

Anisotropic π Bonding in Bis(iminoxolene)ruthenium: Consequences for Alkene and Alkyne Binding

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Cite This: *Organometallics* 2024, 43, 1889–1903



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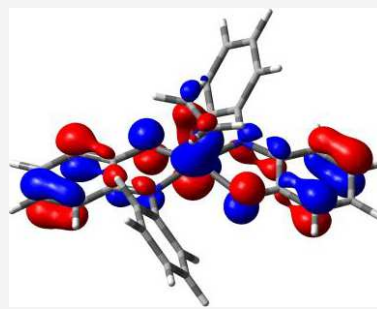


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ABSTRACT: Orientational preferences in alkene and alkyne complexes arise from differences in the π backbonding capabilities of the relevant $d\pi$ orbitals, which typically are engendered by an unsymmetrical arrangement of ancillary ligands. The metal *trans*-bis(iminoxolene) fragment is C_2 -symmetric but discriminates between perpendicular $d\pi$ orbitals because only one of them has a strong π interaction with the iminoxolenes. To assess this effect, square pyramidal bis(iminoxolene) alkene and alkyne complexes (Diso) $_2$ Ru(L) (Diso = *N*-(2,6-diisopropylphenyl)-4,6-di-*tert*-butyl-*o*-iminobenzoquinone) are prepared via the bis-acetonitrile complex *cis*-(Diso) $_2$ Ru(NCCH $_3$) $_2$. The alkenes and alkynes align roughly along the O–Ru–O axis but are turned slightly toward the cleft between the iminoxolene ligands, which orients the ligand π^* orbital with the $d\pi$ orbital that is not engaged in bonding with the iminoxolenes. In the alkyne complexes, π donation from the alkyne competes effectively with the ruthenium-iminoxolene π bonding, forming a favorable four-electron, three-orbital system. The barrier to rotation in the 1-hexyne complex is 19.0 kcal mol $^{-1}$, while allylbenzene dissociates more readily than it undergoes rotation, with a barrier of 17.4 kcal mol $^{-1}$. The strong orientational preference leads to high facial selectivity of alkene binding, with only one diastereomer of the 1-alkene adducts observed by NMR (>30:1 selectivity).



Only (A,S) diastereomer of α -olefin complexes observed

$$\Delta\Delta G^\circ_{\text{calc}} = 4.6 \text{ kcal mol}^{-1}$$

INTRODUCTION

In the bonding of alkenes and alkynes to transition metals, π interactions play a major role. For both classes of ligands, backbonding of filled $d\pi$ orbitals into empty carbon–carbon π^* orbitals usually contributes significantly to the energetics of binding.¹ Alkynes may also have a π donor interaction from the alkyne π bonding orbital perpendicular to the metal–alkyne plane.²

The presence of π bonding introduces the possibility of electronically driven orientational preferences and corresponding barriers to rotation. If the two possible $d\pi$ orbitals that can potentially backbond (d_{xz} and d_{yz} , if the z -axis is taken as the vector between the metal and the centroid of the alkene or alkyne) are degenerate, as in axially symmetric compounds such as W(CO) $_5$ (alkene),³ then there is no difference in the energetics of π bonding with respect to orientation and barriers to rotation are small.⁴ Engendering a preferred orientation requires an unsymmetrical coordination sphere, where the degree of orientational preference depends on the electronic differentiation between the d_{xz} and d_{yz} orbitals. For example, in the pseudo-octahedral d^6 mononitrosyl complex [CpRe(NO)(PPh $_3$)(C $_2$ H $_4$)] $^+$, the alkene prefers to have its C–C bond perpendicular to the nitrosyl linkage, allowing it to backbond with the $d\pi$ orbital that is not also backbonding to the strongly π accepting nitrosyl (Figure 1). The barrier to alkene rotation is 16.4 kcal mol $^{-1}$ (369 K).⁵ When the asymmetry between $d\pi$ orbitals is less, as when the weaker π acceptor CO is present in

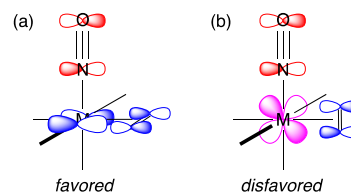


Figure 1. Possible alkene orientations in an octahedral d^6 mononitrosyl complex. (a) Favored orientation, where the backbonding $d\pi$ orbital does not interact with the nitrosyl. (b) Disfavored orientation, where backbonding to the alkene takes place from a $d\pi$ orbital that is also backbonding to the strongly π -accepting nitrosyl ligand.

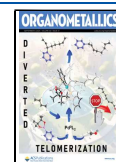
TpRe(CO)(PMe $_3$)(C $_2$ H $_4$), the rotation barrier is correspondingly lower ($\Delta G^\ddagger = 10.0$ kcal mol $^{-1}$).⁶ In an extreme case, in octahedral d^2 -monooxo complexes, only the d orbital of δ symmetry with respect to the oxo group is occupied, so backbonding to the alkene is only possible if its C–C bond is perpendicular to the M=O bond. Accordingly, the tungsten-

Received: June 16, 2024

Revised: July 26, 2024

Accepted: August 5, 2024

Published: August 10, 2024



(IV) complex $W(O)(PMePh_2)_2Cl_2(C_2H_4)$ is rigid on the NMR time scale up to 353 K,⁷ with a barrier to rotation of over 20 kcal mol⁻¹.⁸

A strong orientational preference can foster enantiofacially selective binding of prochiral alkenes, if it forces the alkene substituents in one of the diastereomeric complexes into sterically unfavorable positions in order to maintain the electronically favored orientation. For example, complexes of the diastereomers of monosubstituted alkene complexes $[CpRe(NO)(PPh_3)(RCH=CH_2)]^+$ maintain nearly identical core geometries,⁹ forcing the alkene substituent to approach either the nitrosyl or the cyclopentadienyl substituent. The former diastereomer is favored thermodynamically, by 32:1 in the cyclopentadienyl complex¹⁰ and over 99:1 in the pentamethylcyclopentadienyl complex¹¹ of 1-pentene.

Often, privileged structures that can give rise to high enantioselectivity in binding or reactivity have C_2 symmetry.¹² This point group is not readily compatible with the unsymmetrical structures described above that favor strong orientational preferences in alkene binding. A potential exception to this generalization would be the *trans*-bis(iminoxolene) metal fragment (Figure 2), where the

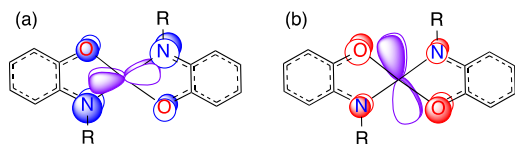


Figure 2. Filled π orbitals in the C_2 -symmetric *trans*-bis(iminoxolene)metal moiety, viewed down the 2-fold axis. (a) Strongly bonding combination of metal $d\pi$ orbital with B -symmetry RAO combination. (b) Modestly antibonding combination of metal $d\pi$ orbital with B -symmetry SJO combination.

particularities of the metal–ligand π bonding discriminate between the two d orbitals that are of π symmetry with respect to the C_2 axis. One of the d orbitals, aligned roughly along the axis connecting the two iminoxolenes, interacts strongly with the B -symmetry combination of the frontier iminoxolene π orbitals, the so-called redox-active orbital (RAO). The RAO is quite close in energy to the d orbitals of elements in the middle of the d block,¹³ so the interaction forms a bonding combination (Figure 2a) that is typically filled and an antibonding combination that is typically empty. In contrast, the d orbital aligned roughly between the iminoxolenes does not overlap with the RAO combinations, but rather is raised in energy by its antibonding interaction with the lower-lying ligand π orbital with out-of-phase oxygen and nitrogen p orbitals¹⁴ (the so-called subadjacent orbital or SJO¹⁵). This filled, high-energy orbital should thus be much better suited to backbonding than the lower-lying π bonding orbital (which also has significantly less metal character). The effects of the π anisotropy of the *trans*-bis(iminoxolene) fragment have been documented in the spectroscopy^{16,17} and reactivity¹⁸ of oxoosmium complexes.

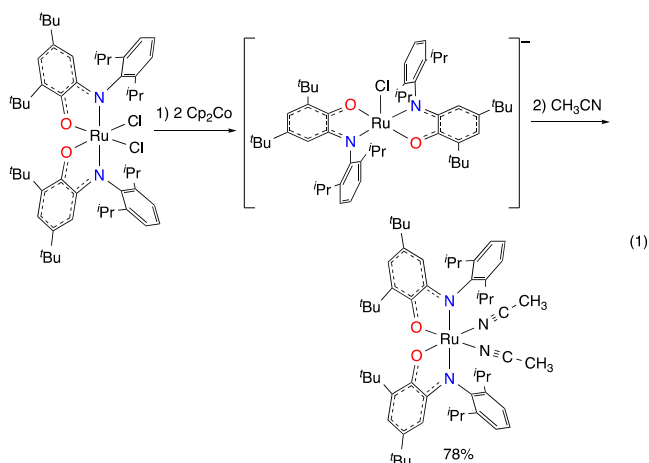
Here we describe the preparation of a reduced *cis*-bis(iminoxolene)ruthenium bis(acetonitrile) complex that serves as a precursor for five-coordinate *trans*-bis(iminoxolene)ruthenium complexes of alkynes and monosubstituted alkenes. Structural studies confirm that the unsaturated ligands are aligned to maximize backbonding from the higher-energy $d\pi$ orbital. Dynamic NMR studies show that there are large barriers to rotation for both alkenes and alkynes,

indicating a strong preference for one particular orientation of the alkene or alkyne. Consonant with this, only one diastereomer is observed by 1H NMR spectroscopy in complexes with monosubstituted alkenes.

RESULTS AND DISCUSSION

Synthesis and Characterization of a *cis*-Bis(iminoxolene)ruthenium Bis(acetonitrile) Complex.

The neutral bis(iminoxolene)ruthenium complex $(Diso)_2Ru(PPh_3)$ ($Diso = N$ -(2,6-diisopropylphenyl)-4,6-di-*tert*-butyl-*o*-iminobenzoquinone) may be prepared by two-electron reduction of $(Diso)_2RuCl_2$ followed by the addition of triphenylphosphine.¹⁹ In the case of the alkene and alkyne adducts, it is more synthetically convenient to prepare an isolable precursor with volatile, labile ligands, namely *cis*- $(Diso)_2Ru(NCCH_3)_2$ (eq 1). The synthesis is achieved by



cobaltocene reduction of either *cis*- or *trans*- $(Diso)_2RuCl_2$, which appears to generate diamagnetic, C_2 -symmetric $[(Diso)_2RuCl]^-$ in solution. Addition of excess acetonitrile to the chloro anion generated in situ affords the crystalline neutral bis(acetonitrile) complex in good yield. The compound is *cis* in solution, as shown by the symmetry of its NMR spectra (for example, two isopropyl methine signals are seen rather than the one expected for the C_{2h} -symmetric *trans* isomer).

The *cis* geometry is confirmed by the solid-state structure of $(Diso)_2Ru(NCCH_3)_2 \cdot 2CH_3CN$ (Table S1 and Figure 3). The intraligand distances in iminoxolene groups are informative because they respond systematically to the electron density in the ligand redox-active orbital (RAO) and can be analyzed to provide an estimate of the apparent or metrical oxidation state (MOS).²⁰ *cis*- $(Diso)_2Ru(NCCH_3)_2$ displays an MOS of $-1.28(5)$ for each iminoxolene ligand (Table 1). Compared to the MOS value of $-0.78(4)$ per iminoxolene in *cis*- $(Diso)_2RuCl_2$, this indicates that the overall two-electron reduction of the dichloride complex is split equally between reduction of the metal and of the ligands, consistent with a highly covalent ruthenium–iminoxolene interaction. Indeed, the observed MOS value is close to the value of -1.34 predicted for a complex with a π bond order of 0.5 per iminoxolene.¹³

Formation of both *trans* and *cis* isomers is preceded for bis(iminoxolene)ruthenium or -osmium complexes with two neutral donor ligands.¹⁸ In the case of isoelectronic $(Diso)_2Ir(py)Cl$, both the *cis* and *trans* isomers are observed, with the *cis* isomer favored by 6.1 kcal mol⁻¹.²¹ The greater stability of the

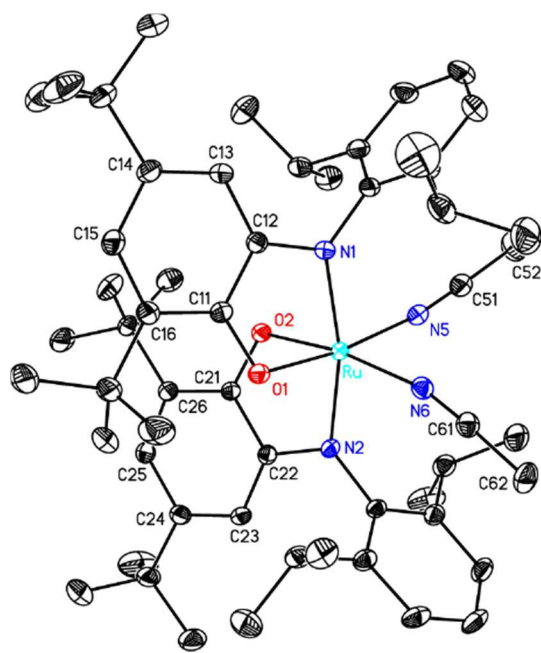


Figure 3. Thermal ellipsoid plot of *cis*-(Diso)₂Ru(NCCH₃)₂ · 2CH₃CN. Hydrogen atoms and lattice solvents are omitted for clarity.

Table 1. Selected Distances (Å) and Metrical Oxidation States (MOS)²⁰ for *cis*-(Diso)₂Ru(NCCH₃)₂^a

	X-ray	DFT
Ru–O1	2.0036(11)	2.025
Ru–N1	2.014(10)	2.050
Ru–N5	2.0376(14)	2.024
C51–N5	1.142(3)	1.157
O1–C11	1.326(3)	1.313
N1–C12	1.368(5)	1.370
C11–C12	1.432(2)	1.441
C12–C13	1.416(2)	1.418
C13–C14	1.377(3)	1.383
C14–C15	1.419(5)	1.414
C15–C16	1.384(2)	1.385
C16–C11	1.423(5)	1.412
MOS	−1.28(5)	−1.24(7)

^aValues in roman type are measured crystallographically; values in italics are from DFT calculations (B3LYP, SDD basis set for Ru and 6-31G* basis set for other atoms) on the complex with *tert*-butyl, isopropyl, and methyl groups replaced with hydrogen atoms. Metrical data are averaged among chemically equivalent values, with stated esd's reflecting both the variance in the measured values and the statistical uncertainty of the crystallographic model.

cis isomer is attributed to steric effects, with electronic effects favoring the *trans* isomer, as judged by the greater computed stability of the *trans* isomer of unhindered (ap)₂Ir(py)Cl (ap = 1,2-C₆H₄(O)(NPh)). A similar explanation likely holds for the ruthenium bis(acetonitrile) complex, as the simplified model hydrogen cyanide complex *trans*-(ap)₂Ru(NCH)₂ is calculated to be 2.0 kcal mol^{−1} more stable than the *cis* isomer.

As has been seen in previously prepared *cis*-bis(iminoxolene)ruthenium bipyridine complexes,²² the optical spectrum of *cis*-(Diso)₂Ru(NCCH₃)₂ features a prominent, intense absorption in the near-IR (λ_{max} = 1084 nm, Figure S20). With the aid of TDDFT calculations, this band is attributed to a HOMO (*B*-symmetry RAO nonbonding

orbital) to LUMO (*A*-symmetry Ru–RAO π^* orbital) transition (Figure 4). The Ru–RAO π bonding orbital is identified as the HOMO–4 orbital, with the $\pi \rightarrow \pi^*$ transition assigned to the 420 nm band.

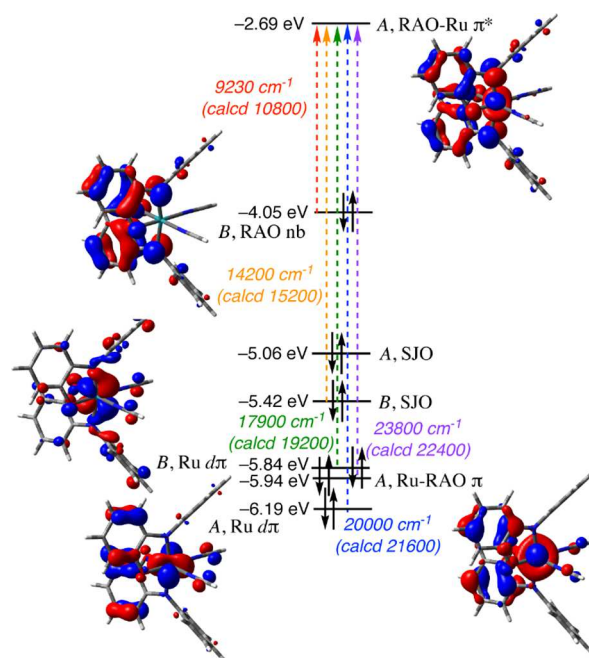


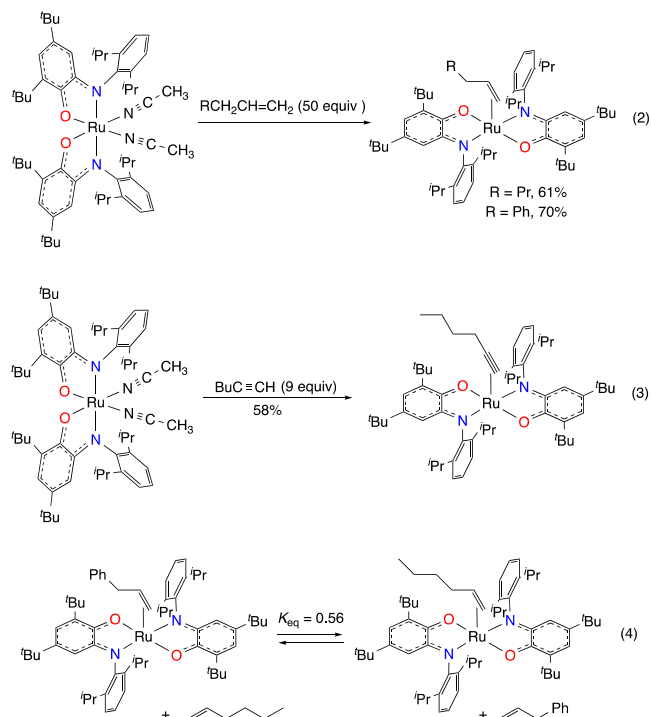
Figure 4. MO diagram of *cis*-(ap)₂Ru(NCH)₂. The HOMO–1 and HOMO–2, which are principally ligand in character, are not pictured.

The orbitals identified as principally Ru $d\pi$ in character, notably the *B*-symmetry HOMO–3 and *A*-symmetry HOMO–5, show some degree of backbonding to the π^* orbitals of the nitrile ligands. This apparent mild π basicity of the *cis*-(Diso)₂Ru fragment is consistent with its IR spectrum, where the nitrile stretches are observed at 2275 cm^{−1}, only slightly raised over the free ligand (2268 cm^{−1} in the gas phase²³) and consistent with a modestly backbonding ruthenium center (similar to the 2276 cm^{−1} observed for [CpRu(PMe₃)(NCCH₃)₂]⁺).²⁴ A useful comparison is *cis*-(acac)₂Ru(NCCH₃)₂, which shares the same charge and geometry with (Diso)₂Ru(NCCH₃)₂ and also has oxygen donors *trans* to acetonitrile. The acetylacetonate complex absorbs at 2250 cm^{−1},²⁵ slightly lower than the iminoxolene complex (for reference, (acac)₂Ru(CO)₂ has ν_{CO} = 2056, 1988 cm^{−1}).²⁶ The fact that the (acac)₂Ru fragment is a slightly better π donor than (Diso)₂Ru is consistent with the ability of the iminoxolenes to withdraw electron density from the metal center as π acceptors themselves.

NMR spectra of *cis*-(Diso)₂Ru(NCCH₃)₂ at ambient temperatures show distinct signals for bound and free acetonitrile, but these signals broaden and coalesce as the temperature is raised, indicating facile ligand exchange (Figure S22). Exchange is dissociative, as the line width of the bound CH₃CN peak is unaffected by the concentration of free CH₃CN. Dissociative exchange is also consistent with the activation parameters determined by Eyring analysis of the dynamic NMR data (Figure S23), with $\Delta H^\ddagger$ = 20.3(5) kcal mol^{−1} and $\Delta S^\ddagger$ = 9.6(13) cal mol^{−1} K^{−1}. The extrapolated $\Delta G^\ddagger$ at 298 K, 17.4 kcal mol^{−1}, corresponds to a rate constant for exchange of about 1 s^{−1} at 298 K. This is about 10⁵ times faster than acetonitrile exchange in *cis*-(acac)₂Ru(NCCH₃)₂.²⁵ Note

that the peaks due to the iminoxolene ligands in the complex are not affected by the dissociation of acetonitrile. This indicates that reassociation of acetonitrile to the five-coordinate intermediate must be faster than formation of *trans*-(Diso)₂Ru(NCCH₃)₂ from that intermediate. Such stereoretentive ligand exchange is also observed for *cis*-(Diso)₂Ir(py)Cl.²¹

Preparation and Characterization of Five-Coordinate Alkene and Alkyne Complexes. Treatment of *cis*-(Diso)₂Ru(NCCH₃)₂ with monosubstituted alkenes such as 1-hexene or allylbenzene, or alkynes such as 1-hexyne, results in displacement of acetonitrile and formation of five-coordinate ruthenium complexes (eqs 2–3). Coordination of a second



equivalent of alkene or alkyne is not observed even in the presence of a large excess of ligand. The internal alkynes 3-hexyne and diphenylacetylene react similarly to 1-hexyne, but the internal alkene 2-hexene binds only weakly, partially displacing acetonitrile from (Diso)₂Ru(NCCH₃)₂, and stilbene does not react at all. Allylbenzene and 1-hexene bind with similar affinities (*K*₄ = 0.56 for displacement of allylbenzene by 1-hexene in CD₂Cl₂ at 293 K, eq 4). Alkynes bind more

strongly than alkenes, with 3-hexyne quantitatively displacing allylbenzene from (Diso)₂Ru(CH₂=CHCH₂Ph).

NMR spectroscopy of the alkene and alkyne complexes show that the two iminoxolene ligands are inequivalent (*C*₁ symmetry), consistent with slow rotation of the alkene or alkyne ligand. The alkene hydrogens appear at very disparate chemical shifts, with the 2-H and the *cis*-1-H resonating at approximately 5 ppm, while the *trans*-1-H appears far upfield (δ 1.83 in (Diso)₂Ru(CH₂=CHBu)). One of the allylic hydrogens also resonates at unusually high field (δ 0.13 for (Diso)₂Ru(CH₂=CHCHH'Pr)). Hydrogens in metal–alkene complexes typically appear upfield of their positions in the free alkenes, but the large difference in chemical shift between the two terminal alkene hydrogens, as well as the upfield shift of one of the diastereotopic allylic hydrogens, suggests that in these compounds the (Diso)₂Ru fragment has a large magnetic anisotropy that dominates the observed chemical shifts. The ¹³C NMR signals of terminal and internal alkene carbons of bound 1-hexene are observed at δ 61.3 and 75.7 ppm, respectively, in the typical region for bound olefins.

The terminal hydrogen of the 1-hexyne complex is observed at δ 7.73 ppm and the diastereotopic propargylic hydrogens at δ 2.92 and 3.16 ppm (²*J* = 17.1 Hz) in the ¹H NMR spectrum. As measured by single- and multiple-bond ¹H–¹³C correlation spectroscopy, the terminal alkyne carbon resonates at 116.2 and the internal carbon at 140.0 ppm. Formation of metal vinylidenes from terminal alkynes is well preceded by ruthenium,²⁷ but the α carbons of ruthenium vinylidenes invariably resonate downfield of 250 ppm,²⁸ so the data for the present compound rule out vinylidene formation and are consistent with the presence of an intact alkyne. No C≡C stretch could be observed in the IR spectrum of (Diso)₂Ru(HCCBu), presumably because of its low intensity. The alkyne stretch in (ap)₂Ru(HCCH) is calculated to be at a scaled²⁹ frequency of 1669 cm^{−1}.

Structure and Bonding in Bis-iminoxolene Ruthenium Alkyne and Alkene Complexes. The (Diso)₂Ru complexes of 1-hexene, allylbenzene, and 3-hexyne all crystallize as five-coordinate monomers (Figure 5) that are well described as square pyramids with the η^2 ligands in the apical position (Reedijk τ values³⁰ close to zero, Table 2). The orientations of the unsaturated ligands in the alkene and alkyne complexes, as determined by X-ray crystallography, are strikingly similar (Figure 5). In each case the bound C–C bond is roughly aligned with the O–Ru–O axis, but canted slightly toward the cleft between the two iminoxolene ligands,

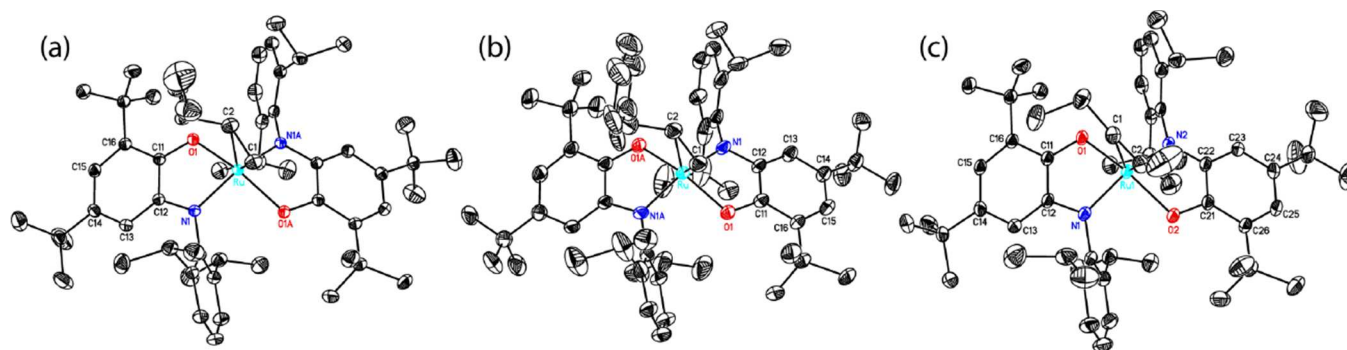


Figure 5. Thermal ellipsoid plots of (a) (Diso)₂Ru(CH₂=CHBu); (b) (Diso)₂Ru(CH₂=CHCH₂Ph); and (c) (Diso)₂Ru(EtC≡CEt). Hydrogen atoms, lattice solvents, and minor components of disordered groups are omitted for clarity. Only one of the two crystallographically inequivalent molecules of (Diso)₂Ru(EtC≡CEt) is shown.

Table 2. Selected Distances (Å), Dihedral Angles (deg), Metrical Oxidation States (MOS) per Iminoxolene Ligand,²⁰ and τ Values³⁰ for Bis(iminoxolene)ruthenium Alkene and Alkyne complexes^a

	(Diso) ₂ Ru (CH ₂ =CHBu) X-ray	(Diso) ₂ Ru (CH ₂ =CHCH ₂ Ph) X-ray	(ap) ₂ Ru (CH ₂ =CH ₂) DFT	(Diso) ₂ Ru (EtC≡CEt) X-ray ^b	(ap) ₂ Ru (HC≡CH) DFT
Ru–O1	2.0399(13)	2.027(2)	2.035	2.042(4)	2.048
Ru–N1	1.9427(16)	1.943(3)	2.008	1.930(4)	1.963
Ru–C1	2.134(13)	2.130(24)	2.133	2.030(5)	2.044
Ru–C2	2.174(12)	2.151(19)			
C1–C2	1.410(6)	1.393(9)	1.419	1.265(3)	1.275
O1–C11	1.317(2)	1.316(4)	1.310	1.327(2)	1.319
N1–C12	1.385(2)	1.382(4)	1.373	1.398(3)	1.391
C11–C12	1.419(3)	1.419(4)	1.434	1.411(4)	1.424
C12–C13	1.405(3)	1.407(4)	1.418	1.403(4)	1.411
C13–C14	1.378(3)	1.372(4)	1.382	1.382(6)	1.387
C14–C15	1.417(3)	1.417(5)	1.415	1.409(6)	1.409
C15–C16	1.386(3)	1.381(5)	1.383	1.391(3)	1.387
C16–C11	1.431(3)	1.426(4)	1.413	1.419(3)	1.409
O1–Ru–C1–C2	−19.4	−15.5	−27.6	−5.5	−15.1
MOS	−1.36(9)	−1.33(8)	−1.26(7)	−1.56(10)	−1.46(9)
τ	0.13	0.10	0.19	0.20	0.09

^aCrystallographically determined values for (Diso)₂Ru(L) are given in roman type, while those calculated by DFT on (ap)₂Ru(L) are given in italic type. ^bValues are averaged among chemically equivalent instances in the two crystallographically inequivalent molecules in the unit cell. Esd's reflect both the statistically estimated uncertainties and the variance in the measured values.

with O–Ru–C1–C2 dihedral angles of roughly 15° (Table 2). This is doubtless an electronic effect, as it is also observed computationally with unhindered *N*-phenyl groups and ethene or ethyne ligands. It is consistent with an orientation that maximizes backbonding, lining up the ligand π^* orbital with position of the high-energy $d\pi$ orbital in, for example, (Diso)₂Ru(PPh₃).¹⁹

Structurally, signatures for backbonding to alkenes include the carbon–carbon distance (elongated with greater backbonding) and the metal–carbon distances (shortened with greater backbonding). Structural data on neutral ruthenium complexes of unchelated monosubstituted alkenes that do not have strongly electron-withdrawing substituents (Table S2) are very similar to those shown by (Diso)₂Ru(1-alkene) complexes, suggesting that the (Diso)₂Ru fragment is similar in its backbonding abilities to other neutral low-valent Ru fragments such as Cp*Ru(η^3 -allyl).³¹

In alkyne complexes, both backbonding to the alkyne π^* and π donation from the alkyne $\pi_{\perp}$ orbital have distinctive structural and spectroscopic indicia. Backbonding elongates the C≡C bond and decreases the alkyne stretching frequency; these metrics do not appear to be sensitive to the extent of π donation of the alkyne.^{32,33} In (Diso)₂Ru(HC≡CBu), the C≡C stretch could not be located in the IR, but the C≡C distance of 1.265(3) Å is typical of ruthenium alkyne complexes (Table S3), such as for example Cp*Ru(η^3 -C₃H₅)(PhC≡CPh), $d(\text{C}\equiv\text{C}) = 1.261(3)$ Å.³⁴

Alkyne π donation to the metal is marked by shortened metal–carbon distances and by downfield shifts in the ¹³C NMR resonances of the alkyne carbons.² Both of these metrics appear to scale with the degree of π donation. For example, in complexes of Mo and W, two-electron donor alkynes resonate at $\sim\delta$ 120 ppm³⁵ and have metal–carbon distances of ~ 2.14 Å, while four-electron donor alkynes resonate at $\sim\delta$ 200 ppm and have metal–carbon distances of ~ 2.03 Å. When one π bond is shared between two alkynes donating to a single metal d orbital (a so-called 3-electron donor alkyne), the metrics are almost exactly halfway in between, with $\delta \sim 160$ ppm and

$d(\text{M}–\text{C}) \approx 2.09$ Å. This scaling also appears to apply in cases where competition is not required by symmetry to be equal. For example, in W(IV) oxo-alkyne complexes, the alkyne invariably lies perpendicular to the M=O vector, so the alkyne $\pi_{\perp}$ orbital competes with one of the oxygen p_{π} orbitals to donate to an empty metal $d\pi$ orbital. In such complexes, $\delta(^{13}\text{C}) = 159(8)$ ppm and $d(\text{W}–\text{C}) = 2.094(15)$ Å (Table S4). These are indistinguishable from the values seen in bis(alkyne) complexes, so the alkyne competes on an equal footing with the oxo for π donation to the metal, leading to the characterization of these alkynes as three-electron donors.^{36,37}

For reported two-electron donor alkyne complexes of ruthenium, $\delta(^{13}\text{C}) = 82(12)$ ppm and $d(\text{Ru}–\text{C}) = 2.18(5)$ Å, while four-electron alkyne complexes have $\delta(^{13}\text{C}) = 140(10)$ ppm and $d(\text{Ru}–\text{C}) = 2.06(4)$ Å (Table S3). The one structurally characterized ruthenium alkyne that could be considered to have a three-electron interaction has an intermediate Ru–C distance of 2.11 Å.³⁸ According to these metrics, (Diso)₂Ru(EtC≡CEt) appears very similar to literature examples of four-electron donor alkynes, with $\delta(^{13}\text{C}) = 139.7$ ppm and $d(\text{Ru}–\text{C}) = 2.030(5)$ Å. However, the fact that the ¹³C chemical shifts of the ruthenium alkyne complexes are so far upfield of those shown by four-electron donor alkynes in molybdenum and tungsten complexes, and to a lesser extent the longer ruthenium–carbon distances, suggests that π donation in the ruthenium alkynes is not as strong as it is in the group 6 complexes. In fact, all but one of the structurally characterized “four-electron donor” Ru alkyne complexes are of the form CpRuCl(RC≡CR').^{39,40} In contrast to the octahedral Mo(II) or W(II) complexes, where the d orbital into which the alkyne donates is strictly π in character, the d orbital in the two-legged piano stool complex has a σ^* interaction with the cyclopentadienyl group (see Figure S26 for the relevant molecular orbitals calculated for CpRuCl[HCCH]). This reduces the π bond order to the alkyne to the point where it looks spectroscopically and structurally similar to a three-electron donor alkyne on a group 6 metal. (The one nonpiano-stool “four-electron donor”

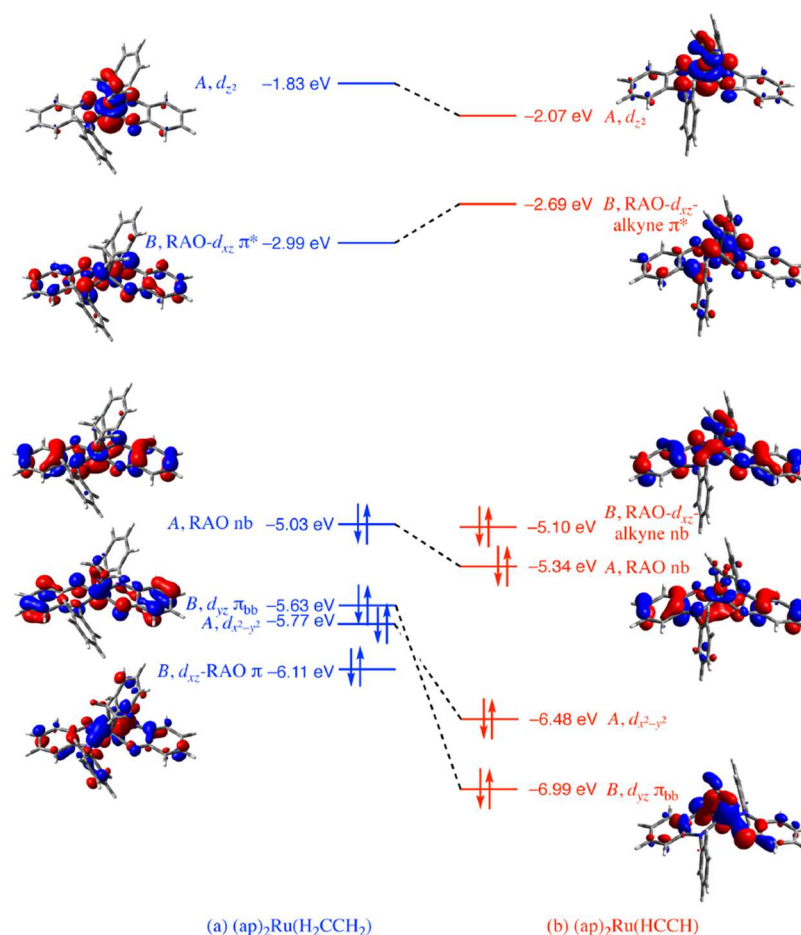


Figure 6. Molecular orbital diagrams for (a) $(\text{ap})_2\text{Ru}(\text{H}_2\text{C}=\text{CH}_2)$ and (b) $(\text{ap})_2\text{Ru}(\text{HC}\equiv\text{CH})$. Only orbitals with significant metal $d\pi$ or iminoxolene RAO character are listed. The A-symmetry $d_{x^2-y^2}$ orbitals are not pictured.

ruthenium complex, $(\text{MesPDI})\text{Ru}(\text{HC}\equiv\text{CH})$,⁴¹ has an analogous issue with poor π bonding to the alkyne, as a square planar complex would not have an empty π orbital suitable for interacting with the alkyne.⁴² The structural and spectroscopic characterization of $(\text{Diso})_2\text{Ru}(\text{EtC}\equiv\text{CEt})$ thus suggests not that the alkyne donates fully to the ruthenium, but rather that it competes about as effectively with the π donation from the iminoxolenes as it does with the σ bonding from the cyclopentadienyl ligand in $\text{CpRuCl}(\text{RC}\equiv\text{CR}')$.

This analysis agrees with the structural characteristics of the iminoxolene ligands. The alkene complexes have MOS values of $-1.36(9)$ (hexene) and $-1.33(8)$ (allylbenzene), close to the MOS value of -1.34 expected for a complex having an overall metal–iminoxolene π bond order of 1.0. In contrast, the MOS of the alkyne complex $(\text{Diso})_2\text{Ru}(\text{EtC}\equiv\text{CEt})$ is significantly more negative, at $-1.56(10)$. This indicates that the metal–iminoxolene bonding orbital has shifted its electron density to be more on the ligand, consistent with donation from the alkyne $\pi_\perp$ into this orbital. A similar effect is seen in a series of bis(iminoxolene)osmium compounds, where increasing the π donor ability of the ancillary ligands from dichloride to ethylene glycolate to oxo produces a change in MOS from -0.94 to -1.47 to -1.98 .¹⁶ Quantitatively, one can use the correlation between π bond order and MOS in Ru iminoxolenes¹³ to estimate that the overall Ru–iminoxolene π bond order in $(\text{Diso})_2\text{Ru}(\text{EtC}\equiv\text{CEt})$ is 0.67. This suggests that π donation from the alkyne competes with that from the iminoxolene, but not quite on an equal footing. This is

consistent with the spectroscopic data, particularly the ^{13}C chemical shift, which is noticeably upfield of the ^{13}C shifts in three-electron donor alkynes.

Density functional theory calculations paint a picture of the bonding in the alkene and alkyne complexes that is in good agreement with this analysis (Figure 6). The B symmetry RAO combination is strongly engaged in π bonding with the Ru d_{xz} orbital (the antibonding combination is the LUMO in both complexes), but in the acetylene complex this π interaction also involves the alkyne $\pi_\perp$ orbital. This converts the interaction into a three-orbital, four-electron system, which has the result of raising the energy of the π^* orbital noticeably (relative to its position in the ethylene complex) and introducing a π_{nb} orbital as the HOMO of $(\text{ap})_2\text{Ru}(\text{HC}\equiv\text{CH})$, with the significant participation of both the alkyne and iminoxolene π orbitals in this latter MO attesting to the competition of both ligands for π bonding as discussed above. In both complexes, the A-symmetry RAO combination is largely nonbonding, but shows some amount of π donation to the d_{z^2} orbital, which is relatively low in energy in these square pyramidal complexes (LUMO+1 in both compounds). As is typical of *trans*-bis-iminoxolene complexes,⁴³ the optical spectra show very intense absorptions in the red (Figure 7), which are assigned as A (RAO) $\rightarrow$ B (RAO- d_{xz} π^*) transitions. The absorption maxima predicted by TDDFT calculations (661 and 517 nm for the alkene and alkyne complexes, respectively) are in reasonable agreement with those observed experimentally (700 and 593 nm, respectively).

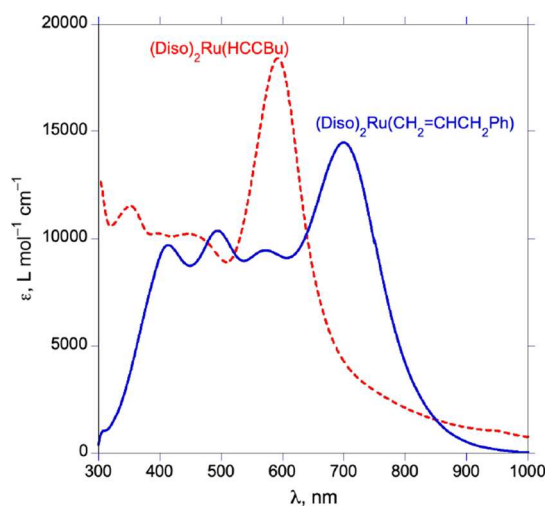


Figure 7. Optical spectra in toluene of $(\text{Diso})_2\text{Ru}(\text{CH}_2=\text{CHCH}_2\text{Ph})$ (blue solid line) and $(\text{Diso})_2\text{Ru}(\text{HC}\equiv\text{CBu})$ (red dashed line).

It is worth contrasting the bonding of the alkyne in $(\text{Diso})_2\text{Ru}(\text{RC}\equiv\text{CR})$ with that of the intramolecularly coordinated alkyne in $(\kappa^2, \eta^2\text{-Tiksi})(3,5\text{-}t\text{Bu}_2\text{Cat})\text{IrCl}$ (Tiksi = *N*-(2,6-bis(triisopropylsilyl)ethynyl)phenyl)-4,6-di-*tert*-butyl-2-imino-*o*-benzoquinone). Despite the fact that IrCl is nominally isoelectronic with Ru, the alkyne bonding in the two compounds is strikingly different. While the Ru compound shows both significant π backbonding to, and appreciable π donation from, the alkyne, the coordinated alkyne in the Ir compound is neither a significant donor nor acceptor of π electrons (a Polonius-type alkyne).⁴⁴ Two factors probably contribute to this stark difference in bonding. The first is that the *mer* geometry of the intramolecularly coordinated iminoxolene-alkyne ligand constrains the orientation of the alkyne so that its alignment with the relevant metal $d\pi$ orbitals is suboptimal.

The second factor is that the iridium compound is notably more electron-poor than the ruthenium compound. This is due to the presence of one dioxolene ligand on the iridium compound, to the intrinsically higher electronegativity of the element farther to the right in the periodic table, and to the higher oxidation state of iridium compared to ruthenium required if the two elements are to have the same electron count.⁴⁵ Clearly, the more electron-poor iridium center will be a poorer backboner than ruthenium. It is less clear why alkyne-to-metal π donation should be diminished at an electron-poor center. Indeed, the limited data available suggest that π donation is not much affected intrinsically by moving to the right in the periodic table. For example, the octahedral tungsten(II) complex $\text{Tp}^*\text{W}(\text{CO})\text{I}(\text{MeC}\equiv\text{CMe})$ ($\delta_{13\text{C}}$ avg. = 207.6)⁴⁶ appears to have very similar π donation compared to

the rhenium(III) complex $\text{TpReCl}_2(\text{EtC}\equiv\text{CEt})$ ($\delta_{13\text{C}}$ = 212.9),⁴⁷ and the pseudotetrahedral tris(alkyne)tungsten(0) complex $(\text{EtC}\equiv\text{CEt})_3\text{W}(\text{CO})$ ($\delta_{13\text{C}}$ avg. = 181.0)³⁶ is very similar to the rhenium(I) complex $[(\text{EtC}\equiv\text{CEt})_3\text{Re}(\text{PMe}_3)]\text{OTf}$ ($\delta_{13\text{C}}$ avg. = 173.6).⁴⁸ But the ability of an alkyne to compete with an oxo group does appear to diminish on moving to the right in the periodic table. Thus, the butyne ligand in the tungsten(IV) oxo-alkyne complex $\text{Tp}^*\text{W}(\text{O})\text{I}(\text{MeC}\equiv\text{CMe})$ ($\delta_{13\text{C}}$ avg. = 162.4)³⁷ appears to donate significantly more strongly than the butyne in the rhenium(V) oxo-alkyne complex $\text{Re}(\text{O})\text{Me}_3(\text{MeC}\equiv\text{CMe})$ ($\delta_{13\text{C}}$ = 143.5).⁴⁹ Possibly the poorer backbonding from the higher-valent later metal (see, e.g., $\nu_{\text{C}\equiv\text{C}}$ = 1741 cm^{-1} in $[(\text{EtC}\equiv\text{CEt})_3\text{Re}(\text{PMe}_3)]\text{OTf}$ ⁴⁹ vs 1702 cm^{-1} in $(\text{EtC}\equiv\text{CEt})_3\text{W}(\text{CO})$ ⁵⁰) contracts the $\text{C}\equiv\text{C}$ bond, lowering the energy of the π orbital and making it a poorer donor. In contrast, the π bonding to the oxo or iminoxolene ligand is strengthened as the d orbital energies of the metal fall, becoming closer to the energies of the oxygen- or nitrogen-containing orbitals.

Energetics of Alkene and Alkyne Rotation. The alkene or alkyne ligands bonded to Ru are aligned to maximize π backbonding, so rotation of the unsaturated ligand is expected to incur a significant energetic penalty. This is observed computationally in $(\text{ap})_2\text{Ru}(\text{H}_2\text{C}=\text{CH}_2)$, which has a calculated $\Delta G^\ddagger$ = 12.4 kcal mol^{-1} for rotation of ethylene about the metal-centroid axis. In the transition state for bond rotation, the alkene is aligned so that it cannot backbond with the high-lying Ru $d\pi$ orbital (Figure 8a), and structural data are consistent with an appreciable decrease in the degree of backbonding to the alkene (Table 3). In contrast to the calculated C_2 -symmetric equilibrium geometry, the transition state shows a slight distortion in the ruthenium-iminoxolene bonds, with Ru–O1 and –N2 bond lengths about 0.01 Å shorter than the Ru–O2 and –N1 bonds, consistent with the alkene becoming essentially a pure σ donor in the transition state and fostering a distortion like that observed in the phosphine complex $(\text{Diso})_2\text{Ru}(\text{PPh}_3)$.¹⁹

The orbital mismatch in the transition state is even more evident in the alkyne complex $(\text{ap})_2\text{Ru}(\text{HC}\equiv\text{CH})$. The HOMO is not backbonding but rather has an unfavorable filled–filled interaction with the alkyne π_1 orbital (Figure 8b). Instead, it is the empty Ru–RAO π^* LUMO that can interact with the empty alkyne π^* (Figure 8c). The loss of backbonding in the transition state is marked by the contraction of the $\text{C}\equiv\text{C}$ bond (by 0.034 Å) and increase in the calculated $\text{C}\equiv\text{C}$ stretching frequency (from 1669 to 1811 cm^{-1}). The loss of π donation in the transition state is marked by the elongation of the Ru–C distances by 0.16 Å. The MOS values of the iminoxolenes also become significantly more positive, with the value of –1.15(9) consistent with a σ -only ligand lacking the π bonding that competes with the iminoxolene–metal π

Table 3. Selected Parameters of the Calculated Transition States for Rotation of the Hydrocarbon Ligand in $(\text{ap})_2\text{Ru}(\text{H}_n\text{CCH}_n)$ ($n = 1, 2$)

parameter	$[(\text{ap})_2\text{Ru}(\text{H}_2\text{C}=\text{CH}_2)]^\ddagger$	change from equilibrium geometry	$[(\text{ap})_2\text{Ru}(\text{HC}\equiv\text{CH})]^\ddagger$	change from equilibrium geometry
$d(\text{CC})$	1.393 Å	–0.026 Å	1.241 Å	–0.034 Å
$d(\text{RuC})$	2.218 Å	+0.085 Å	2.204 Å	+0.160 Å
$\phi(\text{O1–Ru–C1–C2})$	48.9°	+76.5°	53.2°	+68.3°
MOS	–1.18(8)	+0.08	–1.15(9)	+0.41
τ	0.16	–0.03	0.25	+0.16
$\Delta G^\ddagger$	12.4 kcal mol^{-1}		18.7 kcal mol^{-1}	

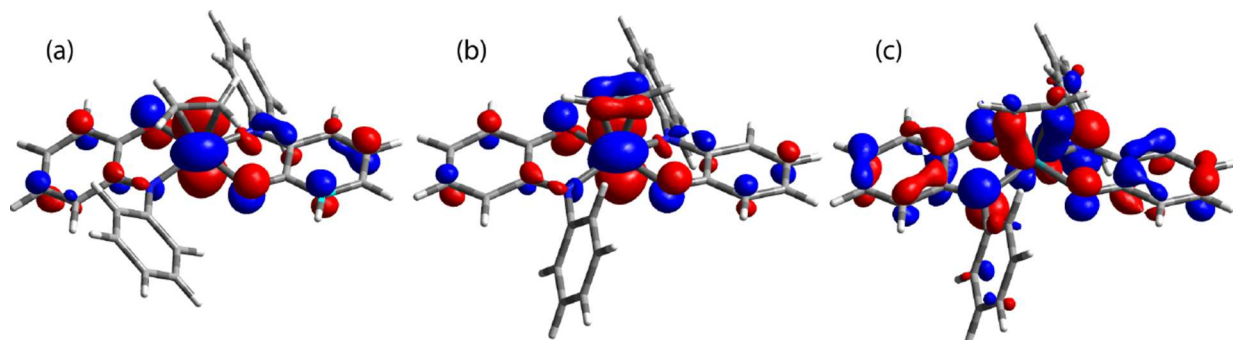


Figure 8. Selected Kohn–Sham orbitals calculated for the transition states for ligand rotations. (a) HOMO–1 of $[(ap)_2Ru(H_2C=CH_2)]^\ddagger$. (b) HOMO of $[(ap)_2Ru(HC\equiv CH)]^\ddagger$. (c) LUMO of $[(ap)_2Ru(HC\equiv CH)]^\ddagger$.

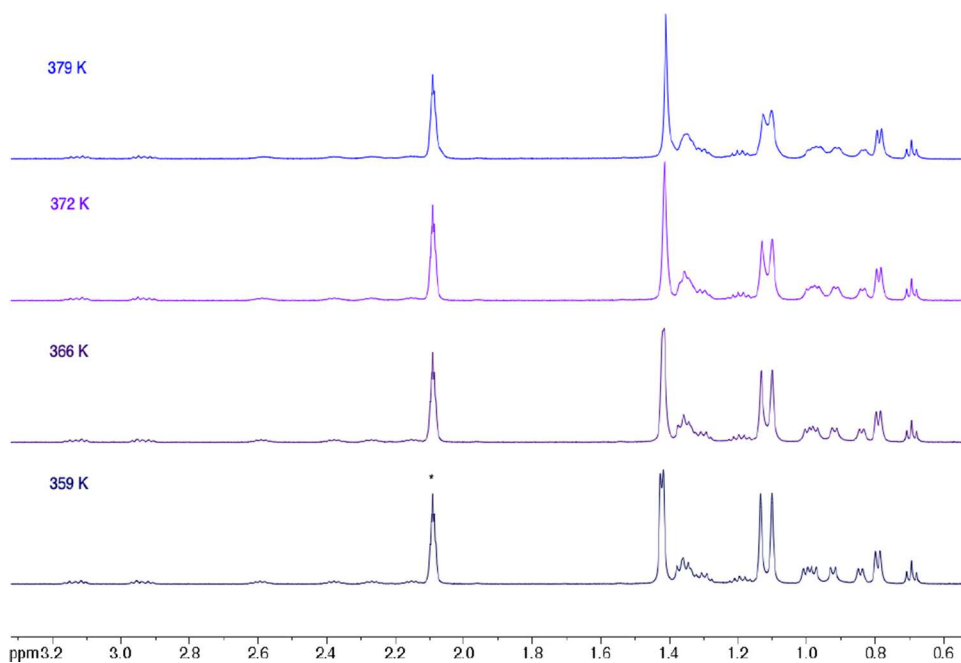


Figure 9. 1H NMR spectra of $(Diso)_2Ru(HC\equiv CBu)$ (toluene- d_8 , 500 MHz). The toluene residual peak at δ 2.09 ppm is marked with *.

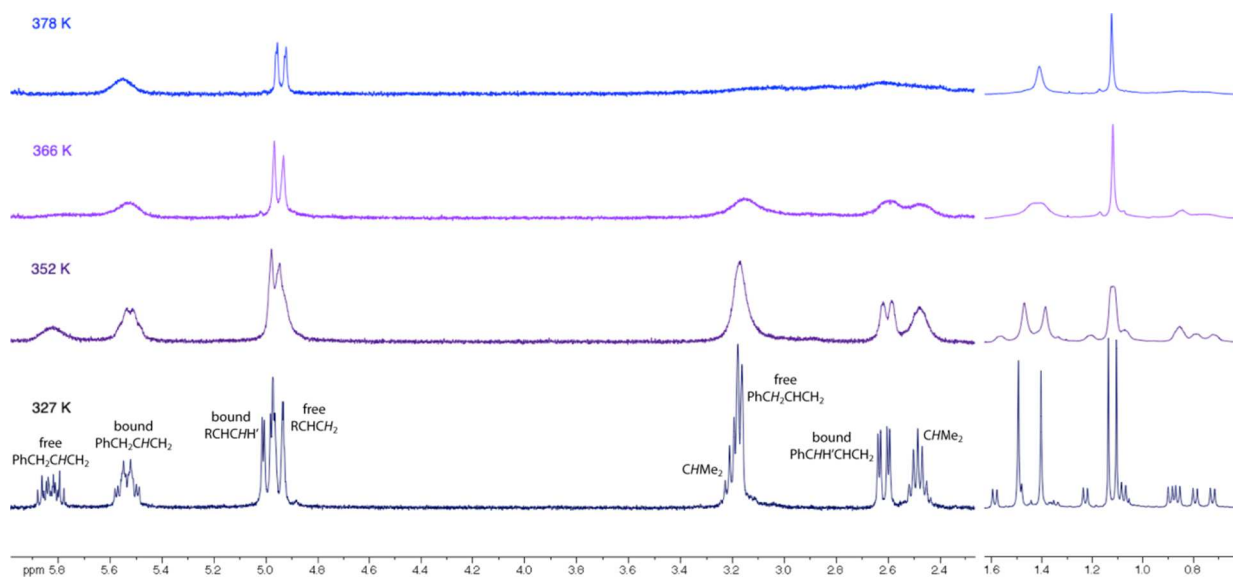


Figure 10. 1H NMR spectra of $(Diso)_2Ru(CH_2=CHCH_2Ph)$ in the presence of 0.4 equiv free $CH_2=CHCH_2Ph$ (toluene- d_8 , 500 MHz). The vertical scale for the upfield region is reduced by a factor of 12 compared to the downfield region.

Table 4. Barriers to Rotation of Alkenes and Alkynes in Selected Complexes

compound	co-ligand or other factor governing alignment of alkene/alkyne	$\Delta G^\ddagger$ (kcal mol ⁻¹) [T, K]	ref
alkene complexes			
TpRe(CO)(PMe ₃)(CH ₂ =CH ₂)	CO	10.0 [188]	6
<i>trans</i> -W(CO) ₄ (CH ₂ =CHBu) ₂	CH ₂ =CHBu	11.3 [237]	52
CpFe(CO)(SnMe ₃)(CH ₂ =CH ₂)	CO	12.8 [223]	53
(Me ₃ P)Pt(CH ₂ =CH ₂) ₂	trigonal geometry	13.0 [269]	54
[CpRe(NO)(PPh ₃)(CH ₂ =CH ₂)]BF ₄	NO	16.4 [369]	5
(Diso) ₂ Ru(CH ₂ =CHCH ₂ Ph)	iminoxolene π bonding anisotropy	>17.3 [379]	this work
(Me ₂ phen)PtI ₂ (CH ₂ =CHMe)	tbp geometry (equatorial alkene)	20.5 [383]	55
W(O)Cl ₂ (CH ₂ =CH ₂)(PMePh ₂) ₂	O	>20 [353]	7
[Cp ₂ W(H)(CH ₂ =CHCH ₃)]PF ₆	Cp ₂ wedge	23.6 [298]	56
alkyne complexes			
(Me ₃ NCS ₂) ₂ W(CO)(HC≡CH)	CO	11.9 [246]	57
(Me ₃ nacnac)Cu(PhC≡CH)	trigonal geometry	13.4 [263]	58
(Me ₂ NCS ₂) ₂ Mo(EtC≡CEt) ₂	EtC≡CEt	15.4 [373]	59
(Me ₂ Phen)PtI ₂ (MeC≡CH)	tbp geometry, equatorial alkyne	17.1 [333]	60
CpW(CH ₃)(CO)(HC≡CH)	CO	18.2 [364]	61
Tp*W(I)(CO)(HC≡CH)	CO	18.6 [343]	62
(Diso) ₂ Ru(HC≡CBu)	iminoxolene π bonding anisotropy	19.0 [379]	this work
[CpRe(NO)(PPh ₃)(EtC≡CEt)]BF ₄	NO	>22.6 [453]	63
Tp*W(O)(I)(HC≡CH)	O	>25 [433]	37

bonding. Consistent with weakening of both backbonding and π donation in the ethyne complex, the calculated rotation barrier of 18.7 kcal mol⁻¹ is greater than that in the ethene complex.

Experimentally, the barriers to rotation can be measured by dynamic NMR spectroscopy. The terminal alkyne complex (Diso)₂Ru(HC≡CBu) shows inequivalent iminoxolene ligands at room temperature, but the iminoxolene resonances broaden and coalesce at higher temperatures (Figure 9). The peaks due to the bound alkyne, such as the diastereotopic propargylic hydrogens at δ 2.9 and 3.1 ppm, are not affected by changing the temperature, nor does the presence of free alkyne affect the spectrum. These observations indicate that the dynamic process involves neither association nor dissociation of alkyne, consistent with its being a rotation of the alkyne ligand. The rate constant of 20 s⁻¹ at 379 K corresponds to $\Delta G^\ddagger = 19.0$ kcal mol⁻¹, in close agreement with the value calculated for (ap)₂Ru(HC≡CH).

The alkene complex (Diso)₂Ru(CH₂=CHCH₂Ph) also shows exchange above 340 K between the two iminoxolene environments, which are inequivalent at room temperature (Figure 10). In contrast to the alkyne complex, iminoxolene exchange in the allylbenzene complex is concurrent with exchange between free and bound alkene. Quantitatively, the rate constant obtained from line shape analysis of the *tert*-butyl hydrogens (k_{exch}) is consistently one-half the value of the dissociative rate constant obtained from analysis of the exchange of bound and free allylbenzene (k_{diss}). This is most consistent with a mechanism where alkene dissociates to give a four-coordinate (Diso)₂Ru intermediate. Rebinding of alkene would take place with an equal probability of the alkene C1 overlying either of the two iminoxolene ligands. This means that every dissociation event would always lead to exchange between bound and free alkene, but would only result in exchange between *tert*-butyl hydrogens half the time, accounting for the quantitative relationship between the two rate constants. Alkene rotation must take place much more slowly than alkene dissociation. Because alkene rotation would lead to *tert*-butyl group exchange but not exchange between

bound and free alkene, if alkene rotation took place at a significant rate, the rate constant for *tert*-butyl group exchange would be greater than half that of alkene dissociation.

The putative four-coordinate intermediate is calculated by DFT to have a square planar geometry. This suggests that alkene rebinding could take place not just with either possible orientation of the alkene, but also with either possible face of the intermediate. It was not possible to confirm this by dynamic NMR, but EXSY spectroscopy at 328 K clearly indicates that exchange proceeds through an intermediate with effective C_{2h} symmetry, with all four isopropyl methine hydrogens exchanging with each other and the isopropyl methyl doublets exchanging in two sets of four peaks (Figure S15). The exchange is dissociative rather than associative, as indicated by the fact that the line widths of (Diso)₂Ru(allylbenzene) are independent of the concentration of the free alkene in the slow exchange regime, as well as by the activation parameters determined from an Eyring plot ($\Delta H^\ddagger = 27.3(14)$ kcal mol⁻¹, $\Delta S^\ddagger = 26(4)$ cal mol⁻¹ K⁻¹, Figure S25).

Because rotation is slower than alkene dissociation, the barrier to alkene rotation must be greater than the $\Delta G^\ddagger$ (379 K) = 17.3 kcal mol⁻¹. This is substantially greater than the calculated barrier to ethylene rotation in (ap)₂Ru(CH₂=CH₂) ($\Delta G^\ddagger = 12.4$ kcal mol⁻¹), probably because steric interactions between the alkene substituent and the ligand isopropyl groups in the transition state significantly slow rotation compared to the unhindered computational model. The fact that $\Delta G^\ddagger_{\text{diss}}$ of the allylbenzene complex is lower than that of the 1-hexyne complex, whose $\Delta G^\ddagger_{\text{rotn}}$ of 19.0 kcal mol⁻¹ at 379 K must be less than its $\Delta G^\ddagger_{\text{diss}}$, is consistent with the experimental observation that alkynes bind more strongly to (Diso)₂Ru than alkenes. The calculated ΔG° for dissociation of ethylene from (ap)₂Ru(CH₂=CH₂), 19.9 kcal mol⁻¹, is in good agreement with the observed $\Delta G^\ddagger$ for dissociation of alkene from (Diso)₂Ru(CH₂=CHCH₂Ph) extrapolated to 298 K of 19.5 kcal mol⁻¹.

Barriers to rotation in alkene and alkyne complexes arise from differences in energy of the two $d\pi$ orbitals that can potentially interact with the unsaturated ligand. In some cases,

this is due to the geometry of the complex. Examples of this include d^{10} trigonal planar complexes and d^8 trigonal bipyramidal species (with the alkene equatorial), where σ^* interactions raise the energy of the filled in-plane $d\pi$ orbital, optimizing backbonding when the alkene (or alkyne) lies in the trigonal plane.⁵¹ In more symmetrical geometries, the barriers to rotation generally reflect the asymmetry in the bonding, for example with the need to compete with nitrosyl showing larger barriers than when the competition is with carbonyl (Table 4).

The geometry of the $(\text{Diso})_2\text{Ru}$ fragment (square pyramidal with apical unsaturated ligand) does not intrinsically foster any differentiation between the relevant $d\pi$ orbitals, which transform as an E set in C_{4v} symmetry, nor does it have a strong π acceptor ligand to desymmetrize the $d\pi$ orbitals as is typical in octahedral complexes with large barriers to alkene or alkyne rotation. Instead, the $d\pi$ orbitals are distinguished by the π bonding anisotropy of the bis(iminoxolene) fragment,¹⁸ which means that only one $d\pi$ orbital is strongly engaged in π bonding and so is much lower in energy than the second one. This novel mechanism appears to differentiate the $d\pi$ orbitals more strongly than a *cis* carbonyl and is energetically comparable to a *cis* nitrosyl or to the effect of a trigonal bipyramidal ligand geometry. It is, unsurprisingly, less effective than in d^2 complexes with *cis* oxo groups^{7,37} or bent metallocene geometries,⁵⁷ where there is only one filled $d\pi$ orbital.

Stereoselective Alkene Binding by Bis(iminoxolene)-ruthenium. Because both the $(\text{Diso})_2\text{Ru}$ fragment and the 1-alkene are prochiral, there are two possible diastereomers of $(\text{Diso})_2\text{Ru}(\text{CH}_2=\text{CHR})$. For both the allylbenzene and the 1-hexene complex, only one diastereomer can be observed by ^1H NMR spectroscopy ($dr > 30:1$). The observed species is assigned on the basis of the solid-state structures as the (A,S) diastereomer.⁶⁴ Since alkene dissociation is fast enough to be observable on the NMR time scale at only moderately elevated temperatures, this selectivity must represent a thermodynamic preference.

Although the minor diastereomer cannot be observed experimentally, its properties can be assessed by calculations on the diastereomers of the propene complexes $(\text{C}_6\text{H}_4[\text{NR}]\text{O})_2\text{Ru}(\text{CH}_2=\text{CHMe})$. Calculated structures of $(\text{diso})_2\text{Ru}(\text{CH}_2=\text{CHMe})$, with the sterically realistic $\text{R} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$ (Figure 11), clearly show the steric clash between the *N*-aryl substituent and the alkene substituent in the (A,R)

diastereomer that is avoided in the (A,S) isomer. This is consistent with the experimental observation that only the latter isomer is observed; computationally the difference in free energy for the two diastereomers of $(\text{diso})_2\text{Ru}(\text{CH}_2=\text{CHMe})$ is $4.6 \text{ kcal mol}^{-1}$. The size of the nitrogen substituent is important energetically, as the compound with $\text{R} = \text{Ph}$, $(\text{ap})_2\text{Ru}(\text{CH}_2=\text{CHMe})$, is calculated to have the (A,S) isomer only $1.6 \text{ kcal mol}^{-1}$ more stable than the (A,R) isomer. In the case of the sterically negligible $\text{R} = \text{H}$, the diastereomers of $(\text{hap})_2\text{Ru}(\text{CH}_2=\text{CHMe})$ are essentially isoenergetic, with the (A,R) isomer lower in free energy by $0.1 \text{ kcal mol}^{-1}$.

In all of the calculated propene isomers the electronically preferred orientation of the alkene is adopted. There is some variation, with increasing steric strain pushing the alkene toward more positive dihedral angles (e.g., $\phi[\text{O1-Ru-C1-C2}] = -18.8^\circ$ vs -1.8° in (A,S) - and (A,R) - $(\text{diso})_2\text{Ru}(\text{CH}_2=\text{CHMe})$, respectively), but in all cases the alkene is aligned in the cleft between the iminoxolene ligands, and inclined more toward the O-Ru-O axis. This electronic constraint is key to the high facial selectivity, for without it, both isomers would presumably rotate the alkene to a position with minimal, and similar, steric interactions.

Stereoselective alkene binding to C_2 -symmetric metal centers is uncommon. The closest analogies to the present work are chiral diamine-ligated trigonal planar copper(I)^{65,66} or trigonal bipyramidal platinum(II) complexes.⁶⁷ In these systems, the coordination geometry imposes an electronic preference for the alkenes to lie in the trigonal plane, and the substituents on the alkene can then experience the dissymmetric environment of the diamine ligands. It is worth noting that these diamine-ligated metal centers do not give high stereoselectivities in binding simple α -olefins. High ($>10:1$) stereoselectivity requires additional interactions such as arene–arene contacts from styrenes⁶⁵ or metal–oxygen binding from allyl alcohols.⁶⁶ The $(\text{Diso})_2\text{Ru}$ fragment has an intrinsically closer approach of the ancillary ligands (90° in the square pyramid vs 120° in the trigonal geometries), and the *ortho* substituents on the *N*-aryl groups are directed toward the alkene. The combination of the significant steric profile of the iminoxolene ligands, coupled with the electronic anisotropy of the bis(iminoxolene) fragment to fix the orientation of the $\text{C}=\text{C}$ bond, allows C_2 -symmetric $(\text{Diso})_2\text{Ru}$ to have a stereoselectivity in binding α -olefins that is comparable to C_1 -symmetric octahedral complexes.⁶⁸

CONCLUSIONS

The low-valent iminoxolene complex $(\text{Diso})_2\text{Ru}(\text{NCCH}_3)_2$ has labile acetonitrile ligands that can be displaced by monosubstituted alkenes or by alkynes to give square pyramidal complexes $(\text{Diso})_2\text{Ru}(\text{L})$. The ruthenium center engages in significant π backbonding to both alkenes and alkynes. The alkyne complexes also show significant donation from the alkyne π_1 orbital to ruthenium, although spectroscopic and structural data indicate that alkyne π donation is slightly outcompeted by iminoxolene–ruthenium π bonding. The nature of the π interactions with the two iminoxolenes is such that one d orbital that is π with respect to the apical position in the square pyramid is strongly engaged with the iminoxolene π orbitals and hence is relatively unavailable for backbonding with the alkene or alkyne. This results in alignment of the C-C multiple bond close to the O-Ru-O axis, but canted toward the cleft between the iminoxolene ligands, in order to maximize backbonding from the other $d\pi$

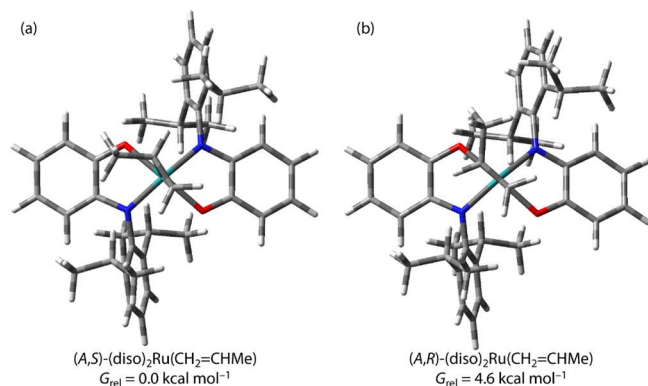


Figure 11. Calculated minimum-energy structures of $(\text{diso})_2\text{Ru}(\text{CH}_2=\text{CHMe})$. (a) (A,S) diastereomer ($G_{\text{rel}} = 0$). (b) (A,R) diastereomer ($G_{\text{rel}} = 4.6 \text{ kcal mol}^{-1}$).

orbital. In this geometry, the alkyne π_1 orbital mixes with the iminoxolene- $d\pi$ orbitals and gives rise to a favorable four-electron, three-orbital interaction. The alignment is strongly energetically favored, as witnessed by large barriers to rotation of the alkene ($\Delta G^\ddagger > 17.3$ kcal mol $^{-1}$ at 379 K for allylbenzene) or alkyne ($\Delta G^\ddagger = 19.0$ kcal mol $^{-1}$ at 379 K for 1-hexyne). For alkenes, the electronic anisotropy of the bis(iminoxolene) group that constrains the C=C orientation combines with the positioning of the diisopropylphenyl groups relative to the alkene substituent to give high diastereoselectivity in binding of 1-alkenes, with only one diastereomer observed by ^1H NMR (selectivity of greater than 30:1).

EXPERIMENTAL SECTION

General Procedures. Unless otherwise noted, all procedures were carried out in a drybox under a nitrogen atmosphere. Dried solvents were purchased from Acros Organics and were stored in a nitrogen-filled drybox until use. Deuterated solvents were obtained from Cambridge Isotope Laboratories. When dry C_6D_6 was needed, it was dried over sodium and vacuum transferred away from the drying agents and stored in the drybox prior to use. NMR spectra were measured on a Bruker Avance DPX 400 or 500 MHz spectrometer. Chemical shifts for ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra are reported in ppm downfield of TMS, with spectra referenced using the known chemical shifts of the solvent residuals. Infrared spectra were recorded by ATR on a Jasco 6300 FT-IR spectrometer and are reported in wavenumbers. UV–visible–NIR spectra were recorded in 1 cm quartz cells on an Agilent 8453 diode array spectrophotometer or a Jasco V-670 spectrophotometer. Elemental analyses were performed by Robertson Microлит Laboratories (Ledge wood, NJ) or Midwest Microлит (Indianapolis, IN).

***cis*-(Diso) $_2$ Ru(NCMe) $_2$.** In a scintillation vial, 175.5 mg of *cis*-(Diso) $_2$ RuCl $_2$ 19 (0.1885 mmol) and 80.1 mg of Cp $_2$ Co (0.424 mmol, 2.25 equiv) are dissolved in 5 mL CH $_2$ Cl $_2$. The vial is capped and shaken. The solution immediately turns purple, whereupon 10 mL CH $_3$ CN is added. The vial is capped and shaken, and allowed to stand at room temperature overnight. The solution is transferred into a round-bottom flask attached to a needle valve, and the solvent is evaporated on the vacuum line. The purple residue is slurried in 4 mL CH $_3$ CN and filtered on a glass frit. After washing with 3 $\times$ 2 mL CH $_3$ CN, the solid is air-dried for 30 min, and 141.3 mg of *cis*-(Diso) $_2$ Ru(NCMe) $_2$ (78%) is isolated. ^1H NMR (C_6D_6): δ 0.94 (d, 6.7 Hz, 6H, CH(CH $_3$)Me), 1.03 (d, 6.9 Hz, 6H, CH(CH $_3$)Me), 1.05 (s, 6H, CH $_3$ CN), 1.23 (d, 6.8 Hz, 6H, CH(CH $_3$)Me), 1.37 (s, 18H, 'Bu), 1.40 (s, 18H, 'Bu), 1.57 (d, 6.8 Hz, 6H, CH(CH $_3$)Me), 3.11 (sept, 6.8 Hz, 2H, CHMe $_2$), 4.22 (sept, 6.5 Hz, 2H, CHMe $_2$), 6.97 (s, 2H, iminoxolene 3- or 5-H), 7.33 (m, 6H, aromatic H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 2.77 (CH $_3$ CN), 23.82, 24.31, 25.61, 26.47, 26.51, 27.60, 29.05 (C(CH $_3$) $_3$), 31.38 (C(CH $_3$) $_3$), 34.33 (C(CH $_3$) $_3$), 35.21 (C(CH $_3$) $_3$), 111.27, 117.46, 123.16, 123.72, 124.49 (CH $_3$ CN), 125.39, 136.30, 138.31, 145.04, 146.44, 149.45, 160.24, 173.55 (CO). IR (nujol mull, cm $^{-1}$): 3052 (w), 2275 (m, $\nu_{\text{C}\equiv\text{N}}$), 1710 (w), 1585 (w), 1526 (m), 1444 (m), 1377 (s), 1357 (m), 1349 (m), 1326 (m), 1302 (m), 1275 (w), 1247 (m), 1232 (s), 1193 (s), 1161 (s), 1110 (m), 1098 (m), 1051 (w), 1040 (w), 1024 (m), 992 (m), 949 (w), 910 (w), 859 (w), 828 (w), 796 (m), 769 (w), 741 (m), 647 (m). UV–vis–NIR (toluene): λ_{max} = 1084 nm (ϵ = 11,300 L mol $^{-1}$ cm $^{-1}$), 703 (13500), 558 (11200), 501 (11000), 420 (11400), 352 (7100). The analytical sample contained one acetonitrile of crystallization. Anal. calcd for C $_{58}$ H $_{83}$ N $_3$ O $_2$ Ru: C, 70.84; H, 8.51; N, 7.12. Found: C, 70.71; H, 8.03; N, 7.02.

(Diso) $_2$ Ru(CH $_2$ =CHCH $_2$ Ph). In a round-bottom flask, 102.0 mg of *cis*-(Diso) $_2$ Ru(NCMe) $_2$ (0.1082 mmol) is dissolved in 8 mL dry CH $_2$ Cl $_2$. Allylbenzene (720 μ L, 5.45 mmol, 50 equiv) is added to the purple solution and the flask is swirled to mix. The round-bottom flask is attached to a needle valve. After standing 30 min at room temperature, the solvent is evaporated on the vacuum line. The blue-violet residue is slurried in 2 mL methanol and filtered through a glass

frit. The round-bottom flask is washed with 2 $\times$ 2 mL methanol and the washes filtered through the frit. The solid is air-dried for 30 min to yield 75.1 mg of product (70%). ^1H NMR (C_6D_6): δ 0.75 (d, 6.3 Hz, 3H, CH(CH $_3$)Me), 0.81 (d, 7.3 Hz, 3H, CH(CH $_3$)Me), 0.92 (d, 7.2 Hz, 3H, CH(CH $_3$)Me), 0.95 (d, 7.0 Hz, 3H, CH(CH $_3$)Me), 1.10 (s, 12H, 'Bu + CH(CH $_3$)Me), 1.14 (s, 9H, 'Bu), 1.25 (d, 3H, CH(CH $_3$)Me), 1.43 (dd, 13.8 Hz, 5.0 Hz, 1H, PhCHH'CH=CH $_2$), 1.47 (s, 9H, 'Bu), 1.52 (d, 7.3 Hz, 3H, CH(CH $_3$)Me), 1.57 (s, 12H, 'Bu + CH(CH $_3$)Me), 1.75 (dd, 9.2, 3.2 Hz, 1H, *trans*-PhCH $_2$ CH=CHH'), 1.92 (sept, 7.0 Hz, 1H, CHMe $_2$), 1.99 (sept, 6.8 Hz, 1H, CHMe $_2$), 2.57 (sept, 6.7 Hz, 1H, CHMe $_2$), 2.71 (dd, 3.9, 13.9 Hz, 1H, PhCHH'CH=CH $_2$), 3.23 (sept, 6.5 Hz, 1H, CHMe $_2$), 5.08 (dd, 12.6, 3.3 Hz, 1H, *cis*-PhCH $_2$ CH=CHH'), 5.61 (m, 1H, PhCH $_2$ CH=CH $_2$), 6.80 (d, 1.9 Hz, 1H, iminoxolene 3- or 5-H), 6.84 (d, 2.0 Hz, 1H, iminoxolene 3- or 5-H), 6.99 (m, 1H, *p*-Ph), 7.05–7.14 (m, 6H, *o,m*-Ph + Ar 4-H), 7.30–7.40 (m, 5H, Ar 3,5-H + iminoxolene 3- or 5-H), 7.45 (d, 2.0 Hz, 1H, iminoxolene 3- or 5-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 23.66 (2C, CH(CH $_3$)Me), 23.74 (CH(CH $_3$)Me), 24.72 (CH(CH $_3$)Me), 25.37 (CH(CH $_3$)Me), 25.61 (CH(CH $_3$)Me), 25.66 (CH(CH $_3$)Me), 25.95 (CH(CH $_3$)Me), 28.75 (CHMe $_2$), 28.87 (CHMe $_2$), 29.15 (CHMe $_2$), 29.34 (CHMe $_2$), 30.08 (C(CH $_3$) $_3$), 30.64 (C(CH $_3$) $_3$), 30.95 (C(CH $_3$) $_3$), 31.10 (C(CH $_3$) $_3$), 34.19 (C(CH $_3$) $_3$), 34.23 (C(CH $_3$) $_3$), 35.16 (C(CH $_3$) $_3$), 35.38 (C(CH $_3$) $_3$), 37.66 (PhCH $_2$), 59.66 (H $_2$ C=CH), 73.14 (H $_2$ C=CH), 112.00, 112.50, 121.11, 121.43, 122.89, 124.33, 124.41, 126.06, 128.34, 128.42, 137.85, 138.21, 138.31, 138.78, 141.03, 141.31, 141.66, 142.45, 142.89, 149.72, 150.02, 157.67, 158.87, 170.65 (CO), 171.44 (CO). IR (nujol mull, cm $^{-1}$): 3060 (w), 1541 (w), 1528 (w), 1378 (s), 1356 (w), 1312 (w), 1299 (w), 1247 (m), 1229 (m), 1203 (m), 1154 (m), 1102 (w), 1031 (w), 996 (w), 922 (w), 865 (m), 821 (w), 803 (w), 781 (w), 746 (w), 737 (w), 698 (w), 663 (w), 654 (w). UV–vis (toluene): λ_{max} = 700 nm (ϵ = 14,500 L mol $^{-1}$ cm $^{-1}$), 573 (9400), 494 (10400), 414 (9700). Anal. calcd for C $_{61}$ H $_{84}$ N $_2$ O $_2$ Ru: C, 74.88; H, 8.65; N, 2.86. Found: C, 74.46; H, 8.01; N, 2.65.

(Diso) $_2$ Ru(CH $_2$ =CHBu). The 1-hexene complex is prepared by the method used for the allylbenzene derivative using 51.9 mg of *cis*-(Diso) $_2$ Ru(NCMe) $_2$ (0.0551 mmol) and 350 μ L of 1-hexene (2.81 mmol, 50 equiv) and yields 32.0 mg of (Diso) $_2$ Ru(1-hexene) (61%). ^1H NMR (C_6D_6): δ 0.14 (m, 1H, CH $_3$ (CH $_2$) $_2$ CH=CH $_2$), 0.69 (t, 7.1 Hz, 3H, CH $_3$ (CH $_2$) $_2$ CH=CH $_2$), 0.74 (d, 6.8 Hz, 3H, CH(CH $_3$)Me), 0.79 (d, 6.9 Hz, 3H, CH(CH $_3$)Me), 0.93 (d, 6.6 Hz, 3H, CH(CH $_3$)Me), 0.95 (d, 6.7 Hz, 3H, CH(CH $_3$)Me), 1.11 (s, 9H, 'Bu), 1.12 (s, 9H, 'Bu), 1.18 (d, 6.8 Hz, 3H, CH(CH $_3$)Me), 1.27 (d, 7.2 Hz, 3H, CH(CH $_3$)Me), 1.48 (s, 9H, 'Bu), 1.52 (s, 9H, 'Bu), 1.54 (d, 6.8 Hz, 3H, CH(CH $_3$)Me), 1.59 (d, 6.6 Hz, 3H, CH(CH $_3$)Me), 1.83 (dd, 9.6, 3.2 Hz, 1H, *trans*-CH $_3$ (CH $_2$) $_2$ CH=CHH'), 1.92 (sept, 6.9 Hz, 1H, CHMe $_2$), 1.99 (sept, 7.1 Hz, 1H, CHMe $_2$), 2.61 (sept, 6.6 Hz, 1H, CHMe $_2$), 3.06 (sept, 7.0 Hz, 1H, CHMe $_2$), 4.87 (dd, 13.2, 3.4 Hz, 1H, *cis*-CH $_3$ (CH $_2$) $_2$ CH=CHH'), 5.39 (m, 1H, CH $_3$ (CH $_2$) $_2$ CH=CH $_2$), 6.80 (d, 2.4 Hz, 1H, iminoxolene 3- or 5-H), 6.83 (d, 2.0 Hz, 1H, iminoxolene 3- or 5-H), 7.07–7.11 (m, 2H, Ar 3- or 5-H + Ar 4-H), 7.29–7.37 (m, 4H, Ar 3- and 5-H + Ar 3- or 5-H + Ar 4-H), 7.41 (d, 2.2 Hz, 1H, iminoxolene 3- or 5-H), 7.43 (d, 2.2 Hz, 1H, iminoxolene 3- or 5-H). (Five of the protons from the bound hexene are multiplets that were obscured by the more intense signals from 1 to 2 ppm.) $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 14.29 (CH $_3$ (CH $_2$) $_2$ CH=CH $_2$), 22.76 (CH $_3$ (CH $_2$) $_2$ CH=CH $_2$), 24.39 (CH(CH $_3$)Me), 24.44 (CH(CH $_3$)Me), 24.50 (CH(CH $_3$)Me), 25.27 (CH(CH $_3$)Me), 26.08 (CH(CH $_3$)Me), 26.33 (CH(CH $_3$)Me), 26.56 (CH(CH $_3$)Me), 26.66 (CH(CH $_3$)Me), 29.12 (CHMe $_2$), 29.56 (CHMe $_2$), 29.86 (CHMe $_2$), 30.03 (CHMe $_2$), 30.79 (C(CH $_3$) $_3$), 30.94 (CH $_3$ (CH $_2$) $_2$ CH=CH $_2$), 31.24 (C(CH $_3$) $_3$), 31.73 (C(CH $_3$) $_3$), 31.82 (C(CH $_3$) $_3$), 33.93 (CH $_3$ (CH $_2$) $_2$ CH=CH $_2$), 34.89 (C(CH $_3$) $_3$), 34.98 (C(CH $_3$) $_3$), 35.92 (C(CH $_3$) $_3$), 36.06 (C(CH $_3$) $_3$), 61.44 (BuCH=CH $_2$), 75.83 (BuCH=CH $_2$), 112.77, 113.05, 121.71, 121.89, 123.54, 123.77, 125.08 (2C), 138.32, 138.66, 139.04, 139.47, 141.64, 141.97, 143.16, 143.58, 150.56, 150.89, 158.51, 159.57, 171.07 (CO), 172.14 (CO). Two resonances

are obscured by the C_6D_6 solvent peak. IR (nujol mull, cm^{-1}): 3056 (w), 1576 (w), 1542 (m), 1373 (s), 1356 (s), 1311 (m), 1305 (m), 1221 (s), 1198 (s), 1159 (s), 1097 (w), 1046 (w), 1030 (w), 990 (w), 951 (w), 934 (w), 911 (w), 883 (w), 861 (m), 821 (w), 787 (w), 782 (w), 765 (w), 742 (w), 714 (w). UV–vis (toluene): $\lambda_{max} = 698$ nm ($\epsilon = 13400$ L mol $^{-1}$ cm $^{-1}$), 581 (9000), 492 (9500), 410 (9500). Anal. calcd for $C_{58}H_{86}N_2O_2Ru$: C, 73.76; H, 9.18; N, 2.97. Found: C, 70.47; H, 8.73; N, 2.71.

(Diso) $_2$ Ru(HC $\equiv$ CBu). The 1-hexyne complex is prepared by the method used for the allylbenzene derivative using 65.1 mg of *cis*-(Diso) $_2$ Ru(NCMe) $_2$ (0.0691 mmol) and 73.0 μ L of 1-hexyne (2.81 mmol, 9 equiv) and yields 36.1 mg of (Diso) $_2$ Ru(1-hexyne) (58%). 1H NMR (C_6D_6): δ 0.69 (t, 7.3 Hz, 3H, HC $\equiv$ CCH $_2$ CH $_2$ CH $_2$ CH $_3$) 0.84 (d, 6.3 Hz, 3H, CH(CH $_3$)Me), 0.85 (d, 6.1 Hz, 3H, CH(CH $_3$)Me), 0.91 (d, 6.3 Hz, 3H, CH(CH $_3$)Me), 1.01 (d, 6.3 Hz, 3H, CH(CH $_3$)Me), 1.06 (d, 6.0 Hz, 3H, CH(CH $_3$)Me), 1.09 (d, 6.6 Hz, 3H, CH(CH $_3$)Me), 1.11 (s, 9H, t Bu), 1.14 (m, 2H, HC $\equiv$ CCH $_2$ CH $_2$ CH $_2$ CH $_3$), 1.16 (s, 9H, t Bu), 1.28 (m, 2H, HC $\equiv$ CCH $_2$ CH $_2$ CH $_2$ CH $_3$), 1.36 (d, 6.6 Hz, 3H, CH(CH $_3$)Me), 1.42 (d, 6.6 Hz, 3H, CH(CH $_3$)Me), 1.51 (s, 9H, t Bu), 1.53 (s, 9H, t Bu), 2.21 (sept, 6.6 Hz, 1H, CHMe $_2$), 2.32 (sept, 6.2 Hz, 1H, CHMe $_2$), 2.42 (sept, 6.9 Hz, 1H, CHMe $_2$), 2.69 (sept, 6.6 Hz, 1H, CHMe $_2$), 2.92 (dt, 17.1, 7.1 Hz, 1H, HC $\equiv$ CCHH'CH $_2$ CH $_2$ CH $_3$), 3.16 (dt, 17.1, 6.7 Hz, 1H, HC $\equiv$ CCHH'CH $_2$ CH $_2$ CH $_3$), 6.58 (d, 2.2 Hz, 1H, iminoxolene 3- or 5-H), 6.59 (d, 2.3 Hz, 1H, iminoxolene 3- or 5-H), 7.12 (dd, 8.1, 1.2 Hz, 1H, Ar 3- or 5-H), 7.18 (dd, 7.8, 1.3 Hz, 1H, Ar 3- or 5-H), 7.24 (dd, 7.9, 1.1 Hz, 1H, Ar 3- or 5-H), 7.30–7.39 (m, 5H, 2 Ar 4-H + Ar 3- or 5-H, + iminoxolene 3- and 5-H), 7.73 (s, 1H, HC $\equiv$ CCH $_2$ CH $_2$ CH $_2$ CH $_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 13.40 (HC $\equiv$ CCH $_2$ CH $_2$ CH $_2$ CH $_3$), 21.76 (HC $\equiv$ CCH $_2$ CH $_2$ CH $_2$ CH $_3$), 23.14 (CH(CH $_3$)Me), 23.89 (CH(CH $_3$)Me), 24.52 (CH(CH $_3$)Me), 25.02 (CH(CH $_3$)Me), 25.32 (CH(CH $_3$)Me), 25.41 (CH(CH $_3$)Me), 25.44 (CH(CH $_3$)Me), 25.83 (HC $\equiv$ CCH $_2$ CH $_2$ CH $_2$ CH $_3$), 26.36 (CH(CH $_3$)Me), 27.69 (CHMe $_2$), 27.84 (CHMe $_2$), 28.70 (CHMe $_2$), 28.73 (CHMe $_2$), 30.35 (C(CH $_3$) $_3$), 30.99 (C(CH $_3$) $_3$), 31.54 (C(CH $_3$) $_3$), 31.60 (C(CH $_3$) $_3$), 32.81 (HC $\equiv$ CCH $_2$ CH $_2$ CH $_2$ CH $_3$), 34.18 (C(CH $_3$) $_3$), 34.25 (C(CH $_3$) $_3$), 35.31 (C(CH $_3$) $_3$), 35.42 (C(CH $_3$) $_3$), 111.87, 112.07, 116.17 (HC $\equiv$ CCH $_2$ CH $_2$ CH $_2$ CH $_3$), 120.22, 121.09, 122.89, 123.46, 124.96, 125.15, 136.70, 137.02, 137.86, 138.10, 140.04 (HC $\equiv$ CCH $_2$ CH $_2$ CH $_2$ CH $_3$), 142.77, 143.00, 143.02, 143.24, 148.63, 149.29, 153.91, 154.93, 166.02 (CO), 166.16 (CO). IR (nujol mull, cm^{-1}): 1577 (w), 1543 (w), 1379 (s), 1371 (m), 1311 (w), 1294 (w), 1255 (m), 1224 (m), 1221 (m), 1201 (m), 1160 (m), 1097 (w), 1053 (w), 1029 (w), 997 (w), 933 (w), 918 (w), 904 (w), 867 (m), 829 (w), 798 (m), 767 (w), 729 (w), 721 (m), 696 (w), 667 (w). UV–vis (toluene): $\lambda_{max} = 593$ nm ($\epsilon = 18,400$ L mol $^{-1}$ cm $^{-1}$), 460 (10,200), 402 (sh, 10,300). Anal. calcd for $C_{58}H_{84}N_2O_2Ru$: C, 73.92; H, 8.98; N, 2.97. Found: C, 73.55; H, 8.74; N, 2.92.

(Diso) $_2$ Ru(EtC $\equiv$ CEt) is generated *in situ* by treating 16.2 mg *cis*-(Diso) $_2$ Ru(NCCH $_3$) $_2$ (0.0172 mmol) with 5.0 μ L 3-hexyne (0.0440 mmol, 2.6 equiv) in 0.6 mL CD_2Cl_2 . The blue-violet solution is analyzed by 1H and $^{13}C\{^1H\}$ NMR spectroscopy. 1H NMR (CD_2Cl_2): δ 0.60 (d, 6.8 Hz, 6H, CH(CH $_3$)Me), 0.74 (d, 6.7 Hz, 6H, CH(CH $_3$)Me), 0.77 (d, 6.7 Hz, 6H, CH(CH $_3$)Me), 0.99 (t, 7.4 Hz, 6H, CH $_2$ CH $_3$), 1.06 (s, 18H, t Bu), 1.18 (s, 18H, t Bu), 1.30 (d, 6.8 Hz, 6H, CH(CH $_3$)Me), 2.78 (dq, 16.3, 7.6 Hz, 2H, CHH'CH $_3$), 3.11 (dq, 16.4, 7.5 Hz, 2H, CHH'CH $_3$), 6.14 (d, 2.0 Hz, 2H, iminoxolene 3- or 5-H), 7.02 (d, 2.0 Hz, 2H, iminoxolene 3- or 5-H), 7.17 (d, 7.5 Hz, 2H, Ar 3- or 5-H), 7.24 (d, 7.1 Hz, 2H, Ar 3- or 5-H), 7.35 (t, 7.7 Hz, 2H, Ar 4-H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 15.57 (CH $_2$ CH $_3$), 20.85 (CH(CH $_3$)Me), 23.29 (CH(CH $_3$)Me), 24.96 (CH(CH $_3$)Me), 25.14 (CH(CH $_3$)Me), 25.29 (CH $_2$ CH $_3$), 27.83 (CHMe $_2$), 28.53 (CHMe $_2$), 31.15 (C(CH $_3$) $_3$), 31.59 (C(CH $_3$) $_3$), 34.28 (C(CH $_3$) $_3$), 35.32 (C(CH $_3$) $_3$), 112.37, 120.67, 122.87, 125.16, 127.80, 136.13, 137.18, 139.68 (C $\equiv$ C), 143.28, 143.55, 149.24, 153.89, 164.76 (CO).

Variable-Temperature NMR Spectroscopy. High-temperature NMR spectra were acquired using toluene- d_8 solutions on a Bruker AVANCE DPX-400 MHz NMR spectrometer for (Diso) $_2$ Ru-(CH $_2$ =CHCH $_2$ Ph) and a Bruker AVANCE DPX-500 MHz NMR spectrometer for *cis*-(Diso) $_2$ Ru(NCCH $_3$) $_2$ and (Diso) $_2$ Ru(1-hexyne),

with probe temperatures calibrated using the peak separation in ethylene glycol.⁶⁹ The bound and free acetonitrile resonances of *cis*-(Diso) $_2$ Ru(NCCH $_3$) $_2$, the *tert*-butyl protons and the bound and free H $_2$ C=CHR of the alkene of (Diso) $_2$ Ru(CH $_2$ =CHCH $_2$ Ph), and the *tert*-butyl protons of (Diso) $_2$ Ru(1-hexyne) were simulated using the dynamic NMR simulation routine in Topspin 3.6. For temperatures above the coalescence point, chemical shifts of the *tert*-butyl peaks were estimated by linear extrapolation of the temperature-dependent shifts, and the extrapolated difference in chemical shifts was treated as fixed in the simulation.

X-ray Crystallography. Crystals of (Diso) $_2$ Ru(NCMe) $_2$ ·2CH $_3$ CN were grown by liquid diffusion of acetonitrile into a dichloromethane solution of the complex. Crystals of (Diso) $_2$ Ru-(CH $_2$ =CHCH $_2$ Ph), (Diso) $_2$ Ru(CH $_2$ =CHBu)·CH $_2$ Cl $_2$, and (Diso) $_2$ Ru(EtC $\equiv$ CEt)·0.5CH $_2$ Cl $_2$ were grown from liquid diffusion of methanol into dichloromethane solutions of the complexes. Crystals were placed in inert oil before being transferred to the cold N $_2$ stream of the diffractometer. The data were reduced, correcting for absorption, using the program SADABS.

In (Diso) $_2$ Ru(CH $_2$ =CHBu)·CH $_2$ Cl $_2$, the 1-hexene is disordered about the crystallographic 2-fold axis. Because the 1- and 2-carbons are each close to the other's symmetry equivalent, they were refined with their thermal parameters constrained to be equivalent to each other. The dichloromethane solvent was partially occupied and was arbitrarily assigned an occupancy of 50%. The bound allylbenzene in (Diso) $_2$ Ru(CH $_2$ =CHCH $_2$ Ph) was disordered about the crystallographic 2-fold analogously to the 1-hexene in the hexene complex. Additionally, the *tert*-butyl group centered at C18, C23–C25 of the diisopropylphenyl group, both isopropyl groups, and the phenyl ring of the allylbenzene were all modeled as occupying two different orientations. In each case, the corresponding atoms in the two orientations were constrained to have the same thermal parameters, with the occupancies allowed to refine. The phenyl groups were refined as rigid groups using the AFIX 66 instruction and their thermal parameters were restrained to be similar using the SIMU instruction. In the structure of (Diso) $_2$ Ru(EtC $\equiv$ CEt)·0.5CH $_2$ Cl $_2$, there were two independent ruthenium complexes in the asymmetric unit. In one of them (Ru2), there was a small amount of whole-molecule disorder where there was a small amount of the species with the ruthenium and hexyne on the other side of the bis(iminoxolene) unit. Only the Ru of this orientation was modeled; its thermal parameters were constrained to be equal to those of Ru2 and its occupancy refined to 4.97(4)%. One *tert*-butyl group (centered on C58) was disordered in two different orientations; opposing methyl groups were constrained to have equal thermal parameters and the occupancies allowed to refine. The lattice dichloromethane had one chlorine disordered in two different locations.

All nonhydrogen atoms were refined anisotropically. Hydrogen atoms in *cis*-(Diso) $_2$ Ru(NCMe) $_2$ ·2CH $_3$ CN were found on difference Fourier maps and refined isotropically, while lattice solvent hydrogen atoms were placed in calculated positions. Hydrogen atoms in the remaining three structures were placed in calculated positions with their thermal parameters tied to the isotropic thermal parameters of the atoms to which they are bonded (1.5 $\times$ for methyl, 1.2 $\times$ for all others). Calculations used SHELXTL (Bruker AXS),⁷⁰ with scattering factors and anomalous dispersion terms taken from the literature.⁷¹

Computational Methods. Geometry optimizations were performed on simplified structures in which *tert*-butyl groups were replaced by hydrogen; the nitrogen substituent in the iminoxolene was either hydrogen (hap ligand), phenyl (ap), or 2,6-diisopropylphenyl (diso). Hydrogen cyanide was used in place of acetonitrile in the relevant compounds. Calculations used density functional theory (B3LYP, SDD basis set for Ru, 6-31G* basis set for all other atoms) as implemented in the Gaussian16 suite of programs.⁷² The optimized geometries for stable species were confirmed as minima, and of transition states as first-order saddle points, by calculation of vibrational frequencies. Plots of calculated Kohn–Sham orbitals were generated using Gaussview (v. 6.0.16) with an isovalue of 0.04.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.4c00259>.

Summary of crystal data, NMR spectra, infrared spectra, UV–visible spectra, summaries of spectroscopic and structural data on known ruthenium alkene and alkyne complexes, and calculated structures, energies, and MOS values (PDF)

Cartesian coordinates of optimized structures by DFT (XYZ)

■ Accession Codes

CCDC 2359508–2359511 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

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■ Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the US National Science Foundation (CHE-1955933 and CHE-2400019). We thank Dr. Allen G. Oliver for his assistance with X-ray crystallography, and the NSF for their support of the acquisition of the diffractometer used for the structure of (Diso)₂Ru(EtC≡CEt)-0.5 CH₂Cl₂ (MRI award CHE-2214606). We thank Dr. Evgenii Kovrigin for his help with the NMR experiments.

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