would be expected for an alkene (cf. δ 7.34 in the complex *trans*-[(terpy)OsCl$_2$(NC$_6$H$_8$)]PF$_6$[7]) but identical with that shown by the acyclic azaallenium complex **5q**.

Scheme 2. Reaction of *trans*-[(terpy)OsNCl$_2$]PF$_6$ with 1-Methoxy-1,3-cyclohexadiene To Give Azaallenium Complex 5v, with Full ^{1}H NMR Assignments of the Azaallenium Moiety



L = *trans*-terpy, **5v**

The cyclic dienes 1,4-dimethyl-1,3-cyclohexadiene and α-terpinene also react with *trans*-[(terpy)OsNCl$_2$]PF$_6$ to give azaallenium complexes **5t** and **5u**, respectively, as single regioisomers (eq 10). The spectra of the two compounds are very similar, which suggests that it is

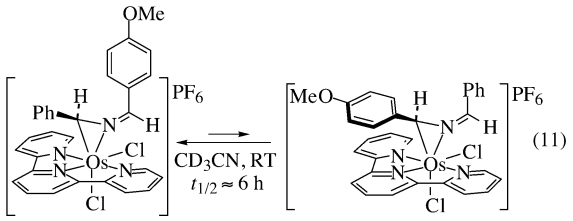


3

R = CH$_3$, 72% (**5t**)
R = ^{i}Pr, 69% (**5u**)

the methyl-substituted double bond of α-terpinene that is cleaved. The assignment of the isomer as the one with the less substituted C═N bond bound to osmium is based on the absence of a downfield-shifted iminium resonance in the ^{1}H NMR and on the ^{13}C NMR, where the iminium carbon resonances (δ 186.17 in **5t**, 186.34 in **5u**) are quaternary and the C_α resonances (δ 42.00, 42.23) are proton-coupled.

Regio- and Stereoisomerizations of Azaallenium Complexes. Isolated samples of the azaallenium complexes **2** generally exist as single regioisomers, with the few exceptions noted above. An important question arises as to whether the observed distribution of isomers is of thermodynamic or kinetic origin. While the observation of sharp, separate resonances for Os*CH* and N═*CH* in *cis*-η^2(*C,N*)-[(terpy)$OsCl_2$(Ph*CH*N═CHPh)]PF_6 (**2a**) indicates that regioisomerization is not occurring on the NMR time scale, other studies indicate that regioisomerization is reasonably facile on the chemical time scale. For example, *p*-methoxystilbene reacts with *cis*-[(terpy)$OsNCl_2$]PF_6 (**1**) to give a 4:1 mixture of regioisomeric azaallenium complexes **2c**, with the major isomer containing the unsubstituted phenyl group on the α-carbon. If this mixture is crystallized slowly, then a pure sample of this major isomer can be obtained. However, on dissolution of the pure major isomer in acetonitrile, the compound isomerizes to the same 4:1 mixture of isomers initially observed with a half-life of about 6 h at room temperature (eq 11).



Thus, the observed distributions of regioisomers formed from para-substituted stilbenes (**2b**−**e**) appear to reflect the thermodynamic stability of the isomers. The preference for the unsubstituted phenyl group for occupying the site attached to the carbon bound to osmium, rather than the iminium carbon, is general, with the preference becoming more marked with the increasing electron-donating ability of the substituent. With the very strongly donating *p*-dimethylamino group, this isomer is the only one observed by NMR (>20:1 preference). The effect can be quantified by a Hammett analysis using the substituent σ values,[21] which gives $\rho = -2.0 \pm 0.2$ (Figure 2).

In a few other cases involving the most reactive alkenes, nonequilibrium distributions of isomers can be observed if reactions of the alkene are monitored by NMR at low temperature. The reaction of *p*-(dimethylamino)-β-methylstyrene with *cis*-[(terpy)$OsNCl_2$]PF_6 is amenable to particularly detailed study, as three of the four possible isomers are observed in kinetically well-separated phases (Scheme 3). The initial exclusive

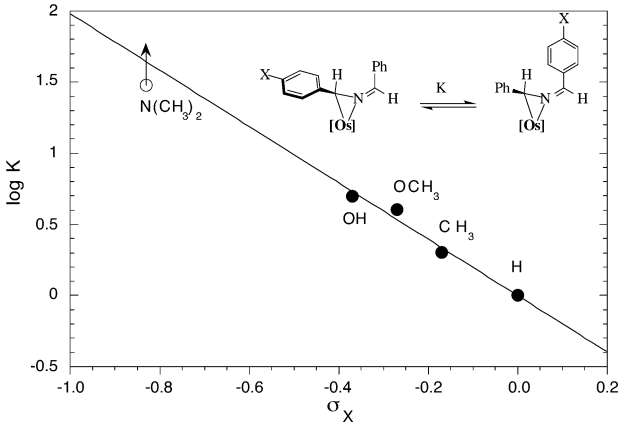
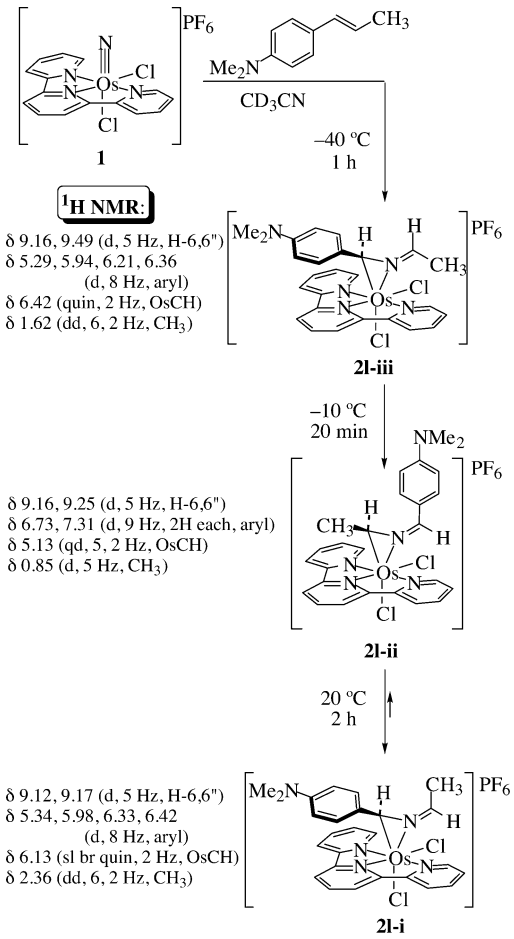


Figure 2. Hammett plot of log *K* for the reaction *cis*-η^2-(*C,N*)-[(terpy)$OsCl_2$([*p*-C_6H_4X]*CH*N═CHPh)]PF_6 ⇄ *cis*-η^2-(*C,N*)-[(terpy)$OsCl_2$(Ph*CH*N═CH[*p*-C_6H_4X])]PF_6 vs σ_X (CD_3-CN). Data for X = NMe_2 represent a lower limit on log *K* and are not included in the correlation. Values for σ_X are taken from ref 21.

Scheme 3. Intermediates in the Reaction of *trans*-*p*-$Me_2NC_6H_4CH$═$CHCH_3$ with *cis*-[(terpy)$OsNCl_2$]PF_6 (1)



(>30:1) product when the reaction is allowed to proceed at −40 °C, **2l-iii**, has the aryl group on the carbon bound to osmium (four aryl resonances in the ^{1}H NMR), the same regiochemistry as that of the major product observed at equilibrium, **2l-i**. **2l-iii** differs from the thermodynamic isomer in having the methyl group on the iminium carbon syn to osmium, as judged by the upfield chemical shift of the methyl group (δ 1.62) and

(18) Taylor, S. D.; Brown, S. N. Unpublished results.
(19) Bothner-By, A. A. *Adv. Magn. Reson.* **1965**, *1*, 195−316.
(20) Barfield, M.; Grant, D. M. *J. Am. Chem. Soc.* **1963**, *85*, 1899−1904.
(21) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−195.

downfield shift of one of the 6,6″-terpy protons (δ 9.49), both characteristic of compounds such as **2m**−**o**, which have syn methyl groups. At higher temperatures, the kinetic isomer **2l-iii** undergoes clean regioisomerization to **2l-ii**, which has the methyl group on C_α (δ 0.80) and the aryl group on the iminium carbon (two aryl resonances) anti to osmium. Formation of **2l-ii** is highly selective at −10 °C, with further equilibration to the equilibrium 5:1 mixture of **2l-i**:**2l-ii** requiring ∼2 h at room temperature. *trans*-Anethole behaves in a manner qualitatively similar to *p*-(dimethylamino)-β-methylstyrene, forming a regioisomer analogous to **2l-iii** at low temperature. Isomerization of the kinetic isomer to the thermodynamic isomer **2k** is slower than that of **2l-iii** to **2l-ii** but faster than that of **2l-ii** to **2l-i**, with a half-life of about 4 h at −5 °C. No intermediate analogous to **2l-ii** is observed in the reaction of the *trans*-anethole.

Nonequilibrium distributions of isomers have also been observed in low-temperature reactions of *cis*-[(terpy)$OsNCl_2$]PF_6 (**1**) with the dienes 1-methoxybutadiene, 2,5-dimethyl-2,4-hexadiene, α-terpinene, and 1,4-dimethyl-1,3-cyclohexadiene. The two acyclic dienes form kinetic product mixtures in which both the isomer present at equilibrium and its regioisomer are observed early in the reaction (in a 1:2 ratio of **2q** to its regioisomer **2q-i** for 1-methoxybutadiene and a 1:3 ratio of **2r** to **2r-i** for 2,5-dimethyl-2,4-hexadiene). The cyclic dienes react to form mixtures in which all the isomers present at equilibrium are formed at low temperature, but in a nonequilibrium ratio. Thus, **1** reacts with α-terpinene to form **2u-i** and **2u-ii** in a 3:1 ratio, equilibrating to 2:1, while dimethylcyclohexadiene forms **2t-i** and **2t-ii** in a roughly 1:1 ratio, equilibrating to 2:1. (Intermediates are also observed prior to formation of azaallenium complexes in both of the reactions with cyclic dienes; the structure of these intermediates will be the subject of a future report.) All of the isomerizations of diene-derived products take place rapidly below room temperature. There is no sign of any isomerization that changes which *alkene* has been cleaved; for example, the ratio of products due to cleavage of the methyl-substituted vs the isopropyl-substituted alkene in α-terpinene (**2u-i** and **2u-ii** vs **2u-iii**) remains unchanged even as the ratio of the regioisomers **2u-i**:**2u-ii** evolves.

The isomerizations observed in the reactions of **1** with excess 2,5-dimethyl-2,4-hexadiene and with excess 1,4-dimethyl-1,3-cyclohexadiene have been monitored by ^{1}H NMR at −10 °C (Figure 3). The time evolution can be fit well to a series of successive first-order (or pseudo-first-order) reactions, as shown for the reaction with 2,5-dimethyl-2,4-hexadiene (eqs 12 and 13) and for 1,4-dimethyl-1,3-cyclohexadiene (eqs 14−16; all rate constants measured in CD_3CN at 263 K). Note that the observed kinetics in the latter reaction rule out the possibility that reversion of the products **2t-i** and **2t-ii** to the intermediate **I** plays a significant role in their interconversion, since the rate of appearance of the products **2t** is only moderately faster than that of their interconversion. If the products reverted to **I** in order to interconvert, then such similar rates would imply that the forward and reverse rate constants for the formation of **2t** from **I** would have to be comparably similar, contradicting the observation that no detectable

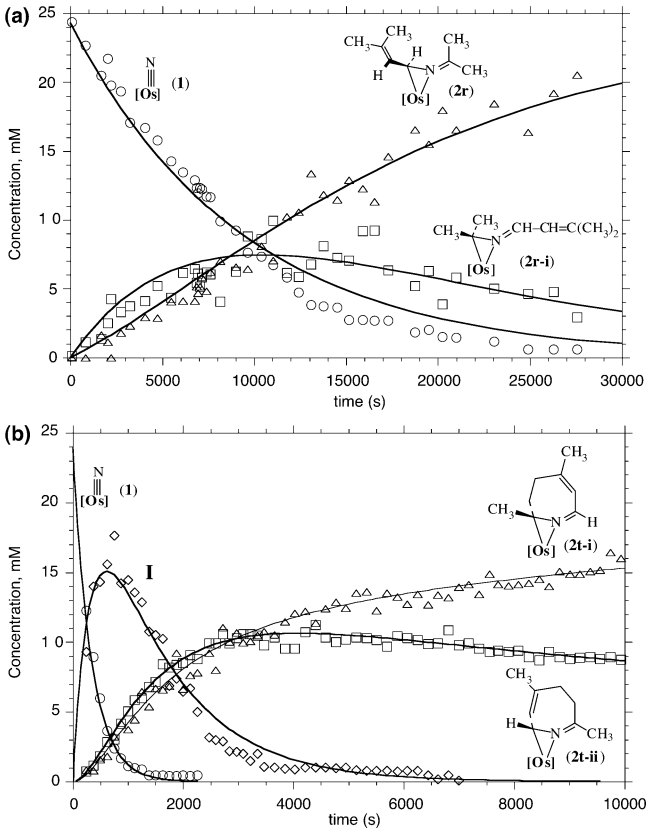
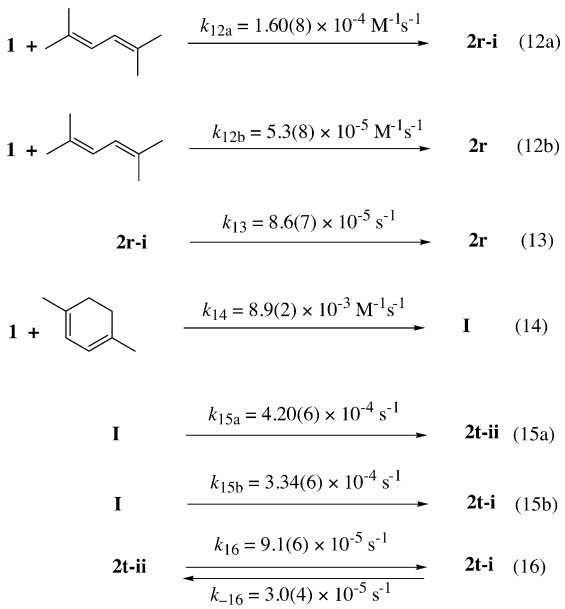


Figure 3. Time evolution of the reactions of *cis*-[(terpy)-$OsNCl_2$]PF_6 with (a) 2,4-dimethyl-2,5-hexadiene and (b) 1,4-dimethyl-1,3-cyclohexadiene (CD_3CN, −10 °C). Solid lines represent the calculated fit to the kinetic schemes of eqs 12 and 13 (a) and eqs 14−16 (b). In Figure 3b, **I** represents an intermediate that precedes azaallenium formation (see text). **[Os]** = *cis*-[(terpy)$OsCl_2$]PF_6.

I is observed at equilibrium. Thus, the equilibration between the regioisomers **2t-i** and **2t-ii** is most probably a direct isomerization. The isomerization rate ($k_{16} + k_{-16}$ = 1.21(7) × 10^{-4} s^{-1} at 263 K) for the cyclic compounds **2t** is remarkably similar to the analogous isomerization of the acyclic complexes **2r** (k_{13} = 0.86(7) × 10^{-4} s^{-1} at 263 K).



Discussion

Scope of Alkene Cleavage by Osmium Nitrides. The cationic terpyridine complex *cis*-[(terpy)$OsNCl_2$]PF_6 (**1**; terpy = 2,2′:6′,2″-terpyridine) reacts with a remarkably wide variety of conjugated alkenes to give azaallenium complexes, the products of net nitrogen atom insertion into a C=C double bond. This nitride complex can thus cleave extremely strong C=C double bonds (BDE ≈ 155 kcal/mol) under remarkably mild conditions (at or below room temperature in most cases). The mechanism of this transformation will be discussed in a forthcoming publication.[22] Yields of the reaction are generally high, and the reactions can be carried out in the presence of air and moisture. Phenyl-substituted alkenes or alkenes substituted with electron-rich aryl groups react readily, with both 1,2-disubstituted and trisubstituted alkenes giving stable products. A variety of acyclic dienes react, as do 1,4-dialkylcyclohexadienes, to give mildly strained complexes with seven-membered azaallenium rings.

In contrast to normal patterns of organometallic reactivity, the more substituted alkenes tend to react more cleanly with **1**. Thus, simple styrenes have so far failed to yield isolable products with **1**, although they do induce decomposition of the osmium nitride. Less substituted dienes, such as butadiene or isoprene, react only very slowly with **1** and have not yielded isolable products. There is a definite preference for electron-rich alkenes, with electron-poor alkenes such as cinnamate esters completely unreactive toward **1**.

Other cationic nitrides, such as *trans*-[(terpy)$OsNCl_2$]PF_6 (**3**) and [(Tpm)$OsNCl_2$]PF_6 (**4**; Tpm = tris(1-pyrazolyl)methane), also react with alkenes to give azaallenium complexes, although the scope of these reactions is more limited. In particular, while a number of dienes react with **3** and **4**, we have not yet been able to isolate any products from the reactions of arylalkenes with these other nitrides. Arylalkenes such as β-methylstyrene do react with these nitrides, although the rate is significantly slower than the rate of reaction with **1**. Indirect evidence suggests that azaallenium complexes are formed in these reactions (for example, the observation of benzaldehyde and acetaldehyde when **4** is heated with β-methylstyrene in the presence of air and moisture). Thus, while the *cis*-terpyridine complex **1** appears to be quantitavely best suited to this reaction, in terms of both rates of reaction and stability of the products, there is nothing that sets this complex qualitatively apart from other cationic osmium nitrides. On the other hand, less electrophilic neutral nitrides such as $TpOsNCl_2$ (Tp = hydridotris(1-pyrazolyl)borate)[23] show little or no reactivity toward alkenes that are readily cleaved by **1**.

Thermodynamic Regioselectivity in Azaallenium Binding. Most of the azaallenium complexes *cis*-[(terpy)$OsCl_2$(RR′C=N=CHR″)]PF_6 (**2**) display substantial regioselectivity with respect to which C=N double bond is bound to osmium. In all cases where we have been able to observe a nonequilibrium mixture of regioisomers, isomerization takes place within hours at room temperature; thus, we presume that the regioselectivity observed in all isolated complexes is thermodynamic in origin. By noting the regioselectivity of the products of reactions of **1** with 1,2-disubstituted alkenes, one can construct a stability scale reflecting the preference of the different substituents for location at C_α (relative to the anti position on the iminium carbon) in complexes **2**, with this preference decreasing in the order Ph > H ≫ *p*-$Me_2NC_6H_4$ ≳ $CH{=}CR_2$ ≳ CH_3. The only potential ambiguity here is in the comparison between H and Ph, since no products have been isolated from simple styrenes. The observation that *cis*-[(terpy)$OsCl_2$(Ph[CH_3]C=N=$CHCH_3$)]PF_6 (**2p**) prefers to have the phenyl-substituted carbon bound to osmium only establishes such a preference conclusively relative to location at the syn position on the iminium carbon. However, a preference for phenyl over hydrogen at C_α seems likely, since it appears to outweigh an otherwise noticeable reluctance to bind a tertiary center to osmium (compare, for example, the exclusive location of the $C(CH_3)_2$ group bonded to nitrogen and $CHCH{=}CMe_2$ bonded to Os in **2r** to the mere 2:1 preference for this location of $CH(CH_3)$ vs CHCH=CHMe in **2s**).

On simple steric grounds, one would expect larger substituents to avoid being located on the carbon bound to osmium. However, apart from H, the reverse trend is observed and is most marked for aryl substituents, with phenyl groups strongly preferred in the α-position over alkenyl or methyl, and probably even over hydrogen. A plausible explanation for the high predilection for placing aryl (and possibly to a lesser extent, alkenyl) groups on C_α is that this allows their electron-rich π systems to interact favorably by a π-stacking interaction with the electron-poor π-system of the terpyridine ligand. The importance of such interactions is suggested by the observed orientation of the phenyl group in the crystal structure of **2h**, which appears to be maintained in solution, judging from the anomalous chemical shifts and hindered rotation observed in aryl-substituted complexes **2a**−**p**. Invoking π-stacking also explains the qualitative trends observed in the aryl group rotation rates of cis-η^2(*C*,*N*)-[(terpy)$OsCl_2$(Ar*C*H=*N*=$CHCH_3$)]PF_6 (**2i**−**l**): the more electron-rich aryl groups should interact more favorably with the terpyridine, and this interaction will be lost in the transition state for aryl group rotation, consistent with the observation that the more electron-rich aryl groups rotate more slowly. Finally, the trans azaallenium complexes **4**, where π-stacking is impossible, show only the expected steric preferences for location at C_α, with H ≫ CH_3 ≫ $CH{=}CR_2$, and no examples of tertiary carbons bound to osmium. While data are limited due to the paucity of trans compounds (no aryl-substituted complexes are available, for instance), the pattern is clearly distinct from that observed with the cis complexes (compare, for example, **2r**−**t** with **5r**−**t**).

Yet if the preference for aryl groups at C_α is due to π-stacking, it is surprising that the more electron-rich aryl groups actually show a *lower* preference for locating at this position. This trend is evident in the regioselectivities of monosubstituted stilbenes (Figure 2) and in the regioselectivity of azaallenium binding in *cis*-[(terpy)$OsCl_2$(ArCH=N=$CHCH_3$)]PF_6 (**2i**−**l**), where only the *p*-dimethylamino compound exhibits any of the α-CH_3 regioisomer at equilibrium. However, electron-donating

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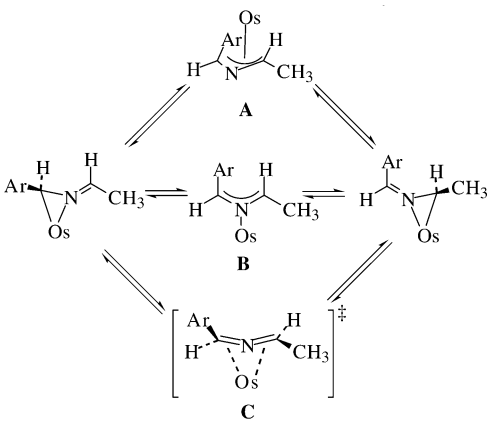
substituents are expected to interact favorably with the electron-poor iminium carbon. For example, organic reactions that involve deconjugation of carbon−heteroatom multiple bonds are typically disfavored by electron-donating groups, such as in the hydration of benzaldehydes ($\rho = +1.7$)[24] or in the addition of methanol to phenylimines of substituted benzaldehydes ($\rho = +1.1$).[25] Apparently, the stabilization of the iminium carbon is more sensitive to the electron-donating ability of the aryl group than is the strength of the π-stacking interaction, which leads to a net preference for more electron-rich aryl groups to be located on the iminium carbon. Nevertheless, all of the data are consistent with a significant interaction due to π-stacking that stabilizes the α-aryl isomers relative to what would be expected on the basis of steric considerations.

Mechanism of Regio- and Stereoisomerizations of Osmium Azaallenium Complexes. Nitrogen atom insertion into C═C double bonds to form azaallenium complexes **2**, **5**, and **6** appears to be irreversible. For example, both *cis*- and *trans*-stilbene react with *cis*-[(terpy)OsNCl$_2$]PF$_6$ (**1**) to form the same azaallenium complex **2a**, but the unreacted stilbene retains its original geometry in both cases. This indicates that dissociation of alkene and reinsertion is not occurring. Even in cases where intramolecular migrations would be possible, the site of nitrogen atom insertion does not appear to be mobile. For example, the insertion products derived from symmetrical butadienes (**2g**,**r**−**t**, **5r**−**t**) invariably show distinct resonances for the groups attached to cleaved and uncleaved double bonds in the NMR. Even on the chemical time scale, the invariance with time of the ratio of products due to cleavage of the methyl-substituted alkene in α-terpinene (**2u-i** and **2u-ii**) to the product due to cleavage of the isopropyl-substituted alkene (**2u-iii**), even as the ratio of **2u-i** to **2u-ii** does change, strongly suggests that the carbon−nitrogen bonds are set irreversibly in the alkene cleavage reaction.

In contrast, a number of azaallenium complexes **2** have been observed to undergo isomerizations affecting the bonding of osmium to the C═N═C unit of the azaallenium moiety. Both regioisomerizations (with the osmium migrating between the two C═N bonds of the azaallenium group in **2c**,**l**,**q**,**r**,**t**,**u**) and stereoisomerizations (interchanging the syn and anti substituents on the iminium group, in **2k**,**l**) have been seen. The most illuminating example of this series of isomerizations is provided by complex **2l**, where regioisomerization and stereoisomerization are both observed (Scheme 3). In this case, the kinetically observed isomer *cis*,*syn*-η^2-(*C*,*N*)-[(terpy)OsCl$_2$(Ar*C*H═*N*═CHCH$_3$)]PF$_6$ (**2l-iii**, Ar = *p*-Me$_2$NC$_6$H$_4$) first undergoes regioisomerization to *cis*,*anti*-η^2(*N*,*C*)-[(terpy)OsCl$_2$(ArCH═*N*═*C*HCH$_3$)]PF$_6$ (**2l-ii**), which subsequently undergoes a second regioisomerization to give the geometric isomer of **2l-iii**, *cis*,*anti*-η^2(*C*,*N*)-[(terpy)OsCl$_2$(Ar*C*H═*N*═CHCH$_3$)]PF$_6$ (**2l-i**). No direct stereoisomerization from **2l-iii** to **2l-i** is observed. Although only stereoisomerization is observed in **2k**, we presume that regioisomerization precedes stereoisomerization as for **2l** but that the relative rate constants differ enough that the intermediate regioisomer never accumulates significantly.

Scheme 4. Possible Mechanisms for Regio- and Stereoisomerizations of Azaallenium Complexes



Three plausible mechanisms for isomerization of the azaallenium group are illustrated in Scheme 4. The three pathways differ in the local symmetry of the intermediates or transition states (neglecting details of the substitution of the carbons): an η^3-azaallyl intermediate (path A) would have local C_s symmetry and an η^1-azaallyl intermediate (path B) would have C_{2v} symmetry, while the transition state in path C would have local C_2 symmetry. The "allene-roll"[26] mechanism of path C, first suggested by Pettit[27] and subsequently investigated in detail by Vrieze[28] and Rosenblum,[29] is well-known in metal−allene chemistry. The all-carbon analogue of path B has also been suggested to explain mutarotation of platinum allene complexes,[30] and while path A is unlikely in the all-carbon case because of the need to develop a σ lone pair on the central carbon, it is reasonable here with nitrogen in the central position. Note that all three pathways predict that stereoisomerization requires a two-step mechanism involving initial regioisomerization followed by a regioreversion accompanied by stereochemical change. Formation of an allyl intermediate would presumably proceed with retention of stereochemistry at the iminium double bond, so accessing the other stereoisomer requires prior coordination to the iminium carbon (with the concomitant twisting of the stereocenter). In the allene-roll mechanism, access to the other face of the initially coordinated C═N bond requires a transit through coordination of the other C═N bond. Thus, while the observation of stepwise isomerization in **2l** is very striking and does rule out gross dissociation of the azaallenium ion from the osmium, it is of no use in discriminating among the intramolecular pathways A−C.

These pathways can be distinguished by contrasting the behavior of the acyclic complex **2r**, derived from 2,5-

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(25) Calculated using substituent constants in ref 21 and equilibrium data from: Toullec, J.; Bennour, S. *J. Org. Chem.* **1994**, *59*, 2831−2839.

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dimethyl-2,4-hexadiene, and its cyclic analogue **2t**, derived from 1,4-dimethyl-1,3-cyclohexadiene. Complex **2t** contains a seven-membered ring, which would be expected to be modestly strained because of the twist of the azaallenium moiety. This strain should be relieved on going to the planar allyl structures in pathways A and B, but not on going to the allene-like transition state of pathway C. Thus, one would expect that relief of strain would cause the cyclic complex **2t** to isomerize substantially faster than the acyclic complex **2r** if mechanism A or B operates. In fact, the two complexes isomerize at very similar rates, with the cyclic complex isomerizing less than 50% faster than the acyclic complex at −10°. This is most consistent with mechanism C.

This analysis closely parallels the studies of Jones and co-workers on iron complexes of 1,2-cycloheptadiene, $[CpFe(CO)(L)(\eta^2\text{-}C_7H_{10})]^+$ (L = CO (**7a**), PPh_3 (**7b**)).[31] NMR experiments showed that allene proton exchange takes place without interconversion of the diastereotopic carbonyls (**7a**) or diastereomeric complexes (**7b**), demonstrating that the complexes isomerize exclusively by the allene-roll mechanism, just as the acyclic analogues do.[28] However, the slow interconversion of the diastereomers of the triphenylphosphine complex indicated that the allyl cation intermediate was accessible, albeit at ∼4−5 kcal/mol higher energy than the allene-roll pathway. Apparently, the osmium azaallenium complexes **2**, like the iron allene complexes, prefer to isomerize by an allene-roll mechanism, and the modest strain in the seven-membered ring is insufficient to divert them into a different mechanism in cyclic **2t** or **7**. One notable difference in the two cases is that, despite following the same mechanism, the cyclic iron complex **7a** does isomerize substantially faster than its acyclic analogues ($\Delta\Delta G^{\ddagger} > \sim 2.4$ kcal/mol),[31a] while the osmium complexes **2r** and **2t** isomerize at very similar rates.

The limited data available on the electronic effects on this isomerization are also consistent with mechanism C. As the metal moves from binding to one C−N bond to the other one, one would expect compensating changes in the electron demand of the two carbons, with C_α becoming less electron-rich and the iminium carbon becoming less electron-poor in the transition state. Thus, electron-donating substituents on C_α should accelerate isomerization and electron-donating substituents on the iminium carbon should slow it down. Indeed, the *p*-(dimethylamino)phenyl-substituted complex **2l** undergoes these reciprocal isomerizations at very different rates, with the isomerization that moves the aryl group from C_α to the iminium carbon (**2l-iii** → **2l-ii**) requiring ∼20 min at −10 °C and the isomerization that moves the aryl group from the iminium carbon to C_α (**2l-ii** → **2l-i**) requiring ∼2 h at 20 °C. The first isomerization is significantly slower for the *p*-methoxyphenyl-substituted compound **2k** ($t_{1/2} \approx 4$ h at −5 °C), and the second apparently significantly faster, since the regioisomeric compound does not accumulate at −5 °C. Note that one would expect mechanism A to be little affected by the electronics at C_α (since that carbon remains bound to Os in the intermediate), while mechanism B should be relatively insensitive to substitution at the iminium carbon (since that carbon remains unbound).

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Conclusions

The cationic nitride complex *cis*-$[(terpy)OsNCl_2]PF_6$ (**1**) reacts with a wide variety of conjugated alkenes by net nitrogen atom insertion to give the η^2-azaallenium complexes **2**. Reactions generally occur in high yield and take place under mild conditions and in the presence of air and moisture. *trans*-$[(terpy)OsNCl_2]PF_6$ (**3**) and $[(Tpm)OsNCl_2]PF_6$ (**4**) react similarly, although the scope of their reactions is more limited. The aryl-substituted azaallenium complexes *cis*-$[(terpy)OsCl_2(\eta^2\text{-}(C,N)\text{-}ArR_1C{=}N{=}CR_2R_3)]PF_6$ (**2a**−**p**) preferentially adopt conformations in which the aryl group lies over the terpyridine ring, both in the solid state and in solution, apparently because of favorable π-stacking interactions. The azaallenium groups in **2** undergo slow regioisomerization, by an allene-roll type mechanism. Net stereoisomerization about the N=C bond is achieved by two successive regioisomerizations, and both steps in this sequence have been observed in one example.

Experimental Section

General Procedures. *cis*-$[(terpy)OsNCl_2]PF_6$ (**1**) and *trans*-$[(terpy)OsNCl_2]PF_6$ (**3**) were prepared by the method of Williams, Coia, and Meyer.[8] Tpm[32] and $[(Tpm)OsNCl_2]PF_6$ (**4**)[33] was prepared according to literature procedures. All anhydrous reactions were performed using oven-dried glassware under nitrogen or argon. When needed during the organic syntheses, anhydrous diethyl ether (Et_2O) and tetrahydrofuran (THF) were obtained by vacuum transfer of the respective solvent from sodium benzophenone ketyl. All organometallic manipulations were performed on the benchtop without precautions to exclude air or moisture. ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on a General Electric GN-300 or a Varian Unity Plus 300 or 500 NMR spectrometer. Unless otherwise noted, all NMR spectra were measured in CD_3CN solution. IR spectra were measured as evaporated films on a Perkin-Elmer PARAGON 1000 FT-IR spectrometer. Fast atom bombardment mass spectra were obtained on a JEOL JMS-AX505HA mass spectrometer using 3-nitrobenzyl alcohol as a matrix. Peaks reported are the mass number of the most intense peak of isotopic envelopes; in all cases isotope patterns were in agreement with values calculated from the molecular formulas. Elemental analyses were performed by M-H-W Laboratories (Phoenix, AZ).

Alkene substrates were commercially available or prepared using literature procedures as noted, except for *p*-methyl-*trans*-*β*-methylstyrene, *p*-(dimethylamino)-*trans*-*β*-methylstyrene, *p*-(dimethylamino)-*trans*-*β*,*β*-dimethylstyrene, and (*E*)-2-phenyl-2-butene, whose preparations are described in the Supporting Information. Details of the preparation of certain key osmium complexes are described in detail below, with other compounds prepared by analogous procedures as noted. Full ^1H and partial $^{13}C\{^1H\}$ NMR and IR data are given for selected compounds. Full synthetic, spectroscopic (^1H and $^{13}C\{^1H\}$ NMR, IR, FABMS), and analytical details are provided for all compounds in the Supporting Information.

***cis*-[(terpy)OsCl$_2$(1,2-η^2-PhCH=N=CHPh)]PF$_6$ (2a).** Into a 50 mL pear-shaped round-bottom flask were weighed 169.8

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mg of *cis*-[(terpy)$OsNCl_2$]PF_6 (0.260 mmol) and 222.0 mg of *cis*-stilbene (Aldrich; 1.23 mmol, 4.7 equiv). A 21 mL portion of acetonitrile was added and the flask capped with a rubber septum. The reaction mixture was heated in a 65 °C oil bath for 17 h, over which time the solution turned dark red. The acetonitrile was evaporated on a rotary evaporator, the residue taken up in ~10 mL of dichloromethane, and the solution set aside. A considerable amount of undissolved material remained in the flask. This was dissolved in CH_3CN, the solution stripped to dryness, and the residue extracted with a second portion of CH_2Cl_2, which was combined with the first extract. The combined CH_2Cl_2 extracts were allowed to stand overnight, and the azaallenium complex was then isolated as a dichloromethane solvate by suction filtration, washing with 10 mL of CH_2Cl_2 and 10 mL of Et_2O, and then air-drying. Yield: 157.1 mg (66%). ^{1}H NMR: δ 5.48 (d, 8 Hz, 1H; ortho OsCH*Ph*); 6.49 (t, 7.5 Hz, 1H; meta OsCH*Ph*), 6.62 (d, 2 Hz, 1H; OsC*H*Ph), 6.72 (d, 7.5 Hz, 1H; ortho′ OsCH*Ph*), 7.02 (t, 7.5 Hz, 1H; meta′ OsCH*Ph*), 7.19 (tt, 7.5, 1 Hz, 1H; para OsCH*Ph*), 7.32 (t, 7.5 Hz, 2H; meta N=CH*Ph*), 7.43 (m, 3H; *o*, *p*-N=CH*Ph*), 7.84 (ddd, 7, 5.5, 2 Hz, 1H; terpy H-5), 7.94 (t, 8 Hz, 1H; terpy H-4′), 7.96 (m, 1H; terpy H-5″), 8.02 (dd, 8, 0.5 Hz, 1H; terpy H-3′), 8.09 (m, 2H; terpy H-3,4), 8.21 (d, 2 Hz, 1H; N=C*H*Ph), 8.23 (dd, 8, 0.5 Hz, 1H; terpy H-5′), 8.26 (m, 2H; terpy H-3″,4″), 9.09 (dd, 5.5, 1 Hz, 1H; terpy H-6), 9.15 (dt, 5.5, 1 Hz, 1H; terpy H-6″). ^{13}C{^{1}H} NMR: δ 163.12 (*C*H=N), 44.75 (Os*C*H). Anal. Calcd for $C_{30}H_{25}Cl_4F_6N_4OsP$: C, 39.23; H, 2.74; N, 6.10. Found: C, 39.04; H, 2.26; N, 6.52.

***cis*-[(terpy)$OsCl_2$(η^2(*C*,*N*)-Ph*C*H=*N*=CH[$C_6H_4CH_3$])]PF_6 (2b).** A mixture of 86.0 mg of *cis*-[(terpy)$OsNCl_2$]PF_6 (0.1316 mmol), 128 mg of 4-methyl-*trans*-stilbene[34] (0.6580 mmol, 5 equiv), a magnetic stirbar, and 9 mL of acetonitrile was stirred in a 25 mL round-bottom flask for 42 h in a 65 °C oil bath. The resulting dark red solution was reduced to half its original volume on the rotary evaporator and then layered with ether. The mixture was allowed to stand overnight in a −20 °C freezer. The crystals were suction-filtered on a frit and washed with 3 × 60 mL of Et_2O to give 83.4 mg of dark red **2b**, as a 2:1 mixture of isomers (total yield 75%). ^{1}H NMR: *major isomer* (Ph on C_α), δ 9.16 (d, 5 Hz, 1H; terpy H-6″), 9.08 (d, 5 Hz, 1H; terpy H-6), 8.50−7.85 (m, 9H; other terpyridine protons), 8.28 (d, 2.5 Hz, 1H; N=C*H*Ar), 7.32 (d, 8.5 Hz, 2H; ortho N=CH*Ar*), 7.26 (t, 8 Hz, 1H; para), 7.08 (d, 8 Hz, 2H; meta N=CH*Ar*), 7.00 (t, 8 Hz, 1H; meta′), 6.86 (d, 8.5 Hz, 1H; ortho′), 6.61 (m, 1H; OsC*H*Ph, partially obscured by minor resonances), 6.48 (t, 7.5 Hz, 1H; meta), 5.64 (d, 8 Hz, 1H; ortho), 2.19 (s, 3H; CH_3); *minor isomer* (*p*-tolyl on C_α, partial), δ 9.14 (d, 5 Hz, 1H; terpy H-6″), 9.06 (d, 5 Hz, 1H; terpy H-6), 8.50−7.85 (other terpyridine resonances, obscured), 8.42 (d, 2.5 Hz, 1H; N=C*H*Ph), 7.45 (d, 8.5 Hz, 2H; ortho), 7.14 (t, 7.5 Hz, 1H; para), 6.83 (d, 8 Hz, 1H; meta *Ar*), 6.61 (m, 2H, *OsCH* and meta′ Ar H, overlapped with major OsC*H*Ph), 6.31 (d, 8 Hz, 1H; ortho′ or ortho *Ar*), 5.52 (d, 8.5 Hz, 1H; ortho′ or ortho *Ar*), 2.04 (s, 3H; CH_3). ^{13}C{^{1}H} NMR: δ 45.37 (Os*C*H, minor) 44.85 (Os*C*H, major), 21.66 (*C*H_3, major), 21.4 (*C*H_3, minor). Anal. Calcd for $C_{30}H_{25}Cl_2F_6N_4OsP$: C, 42.51; H, 2.97; N; 6.61. Found: C, 42.32; H, 3.05; N, 6.43.

Also prepared by this method were *cis*-[(terpy)$OsCl_2$(η^2(*C*,*N*)-Ph*C*H=*N*=CH[$MeOC_6H_4$])]PF_6 (**2c**, 4:1 mixture of isomers, 71%), *cis*-[(terpy)$OsCl_2$(1,2-η^2-[4-$MeOC_6H_4$]CH=N=CH[4-$MeOC_6H_4$])]PF_6 (**2f**, 85%), *cis*-[(terpy)$OsCl_2$(1,2-η^2-PhCH=N=CHCH=CHPh)]PF_6 (**2g**, 79%), and *cis*-[(terpy)$OsCl_2$(1,2-η^2-PhCH=N=CHCH=CHCH=CHPh)]PF_6 (**2h**, 61%).

***cis*-[(terpy)$OsCl_2$(1,2-η^2-PhCH=N=$CHCH_3$)]PF_6 (2i).** Into a screw-cap vial were placed 55.8 mg of *cis*-[(terpy)$OsNCl_2$]PF_6 (0.0854 mmol), 125.6 mg of *trans*-β-methylstyrene (Acros, 1.063 mmol, 12.4 equiv), and 5.5 mL of CH_3CN. The vial was capped and allowed to stand at room temperature for 24 h. The acetonitrile was evaporated from the dark red solution and the residue washed with ether. The red oil was taken up in 1.5 mL of CH_3CN, layered with 5 mL of Et_2O, and allowed to stand overnight. The red crystals were suction filtered on a fritted-glass funnel, washed with 3 × 5 mL of Et_2O, and air-dried to yield 53.1 mg of **2i** (81%). ^{1}H NMR: δ 2.38 (dd, 5.4, 1.5 Hz, 3H; N=CHCH_3), 5.56 (br d, 7 Hz, 1H; ortho), 6.29 (sl br, 1H; OsC*H*Ph), 6.67 (br m, 2H; meta, ortho′), 6.96 (br t, 7 Hz, 1H; meta′), 7.24 (tt, 7, 1 Hz, 1H; para), 7.40 (qd, 5.4, 2.5 Hz, 1H; N=C*H*CH_3), 7.84 (ddd, 7.5, 5.5, 1.5 Hz, 1H; terpy H-5), 7.88 (t, 8 Hz, 1H; terpy H-4′), 7.95 (dd, 8, 1 Hz, 1H; terpy H-3′), 7.98 (ddd, 7, 5.5, 2 Hz, 1H; terpy H-5″), 8.00 (ddd, 8, 1.5, 0.5 Hz, 1H; terpy H-3), 8.08 (td, 7, 1.5 Hz, 1H; terpy H-4), 8.25 (dd, 8, 1 Hz, 1H; terpy H-5′), 8.31 (m, 2H; terpy H-3″,4″), 9.10 (ddd, 5.5, 1.5, 0.5 Hz, 1H; terpy H-6), 9.13 (ddd, 5.5, 2, 1 Hz, 1H; terpy H-6″). ^{13}C{^{1}H} NMR: δ 23.75 (*C*H_3), 42.35 (Os*C*HPh), 168.57 (N=*C*HCH_3). Anal. Calcd for $C_{24}H_{21}Cl_2F_6N_4OsP$: C, 37.36, H, 2.74; N, 7.26. Found: C, 37.18; H, 2.80; N, 7.44.

Also prepared by this route was *cis*-[(terpy)$OsCl_2$(1,2-η^2-[4-$MeOC_6H_4$]CH=N=CMe_2)]PF_6 (**2n**, 71%).

***cis*-[(terpy)$OsCl_2$(η^2(*C*,*N*)-Ph*C*H=*N*=CH[C_6H_4OH])]PF_6 (2d).** A mixture of 95.4 mg of *cis*-[(terpy)$OsNCl_2$]PF_6 (0.1460 mmol), 143 mg of 4-hydroxy-*trans*-stilbene (Pfaltz and Bauer, 0.730 mmol, 5.0 equiv), a magnetic stirbar, and 10 mL of acetonitrile were stirred in a 25 mL round-bottom flask for 36 h at room temperature. The resulting dark solution was reduced to half its original volume on the rotary evaporator and then layered with ether. The mixture was allowed to stand overnight in a −20 °C freezer. The crystals were suction-filtered on a fritted funnel, washed with 3 × 50 mL of Et_2O, and air-dried to give 88.0 mg of **2d** (5:1 mixture of isomers, total yield 71%). ^{1}H NMR: *major isomer* (Ph on C_α), δ 9.20 (dt, 5.5, 1 Hz, 1H; terpy H-6″), 9.13 (dd, 5.5, 1 Hz, 1H; terpy H-6), 8.31−7.95 (m, 7 H), 7.91 (d, 2.1 Hz, 1H; N=C*H*Ar), 7.87 (t, 8 Hz, 1H; terpy H-4′), 7.86 (ddd, 7, 5.5, 2 Hz, 1H; terpy H-5), 7.31 (m, 2H; ortho N=CH*Ar*), 7.21 (t, 7.5 Hz, 1H; para OsCH*Ph*), 7.02 (t, 7.5 Hz, 1H; meta OsCH*Ph*), 6.72 (d, 8.5 Hz, 2H; meta N=CH*Ar*), 6.52 (m, 2H; meta and ortho OsCH*Ph*), 6.48 (d, 2.1 Hz, 1H; OsC*H*Ph), 5.47 (d, 8 Hz, 1H; ortho OsCH*Ph*); *minor isomer* (*p*-HOC_6H_4 on C_α, partial), δ 9.14 (dd, 5.5, 1 Hz, 1H; terpy H-6″), 9.08 (dd, 5.5, 1 Hz, 1H; terpy H-6), 8.31−7.95 (8H, terpy, overlapped with major isomer), 7.82 (ddd, 7, 5.5, 1.5 Hz, 1H; terpy H-5), 7.44 (d, 7.5 Hz, 2H; ortho N=CH*Ph*), 7.33 (tt, 7.5, 1 Hz, 1H; para N=CH*Ph*), 5.95 (dd, 8.5, 2.5 Hz, 1H; meta OsCH*Ar*), 5.33 (dd, 8.5, 2.5 Hz, 1H; ortho OsCH*Ar*). ^{13}C{^{1}H} NMR: *major isomer*, δ 163.83 (N=*C*HAr), 44.98 (Os*C*HPh). IR (cm^{-1}): 3300 (m, v br, ν_{OH}). Anal. Calcd for $C_{29}H_{23}Cl_2F_6N_4OOsP$: C, 41.00; H, 2.73; N, 6.59. Found: C, 40.82; H, 2.55; N, 6.43.

The following compounds were prepared analogously: *cis*-[(terpy)$OsCl_2$(η^2(*C*,*N*)-Ph*C*H=*N*=CH[$C_6H_4NMe_2$])]PF_6 (**2e**, 82%), *cis*-[(terpy)$OsCl_2$(η^2(*C*,*N*)-[MeC_6H_4]*C*H=*N*=CHMe)]PF_6 (**2j**, 78%), *cis*-[(terpy)$OsCl_2$(η^2(*C*,*N*)-[$MeOC_6H_4$]*C*H=*N*=CHMe)]PF_6 (**2k**, 90%), *cis*-[(terpy)$OsCl_2$(η^2(*C*,*N*)-[$Me_2NC_6H_4$]*C*H=*N*=CHMe)]PF_6 (**2l**, 90%), *cis*-[(terpy)$OsCl_2$(η^2(*C*,*N*)-Ph*C*H=*N*=CMe_2)]PF_6 (**2m**, 72%), *cis*-[(terpy)$OsCl_2$(η^2(*C*,*N*)-[$Me_2NC_6H_4$]*C*H=*N*=CMe_2)]PF_6 (**2o**, 86%), *cis*-[(terpy)$OsCl_2$(η^2(*C*,*N*)-Ph(Me)*C*=*N*=CHMe)]PF_6 (**2p**, 76%), *cis*-[(terpy)$OsCl_2$(η^2(*C*,*N*)-H_2C=*N*=CHCH=CHOMe)]PF_6 (**2q**, 88%), and *cis*-[(terpy)$OsCl_2$(η^2(*C*,*N*)-[Me_2C=CH]*C*H=*N*=CMe_2)]PF_6 (**2r**, 87%).

Spectroscopic data for **2l**, as a 5:1 mixture of isomers **2l-i** (*p*-$Me_2NC_6H_4$ on C_α, N=CHCH_3 anti to Os) and **2l-ii** (CH_3 on C_α), are as follows. ^{1}H NMR: **2l-i**, δ 9.12 (ddd, 5.5, 1.5, 0.5 Hz, 1H; terpy H-6″), 9.07 (ddd, 5.5, 1.5, 0.5 Hz, 1H; terpy H-6), 8.48 (br t, 8 Hz, 1H; terpy H-5″), 8.29 (ddd, 8, 1.5, 0.5 Hz, 1H; terpy H-3″), 8.26 (td, 8, 1.5 Hz, 1H; terpy H-4″), 8.21 (dd, 8, 0.5 Hz, 1H; terpy H-5′), 8.07 (td, 8, 1.5 Hz, 1H; terpy H-4), 8.01 (ddd, 8, 1.5, 0.5 Hz, 1H; terpy H-3), 7.95 (dd, 8, 0.5 Hz, 1H; terpy H-3′), 7.85 (t, 8 Hz, 1H; terpy H-4′), 7.76 (ddd, 7.5, 5.5, 1.5 Hz, 1H; terpy H-5), 7.52 (qd, 5.5, 2.5 Hz, 1H;

(34) Reetz, M. T.; Westermann, E.; Lohmer, R.; Lohmer, G. *Tetrahedron Lett.* **1998**, *39*, 8449−8452.

N=C*H*CH$_3$), 6.37 (dd, 9, 2.5 Hz, 1H; meta′), 6.27 (dd, 9, 2.5 Hz, 1H; ortho′), 6.08 (br, 1H; OsC*H*Ar), 5.93 (dd, 9, 2.5 Hz, 1H; meta), 5.29 (dd, 9, 2 Hz, 1H; ortho), 2.88 (s, 6H; N(CH_3)$_2$), 2.31 (dd, 5.5, 2 Hz, 3H; N=CHCH_3); **2l-ii**, δ 9.20 (ddd, 5.5, 1.5, 0.5 Hz, 1H; terpy H-6″), 9.11 (ddd, 5.5, 1.5, 0.5 Hz, 1H; terpy H-6), 8.37 (td, 7.5, 1.5 Hz, 1H; terpy H-4″), 8.37 (dd, 8, 1 Hz, 1H; terpy H-3″), 8.33 (dd, 8, 1 Hz, 1H; terpy H-3), 8.31 (td, 7.5, 1.5 Hz, 1H; terpy H-4), 8.00 (obscured, 1H; terpy H-5″), 7.97−7.73 (m, 3H; terpy H-3′,5′, 5), 7.95 (t, 8 Hz, 1H; terpy H-4′), 7.26 (d, 9.5 Hz, 2H; ortho *Ar*), 7.24 (d, 2 Hz, 1H; N=C*H*Ar), 6.67 (d, 9.5 Hz, 2H; meta *Ar*), 5.08 (qd, 5.5, 2 Hz, 1H; OsC*H*CH$_3$), 3.04 (s, 6H, N(CH_3)$_2$), 0.80 (d, 5.5 Hz, 3H; OsCHCH_3). ^{13}C{^{1}H} NMR ((CD$_3$)$_2$CO, **2l-i** only): δ 168.05 (N=*C*HCH$_3$), 56.00 ([*C*H$_3$]$_2$N), 43.69 (Os*C*HAr), 23.46 (N=CH*C*H$_3$). Anal. Calcd for $C_{26}H_{26}Cl_2F_6N_5OsP$: C, 38.34; H, 3.22; N, 8.60. Found: C, 38.35; H, 3.10; N, 8.50.

Spectroscopic data for **2m** are as follows. ^{1}H NMR: δ 9.51 (ddd, 5.5, 2, 1 Hz, 1H; terpy H-6″), 9.22 (ddd, 5.5, 2, 1 Hz, 1H; terpy H-6), 8.52 (d, 8.5 Hz, 1H; terpy H-3″), 8.44 (td, 8, 1.5 Hz, 1H; terpy H-4″), 8.31 (dd, 8, 0.5 Hz, 1H; terpy H-5′), 8.08 (td, 8, 1.5 Hz, 1H; terpy H-4), 8.03 (ddd, 7, 5.5, 2 Hz, 1H; terpy H-5″), 7.92 (d, 8.5 Hz, 1H; terpy H-3), 7.88 (ddd, 7, 5.5, 2 Hz, 1H; terpy H-5), 7.84 (dd, 8, 0.5 Hz, 1H; terpy H-3′), 7.76 (t, 8 Hz, 1H; terpy H-4′), 7.26 (tt, 7.5, 1 Hz, 1H; para), 6.96 (br td, 7.5, 1 Hz, 1H; meta′), 6.72 (br t, 7.5 Hz, 1H; meta), 6.64 (br d, 8 Hz, 1H; ortho′), 6.48 (br s, 1H; OsC*H*Ph), 5.64 (br d, 8 Hz, 1H; ortho), 2.43 (d, 2 Hz, 3H; N=C[CH_3][CH$_3$] anti to Os), 1.72 (d, 2 Hz, 3H; N=C[CH$_3$][CH_3] syn to Os). ^{13}C{^{1}H} NMR: 184.37 (N=*C*Me$_2$), 47.23 (Os*C*HPh), 31.95 (N=CH[*C*H$_3$][CH$_3$] anti to Os), 21.35 (N=CH[CH$_3$][*C*H$_3$] syn to Os). Anal. Calcd for $C_{25}H_{23}Cl_2F_6N_4OsP$: C, 38.25; H, 2.95; N, 7.13. Found: C, 38.10; H, 3.13; N, 6.98.

Spectroscopic data for **2p** are as follows. ^{1}H NMR: δ 9.43 (ddd, 5.5, 2, 1 Hz, 1H; terpy H-6″), 9.11 (ddd, 5.5, 2, 1 Hz, 1H; terpy H-6), 8.48 (d, 8.5 Hz, 1H; terpy H-3″), 8.41 (td, 8, 1.5 Hz, 1H; terpy H-4″), 8.25 (dd, 8, 0.5 Hz, 1H; terpy H-5′), 8.07 (td, 8, 1.5 Hz, 1H; terpy H-4), 8.02 (ddd, 7, 5.5, 1.5 Hz, 1H; terpy H-5″), 7.98 (d, 8.5 Hz, 1H; terpy H-3), 7.87 (ddd, 7, 5.5, 1.5 Hz, 1H; terpy H-5), 7.82 (dd, 8, 0.5 Hz, 1H; terpy H-3′), 7.76 (t, 8 Hz, 1H; terpy H-4′), 7.32 (q, 5 Hz, 1H; N=*C*HCH$_3$), 7.25 (tt, 7.5, 1 Hz, 1H; para), 6.95 (td, 7.5, 1 Hz, 1H; meta′), 6.73 (br t, 7.5 Hz, 1H; meta), 6.65 (br d, 8 Hz, 1H; ortho′), 5.60 (br d, 8 Hz, 1H; ortho), 2.40 (d, 5 Hz, 3H; N=CHCH_3 anti to Os), 0.94 (s, 3H; OsCPhCH_3). ^{13}C{^{1}H} NMR: 167.43 (N=*C*HCH$_3$), 59.24 (Os*C*PhCH$_3$), 24.89 (N=CH*C*H$_3$), 18.52 (OsCPh*C*H$_3$). Anal. Calcd for $C_{25}H_{23}Cl_2F_6N_4OsP$: C, 38.25; H, 2.95; N, 7.13. Found: C, 38.08; H, 3.21; N, 7.04.

Spectroscopic data for **2q** are as follows. ^{1}H NMR: δ 9.10 (d, 5 Hz, 2H; terpy H-6,6″), 8.46 (d, 8 Hz, 2H; terpy H-3′,5′), 8.33 (m, 4H; terpy H-4,4″,5,5″), 7.99 (t, 8 Hz, 1H; terpy H-4′), 7.94 (ddd, 8, 1.5, 0.5 Hz, 2H; terpy H-3,3″), 7.22 (d, 12 Hz, 1H; N=CHCH=C*H*OMe), 6.97 (dt, 9.6, 1.8 Hz, 1H; N=C*H*CH=CHOMe), 5.82 (dd, 12, 9.6 Hz, 1H; N=CHC*H*=CHOMe), 4.35 (d, 1.8 Hz, 2H; OsCH_2), 3.73 (s, 3H; OCH_3). ^{13}C-{^{1}H} NMR: δ 167.38 (N=*C*HR), 60.10 (O*C*H$_3$), 31.73 (Os*C*H$_2$). Anal. Calcd for $C_{20}H_{19}Cl_2F_6N_4OOsP$: C, 32.57; H, 2.60; N, 7.60. Found: C, 33.00; H, 2.76; N, 7.53.

Spectroscopic data for **2r** are as follows. ^{1}H NMR: δ 9.28 (ddd, 5, 1.5, 0.6 Hz, 1H; terpy H-6″), 9.26 (ddd, 5, 1.5, 0.6 Hz, 1H; terpy H-6), 8.45 (dd, 8, 2 Hz, 1H; terpy H-3 or 3″), 8.41 (dd, 8, 2 Hz, 1H; terpy H-3 or 3″), 8.37 (td, 9, 1.5 Hz, 1H; terpy H-4″), 8.33−8.29 (m, 2H; terpy H-3′,5′), 8.29 (ddd, 7, 5.5, 2 Hz, 1H; terpy H-5″), 7.96 (td, 9, 1.5 Hz, 1H; terpy H-4), 7.92 (t, 8 Hz, 1H; terpy H-4′), 7.80 (ddd, 7, 5.5, 2 Hz, 1H; terpy H-5), 5.63 (sl br d, 10 Hz, 1H; OsC*H*CH=CMe$_2$), 3.92 (d of sp, 10, 1.2 Hz, 1H; OsCHC*H*=CMe$_2$), 2.47 (d, 1.2 Hz, 3H; N=C[CH_3][CH$_3$] anti to Os), 1.73 (d, 1.5 Hz, 3H; N=C[CH$_3$]-[CH_3] syn to Os), 1.40 (d, 0.9 Hz, 3H; OsCHCH=C[CH_3][CH$_3$]), 0.94 (s, sl br, 3H; OsCHCH=C[CH$_3$][CH_3]). ^{13}C{^{1}H} NMR: δ 183.21 (Me$_2$*C*=N), 45.40 (Os*C*HR), 30.51, 27.12, 21.71, 18.76 (*C*H$_3$). Anal. Calcd for $C_{23}H_{25}Cl_2F_6N_4OsP$: C, 36.19; H, 3.30; N, 7.34. Found: C, 35.95; H, 3.48; N, 7.16.

***cis*-[(terpy)OsCl$_2$(η^2(*C,N*)-[MeCH=CH]*C*H=*N*=CHMe)]-PF$_6$ (2s).** Into a 100 mL round-bottom flask were placed 102.0 mg of *cis*-[(terpy)OsNCl$_2$]PF$_6$ (0.1561 mmol), a magnetic stir bar, and 10 mL of CH$_3$CN. A 180 μL portion of 2,4-hexadiene (Aldrich, 90% tech grade mixture of isomers, 1.56 mmol, 10 equiv) was then added via syringe, and the mixture was stirred overnight. The acetonitrile solution was evaporated down to ∼3 mL under reduced pressure, and the dark red solution was then passed down a flash column (silica) under argon, with acetonitrile as eluent, and the volume was reduced again to 2 mL. The red solution was layered with Et$_2$O, stored overnight at −20 °C, and then filtered on a fritted glass funnel. The red crystalline solid was washed with 3 × 30 mL of Et$_2$O and air-dried to yield 52.3 mg of **2s** as a 6:3:1 mixture of isomers **2s-i**, **2s-ii**, and **2s-iii** (0.0709 mmol, 45%). ^{1}H NMR: **2s-i**, δ 8.97 (dd, 5.5, 1.5 Hz, 1H; terpy H-6″), 8.95 (dd, 5.5, 1.5 Hz, 1H; terpy H-6), 8.42 (br d, 8 Hz, 2H; terpy H-3,3″), 8.37 (br d, 8.5 Hz, 1H; terpy H-5′), 8.33 (br d, 7.5 Hz, 1H; terpy H-3′), 8.28 (td, 8, 1.5 Hz, 1H; terpy H-4″), 8.19 (td, 8, 1.5 Hz, 1H; terpy H-4), 8.03 (t, 8 Hz, 1H; terpy H-4′), 7.92 (ddd, 7.5, 5.5, 1 Hz, 1H; terpy H-5″), 7.81 (ddd, 7, 5.5, 1 Hz, 1H; terpy H-5), 7.35 (qd, 5.5, 2.5 Hz, 1H; N=C*H*CH$_3$), 5.52 (dq, 16, 7 Hz, 1H; OsCHCH=C*H*CH$_3$), 5.49 (br d, 10 Hz, 1H; OsC*H*CH=CHCH$_3$), 4.23 (ddq, 16, 9, 2.5 Hz, 1H; OsCHC*H*=CHCH$_3$), 2.40 (dd, 5.5, 1.5 Hz, 3H; N=CHCH_3), 1.96 (dd, 2.5, 1.5 Hz, 3H; OsCHCH=CHCH_3); **2s-ii**, δ 9.08 (dd, 5.5, 1.5 Hz, 1H; terpy H-6″), 9.03 (dd, 5.5, 1 Hz, 1H; terpy H-6), 8.47 (d, 7 Hz, 1H; terpy H-3″), 8.45 (d, 7 Hz, 1H; terpy H-3), 8.37 (br d, 8.5 Hz, 1H; terpy H-5′), 8.34 (td, 7, 1.5 Hz, 1H; terpy H-4″), 8.33 (br d, 7.5 Hz, 1H; terpy H-3′), 8.29 (td, 8, 1.5 Hz, 1H; terpy H-4), 7.97 (ddd, 7.5, 5.5, 1 Hz, 1H; terpy H-5″), 7.90 (ddd, 7, 5.5, 1.5 Hz, 1H; terpy H-5), 7.27 (dd, 9.5, 2.5 Hz, 1H; N=C*H*CH=CHCH$_3$), 6.50 (dq, 15, 7 Hz, 1H; N=CHCH=C*H*CH$_3$), 6.43 (dd, 15, 10 Hz, 1H; N=CHC*H*=CHCH$_3$), 4.87 (br qd, 5, 2.5 Hz, 1H; Os-C*H*CH$_3$), 1.22 (dd, 7, 1.5 Hz, 3H; N=CHCH=CHCH_3), 0.79 (d, 5 Hz, 3H; OsCHCH_3) (terpy H-4′ was not found); **2s-iii**, δ 9.02 (dd, 5, 1 Hz, 1H; terpy H-6″), 8.89 (dd, 5.5, 1.5 Hz, 1H; terpy H-6), 8.24 (td, 8, 1.5 Hz, 1H; terpy H-4″), 8.21 (td, 8, 1.5 Hz, 1H; terpy H-4), 8.07 (t, 8.5 Hz, 1H; terpy H-4′), 7.86 (ddd, 7, 5.5, 1.5 Hz, 1H; terpy H-5″), 7.80 (ddd, 7, 5.5, 1 Hz, 1H; terpy H-5), 7.50 (qd, 5.5, 2.5 Hz, 1H; N=C*H*CH$_3$), 6.13 (dq, 12, 7.5 Hz, 1H; OsCHCH=C*H*CH$_3$), 5.64 (br d, 9.5 Hz, 1H; OsC*H*CH=CHCH$_3$), 4.16 (ddq, 12, 10, 1.5 Hz, 1H; OsCHC*H*=CHCH$_3$), 2.43 (dd, 5.5, 2 Hz, 3H; N=CHCH_3), 0.93 (dd, 7, 1.5 Hz, 3H; OsCHCH=CHCH_3). Anal. Calcd for $C_{21}H_{21}Cl_2F_6N_4OsP$: C, 34.29; H, 2.88; N, 7.62. Found: C, 34.12; H, 3.02; N, 7.48.

Also prepared using analogous procedures were *cis*-[(terpy)-OsCl$_2$(η^2-2-aza-1,5-dimethylcyclohepta-1,2,4-trienium)]PF$_6$ (**2t**) from **1** and 1,4-dimethyl-1,3-cyclohexadiene,[35] isolated as a 2:1 mixture of isomers **2t-i** (η^2-1,2-isomer) and **2t-ii** (η^2-2,3-isomer) in 87% overall yield, and the products of the reaction of **1** with α-terpinene, *cis*-[(terpy)OsCl$_2$(η^2-[2,3]-2-aza-1-methyl-5-isopropylcyclohepta-1,2,4-trienium)]PF$_6$ (**2u-i**), *cis*-[(terpy)OsCl$_2$(η^2-[1,2]-2-aza-1-methyl-5-isopropylcyclohepta-1,2,4-trienium)]-PF$_6$ (**2u-ii**), and *cis*-[(terpy)OsCl$_2$(η^2-[2,3]-2-aza-1-isopropyl-5-methylcyclohepta-1,2,4-trienium)]PF$_6$ (**2u-iii**), isolated as a 2:1:1 mixture in 75% yield. Spectroscopic data for **2t** are as follows. ^{1}H NMR: **2t-i**, δ 9.31 (dd, 5.5, 1.5 Hz, 1H; terpy H-6″), 8.95 (dd, 5.5, 1.5 Hz, 1H; terpy H-6), 8.51 (d, 8 Hz, 1H; terpy H-3″), 8.46 (d, 8 Hz, 1H; terpy H-3), 8.40 (dd, 8, 0.5 Hz, 1H; terpy H-5′), 8.36 (br td, 7.5, 2 Hz, 2H; terpy H-4,4″), 8.35 (dd, 8, 1 Hz, 1H; terpy H-3′), 8.02 (ddd, 7, 5.5, 1 Hz, 1H; terpy H-5″), 7.99 (t, 8 Hz, 1H; terpy H-4′), 7.94 (ddd, 7, 5.5, 1.5 Hz, 1H; terpy H-5), 7.72 (d, 4.5 Hz, 1H; iminium *H*), 6.00 (br, 1H;

(35) 1,4-Dimethyl-1,3-cyclohexadiene was used as a 2:1 mixture with 1,4-dimethyl-1,4-cyclohexadiene; control experiments show that the unconjugated diene is unreactive with **1** at room temperature. Preparation of the mixture of dienes: Brady, W. T.; Norton, S. J.; Ko, J. *Synthesis* **1985**, 704−705.

alkene *H*), 2.46 (td, 14, 3.5 Hz, 1H; methylene), 1.93 (d, 1.5 Hz, 3H; CH_3), 1.77 (td, 13, 5 Hz, 1H; methylene), 1.61 (ddd, 13, 7, 2.5 Hz, 1H; methylene), 1.58 (dtd, 13, 7, 2 Hz, 1H; methylene), 0.69 (s, 3H; CH_3); **2t-ii**, δ 9.24 (dd, 5.5, 1.5 Hz, 1H; terpy H-6″), 9.22 (dd, 5.5, 1.5 Hz, 1H; terpy H-6), 8.48 (d, 8 Hz, 1H; terpy H-3 or -3″), 8.47 (d, 8 Hz, 1H; terpy H-3 or -3″), 8.33 (obscured, 1H; terpy H-4 or -4″), 8.33 (br d, 7.5 Hz, 2H; terpy H-3′,5′), 8.31 (td, 8, 2 Hz, 1H; terpy H-4 or -4″), 7.97 (ddd, 7, 5.5, 1.5 Hz, 1H; terpy H-5″), 7.95 (t, 8 Hz, 1H; terpy H-4′), 7.90 (ddd, 7, 5.5, 1.5 Hz, 1H; terpy H-5), 6.56 (br, 1H; alkene *H*), 4.21 (br, 1H; H_α), 2.99 (td, 13, 3.5 Hz, 1H; methylene), 2.65 (m, 2H; methylene), 2.52 (dddd, 16.5, 7.5, 3, 1.5 Hz, 1H; methylene), 1.71 (d, 2 Hz, 3H; CH_3), 1.32 (br s, 3H; CH_3). Anal. Calcd for $C_{23}H_{23}Cl_2F_6N_4OsP$: C, 36.28; H, 3.04; N, 7.36. Found: C, 36.87; H, 3.34; N, 6.82.

***trans*-[(terpy)OsCl$_2$(η^2(*C*,*N*)-(H$_2$*C*═*N*═CHCH═CHOMe)]PF$_6$ (5q).** Into a 50 mL round-bottom flask were added a magnetic stirbar, *trans*-[(terpy)OsNCl$_2$]PF$_6$ (**3**; 82.1 mg, 0.126 mmol), and 8 mL of acetonitrile. A 130 μL portion of 1-methoxy-1,3-butadiene (Aldrich, 1.28 mmol, 10 equiv) was injected with a 100 μL syringe, and the flask was sealed with Parafilm. The reaction mixture was stirred overnight for 15 h, over which time the solution turned dark brown. The volume of acetonitrile was reduced by half on a rotary evaporator, and the solution was flash-chromatographed on silica gel, with acetonitrile as eluent, to yield a light brown solution. The brown eluate was reduced to half its volume and then layered with ether and stored at −20 °C overnight. The azaallenium complex was then isolated as a brown solid by suction filtration, washed with 50 mL of Et$_2$O, and air-dried. Yield: 80.2 mg (0.109 mmol, 47%). ^{1}H NMR: δ 8.74 (d, 5 Hz, 2H; terpy H-6,6″), 8.60 (d, 8 Hz, 2H; terpy H-3′,5′), 8.57 (dd, 9, 2.5 Hz, 2H; terpy H-3,3″), 8.22 (dt, 10, 1.8 Hz, 1H; N═C*H*CH═CHOMe), 8.16 (t, 8 Hz, 1H; terpy H-4′), 8.10 (td, 7.8, 1.5 Hz, 2H; terpy H-4,4″), 7.78 (ddd, 7, 5.5, 1.5 Hz, 2H; terpy H-5,5″), 7.72 (d, 12 Hz, 1H; N═CHCH═C*H*OMe), 6.62 (dd, 12, 10 Hz, 1H; N═CHC*H*═CHOMe), 5.45 (d, 1.8 Hz, 2H; OsCH_2), 4.01 (s, 3H, OCH_3). ^{13}C{^{1}H} NMR: δ 171.67, 171.36, 157.96, 155.31, 154.25, 141.82, 129.55, 126.26, 124.07, 117.96, 109.23, 60.86 (OCH_3), 46.05 (OsCH_2). Anal. Calcd for $C_{20}H_{19}Cl_2F_6N_4OOsP$: C, 32.57; H, 2.60; N, 7.60. Found: C, 32.69; H, 2.49; N, 7.64.

Also prepared by this method were *trans*-[(terpy)OsCl$_2$(η^2-(*C*,*N*)-Me*C*H═*N*═CH[CH═CHMe])]PF$_6$ (**5s**, 51%), *trans*-[(terpy)-OsCl$_2$(2,3-η^2-2-aza-1,5-dimethylcyclohepta-1,2,4-trienium)]-PF$_6$ (**5t**, 72%), and *trans*-[(terpy)OsCl$_2$(2,3-η^2-2-aza-1-methyl-5-isopropylcyclohepta-1,2,4-trienium)]PF$_6$ (**5u**, 69%). Spectroscopic data for **5s** are as follows. ^{1}H NMR: δ 8.45 (d, 8 Hz, 2H; terpy H-3′,5′), 8.39 (d, 7.5 Hz, 2H; terpy H-3,3″), 8.38 (t, 8 Hz, 1H; terpy H-4′), 8.33 (dd, 10, 2.5 Hz, 1H; iminium), 8.02 (dd, 5.5, 1 Hz, 2H; terpy H-6,6″), 7.96 (td, 8, 1.5 Hz, 2H; terpy H-4,4″), 7.79 (ddd, 7.5, 5.5, 1 Hz, 2H; terpy H-5,5″), 7.17 (ddq, 16, 10, 2.5 Hz, 1H; N═CHC*H*═CHCH$_3$), 6.87 (dq, 16, 7 Hz, 1H; N═CHCH═C*H*CH$_3$), 5.89 (br q, 7 Hz, 1H; OsC*H*CH$_3$), 2.21 (dd, 7, 1 Hz, 3H; N═CHCH═CHC*H*$_3$), 2.08 (d, 5.5 Hz, 3H; OsCHC*H*$_3$). ^{13}C{^{1}H} NMR: δ 161.54 (N═*C*HR), 43.49 (Os-*C*HCH$_3$), 19.13, 18.88 (*C*H$_3$). Anal. Calcd for $C_{21}H_{21}Cl_2F_6N_4$-OsP: C, 34.29; H, 2.88; N, 7.62. Found: C, 34.79; H, 3.14; N, 7.19. Spectroscopic data for **5t** are as follows. ^{1}H NMR: δ 8.36−8.31 (m, 5H; terpy H-3,3′,3″,4′,5′), 7.92−7.86 (m, 4H; terpy H-4,4″,6,6″), 7.54 (br t, 6.6 Hz, 2H; terpy H-5,5″), 7.27 (br s, 1H; alkene H), 6.02 (br s, 1H; H_α), 3.67 (td, 13, 4.5 Hz, 1H; methylene), 3.02 (dt, 13.5, 4 Hz, 1H; methylene), 2.68 (d, 1.5 Hz, 3H; N═CC*H*$_3$), 2.45 (m, 2H; methylene), 1.81 (s, 3H; alkene C*H*$_3$). ^{13}C{^{1}H} NMR: 186.17 (N═*C*R$_2$), 42.00 (Os*C*HR), 39.74, 31.26 (*C*H$_2$), 26.43, 22.92 (*C*H$_3$). Anal. Calcd for $C_{23}H_{23}Cl_2F_6N_4$-OsP: C, 36.28; H, 3.04; N, 7.36. Found: C, 36.87; H, 2.95; N, 6.92.

***trans*-[(terpy)OsCl$_2$(η^2(*C*,*N*)-[Me$_2$C═CH]*C*H═*N*═CMe$_2$)]-PF$_6$ (5r).** A mixture of 54.4 mg of *trans*-[(terpy)OsNCl$_2$]PF$_6$ (**3**; 0.0833 mmol), 65 μL of 2,5-dimethyl-2,4-hexadiene (Aldrich; 0.42 mmol, 5.0 equiv), a magnetic stirbar, and 5 mL of acetonitrile were stirred in a screw-cap vial with a Teflon-lined cap for 9 h. The resulting dark solution was reduced to half its volume on the rotary evaporator and then layered with ether. The mixture was allowed to stand overnight in a −20 °C freezer. The crystals were suction-filtered on a fritted funnel, washed with 3 × 30 mL of Et$_2$O, and air-dried to give 57.0 mg of **5r** (90%). ^{1}H NMR: δ 8.50 (d, 8 Hz, 2H; terpy H-3′,5′), 8.47 (d, 8.5 Hz, 2H; terpy H-3,3″), 8.44 (d, 6 Hz, 2H; terpy H-6,6″), 8.28 (t, 8 Hz, 1H; terpy H-4′), 8.05 (td, 8, 1.5 Hz, 2H; terpy H-4,4″), 7.70 (ddd, 7.5, 5, 1.5 Hz, 2H; terpy H-5,5″), 6.54 (dsp, 10, 1.5 Hz, 1H; OsCHC*H*═CMe$_2$), 5.14 (dsp, 10, 1.5 Hz, 1H; OsC*H*CH═CMe$_2$), 3.06 (d, 1.5 Hz, 3H; OsN═C[C*H*$_3$][CH$_3$]), 2.52 (d, 1.5 Hz, 3H; OsN═C[CH$_3$][C*H*$_3$]), 2.22 (d, 1.5 Hz, 3H; alkene *CH*$_3$), 1.92 (d, 2 Hz, 3H; alkene C*H*$_3$). ^{13}C{^{1}H} NMR: δ 185.31 (Me$_2$*C*═N), 51.02 (Os*C*HR), 29.52, 26.64, 25.53, 19.86 (*C*H$_3$). Anal. Calcd for $C_{23}H_{25}Cl_2F_6N_4OsP$: C, 36.19; H, 3.30; N, 7.34. Found: C, 36.25; H, 3.14; N, 7.32.

***trans*-[(terpy)OsCl$_2$(1,2-η^2-2-aza-5-methoxycyclohepta-1,2,4-trienium)]PF$_6$ (5v).** Into a 25 mL round-bottom flask were placed 81.2 mg *trans*-[(terpy)OsNCl$_2$]PF$_6$ (**3**; 0.133 mmol), 79 μL of 1-methoxy-1,3-cyclohexadiene (Aldrich; 65% pure, 0.43 mmol, 3.2 equiv), a magnetic stirbar, and 5 mL of CH$_3$CN. The mixture was stirred at room temperature for 15 min and then stored at −20 °C for 2 h. The dark solid that formed was suction-filtered, washed three times with Et$_2$O, and air-dried to yield 62.3 mg of **5v** as a black solid (65%). ^{1}H NMR: δ 2.34 (tdd, 13, 9, 3 Hz, 1H; C*H*H′CH″H‴), 2.87 (dtd, 14, 4, 3 Hz, 1H; CH*H*′CH″H‴), 3.00 (dt, 20, 3 Hz, 1H; CHH′C*H*″H‴), 3.35 (dddd, 20, 13, 4, 1.5 Hz, 1H; CHH′CH″*H*‴), 3.89 (s, 3H; OCH_3), 5.92 (dd, 6, 2 Hz, 1H, alkene), 6.53 (dt, 9, 2 Hz, 1H; H_α), 7.80 (ddd, 7.5, 6, 1 Hz, 2H; terpy H-5,5″), 8.10 (t, 8 Hz, 1H; terpy H-4′), 8.11 (td, 8, 1 Hz, 2H, terpy H-4,4″), 8.22 (dd, 6, 2 Hz, 1H; N═C*H*), 8.57 (dd, 8, 1 Hz, 2H; terpy H-3,3″), 8.60 (d, 8 Hz, 2H; terpy H-3′,5′), 8.87 (d, 5.5 Hz, 2H; terpy H-6,6″). Anal. Calcd for $C_{22}H_{21}Cl_2F_6N_4OOsP$: C, 35.35; H, 2.83; N, 7.49. Found: C, 34.98; H, 3.04; N, 7.75.

[(Tpm)OsCl$_2$(η^2(*C*,*N*)-[H$_2$*C*═*N*═CHCH═CHOMe)]PF$_6$ (6q). A mixture of 87.2 mg of [(Tpm)OsNCl$_2$]PF$_6$ (**4**; 0.138 mmol) and 140 μL of 1-methoxy-1,3-butadiene (Aldrich, 1.38 mmol, 10 equiv) in 9 mL of CH$_3$CN were stirred magnetically in a screw-cap vial with a Teflon-lined cap for 3 h. The resulting dark solution was reduced by half its volume on the rotary evaporator and then layered with ether. After the mixture stood overnight in a −20 °C freezer, the crystals were suction-filtered on a fritted funnel, washed with 3 × 60 mL of Et$_2$O, and air-dried to give 91.0 mg of **6q** (92%). ^{1}H NMR: δ 8.93 (s, 1H; pz$_3$C*H*), 8.44 (dt, 10, 1.6 Hz, 1H; N═C*H*CH═CHOMe), 8.42 (obscured, 1H; pz 3,5-*H*), 8.36 (d, 2.7 Hz, 1H; pz 3,5-*H*), 8.25 (d, 3.6 Hz, 2H; pz 3,5-*H*), 7.64 (d, 3.6 Hz, 2H; pz 3,5-*H*), 7.62 (d, 12 Hz, 1H; N═CHCH═C*H*OMe), 6.68 (t, 2.7 Hz, 1H; pz 4-*H* trans to azaallenium), 6.58 (t, 2.7 Hz, 2H; pz 4-*H* cis to azaallenium), 6.26 (dd, 12, 10 Hz, 1H; N═CHC*H*═CHOMe), 4.86 (d, 1.8 Hz, 2H; OsCH_2), 3.91 (s, 3H; OCH_3). ^{13}C-{^{1}H} NMR: δ 167.37 (N═*C*HR), 77.35 (pz$_3$*C*H), 59.90 (OCH_3), 32.54 (OsCH_2). Anal. Calcd for $C_{15}H_{18}Cl_2F_6N_7OOsP$: C, 26.08; H, 2.52; N, 13.25. Found: C, 26.35; H, 2.72; N, 13.00.

Kinetics of Reactions of *cis*-[(terpy)OsNCl$_2$]PF$_6$ with 1,4-Dimethyl-1,3-cyclohexadiene and 2,5-Dimethyl-2,4-hexadiene. Samples consisting of 7.7 mg of *cis*-[(terpy)OsNCl$_2$]-PF$_6$ and ~2 mg of terephthalaldehyde (as an internal standard) dissolved in 0.5 mL of CD$_3$CN were placed in 5 mm NMR tubes with screw-cap tops fitted with Teflon-lined silicone rubber septa. The tubes were cooled in the probe of a 500 MHz NMR instrument to −10 °C. Reactions were initiated by ejecting the sample, injecting 35 μL of the appropriate diene through the septum, and reinserting into the precooled probe. ^{1}H NMR spectra were then acquired periodically over the course of 30 000 s. (In the reaction with 1,4-dimethyl-1,3-cyclohexadiene,[35] the tube was cooled to −40 °C while outside the probe; 5 min was allowed for reequilibration at −10 °C before data collection was initiated.) Concentrations of the various species

were obtained by integration relative to the intensity of the terephthalaldehyde peak at δ 10.10, using the following peaks: **1**, δ 9.80 (2H); the intermediate **I** in the reaction with 1,4-dimethyl-1,3-cyclohexadiene, δ 11.22 (1H); **2t-i**, δ 9.31 (1H); **2t-ii**, δ 9.24 and 9.22 combined (2H). The thermodynamic product in the reaction with 2,5-dimethyl-2,4-hexadiene (**2r**) was measured by integration of its resonance at δ 7.80 (1H); the kinetic product in the reaction was measured by difference, using the overlapped terpy 6,6″-H peaks at δ 9.35 to ascertain the total product concentration. Good mass balance was obtained in all cases, with constant total integrals measured (about ±10%) and no systematic variation of the overall integral with time.

The time courses of the reactions were simulated by nonlinear least-squares fitting to the appropriate analytical expressions for successive first-order (or pseudo-first-order) equations[36] using Microsoft Excel,[37] with uncertainties in the calculated parameters calculated as described in the literature.[38]

Generation and ^{1}H NMR Characterization of Unstable Azaallenium Isomers. The following isomers are thermodynamically unstable and were characterized in situ when generated at low temperature from **1** and an excess of the appropriate alkene. Some resonances are obscured by isomeric products and resonances from excess alkene. ^{1}H NMR data for *cis*,*syn*-[(terpy)$OsCl_2$(η^2(*C*,*N*)-[$Me_2NC_6H_4$]*C*H=*N*=CHMe)]-PF_6 (**2l-iii**) at −40 °C: δ 9.49 (d, 5.5 Hz, 1H; terpy H-6″), 9.16 (d, 5.5 Hz, 1H; terpy H-6), 8.49 (d, 8.5 Hz, 1H; terpy H-3″), 8.42 (td, 7.5, 1.5 Hz, 1H; terpy H-4″), 8.25 (d, 8 Hz, 1H; terpy H-3), 8.24 (qd, 6, 2 Hz, 1H; iminium), 8.03 (m, 2 H; terpy H-5,5″), 7.80 (m, 4H; terpy H-3′,4,5′,4′), 6.42 (quin, 2 Hz, 1H; H_α), 6.36 (d, 8.5 Hz, 1H; Ar H), 6.21 (d, 8.5 Hz, 1H; Ar H), 5.94 (d, 8.5 Hz, 1H; Ar H), 5.29 (d, 8.5 Hz, 1H; Ar H), 1.62 (dd, 6, 2 Hz, 3H; N=CHCH_3). ^{1}H NMR at −5 °C for *cis*,*syn*-[(terpy)-$OsCl_2$(η^2(*C*,*N*)-[$MeOC_6H_4$]*C*H=*N*=CHMe)]PF_6 (**2k-iii**): δ 9.50 (d, 5.5 Hz, 1H; terpy H-6″), 9.20 (d, 5.5 Hz, 1H; terpy H-6), 8.47 (d, 8.5 Hz, 1H; terpy H-3″), 8.42 (td, 7.5, 1.5 Hz, 1H; terpy H-4″), 8.25 (d, 8.5 Hz, 1H; terpy H-5′), 8.22 (qd, 6, 2.5 Hz, 1H; iminium), 8.04 (m, 2 H; terpy H-5,5″), 7.90 (m, 1H; terpy H-3), 7.83 (m, 2H; terpy H-3′,4), 7.75 (t, 8 Hz, 1H; terpy H-4′), 6.64 (quin, 2 Hz, 1H; H_α), 5.48 (br, 1H; Ar H), 1.62 (dd, 5, 2 Hz, 3H; N=CHCH_3). ^{1}H NMR of *cis*-[(terpy)$OsCl_2$(η^2(*N*,*C*)-CH_2=*N*=*C*H(CH=CHOMe)]PF_6 (**2q-i**) at −20 °C: δ 8.92 (d, 5 Hz, 1H; terpy H-6″), 8.26 (td, 8, 1 Hz, 1H; terpy H-4 or 4″), 7.91 (ddd, 7.5, 5.5, 1 Hz, 1H; terpy H-5″), 7.83 (dd, 9, 2.5 Hz, 1H; iminium), 7.80 (ddd, 7.5, 5.5, 1 Hz, 1H; terpy H-5), 7.45 (dd, 9, 2.5 Hz, 1H; iminium). ^{1}H NMR of *cis*-[(terpy)$OsCl_2$(η^2(*C*,*N*)-Me_2*C*H=*N*=CH(CH=CMe_2)]PF_6 (**2r-i**) at −20 °C: δ 9.34 (dd, 5, 1 Hz, 2H; terpy H-6,6″), 8.66 (d, 10.5 Hz, 1H; iminium), 8.51 (d, 8 Hz, 2H; terpy H-3,3″), 8.40 (m, 4H; terpy H-3′,4,4″,5′), 8.03 (m, 3H; terpy H-4′,5,5″), 5.65 (dt, 10.5, 1 Hz, 1H; alkene), 1.97 (sl br s, 3H, CH=C[CH_3][CH_3′]), 1.96 (sl br s, 3H, CH=C[CH_3][CH_3′]), 1.05 (s, 6H; OsC[CH_3]$_2$).

X-ray Crystallography of *cis*-[(terpy)$OsCl_2$(1,2-η^2-Ph-CH=N=CHCH=CHCH=CHPh)]PF_6·$(CD_3)_2CO$ (2h·$(CD_3)_2CO$). Dark red blocks of the complex were grown by slow diffusion of ether into a solution of **2h** in acetone-d_6. A 0.22 × 0.10 × 0.05 mm crystal was glued to the tip of a glass fiber in the air and examined at 20 °C on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation with a graphite monochromator (λ = 0.710 73 Å). The crystal was triclinic (space group $P\bar{1}$). The unit cell was determined on the basis of 25 reflections with 12.0° < θ < 13.0°. A total of 6341 reflections with 2θ < 50° were collected. Crystal quality was monitored by recording 3 standard reflections approximately every 170 reflections measured, and a linear correction was applied to correct for the slight (2%) decay that was observed. An empirical absorption correction was applied (μ = 3.796 mm^{-1}, transmission factors 0.7049−0.8369). The osmium atom was located on a Patterson map. The remaining non-hydrogen atoms were found on difference Fourier syntheses. Hydrogens in the complex were placed in calculated positions, except for the two bonded to C1 and C2, which were located on the difference Fourier maps and refined isotropically. Final full-matrix least-squares refinement on F^2 converged at R = 0.0342 for 5324 reflections with $F_o > 4\sigma(F_o)$ and R = 0.0490 for all data (wR2 = 0.0715, 0.0774, respectively). All calculations used SHELXTL (Bruker Analytical X-ray Systems), with scattering factors and anomalous dispersion terms taken from the literature.[39]

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Supporting Information Available: Text giving full synthetic details and spectroscopic data on all compounds and tables giving and crystallographic data; crystallographic data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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