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Reactions of Grubbs Catalysts with Excess Methoxide: Formation of Novel Methoxyhydride Complexes

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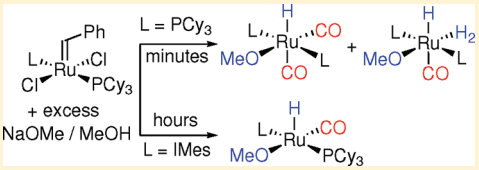
Supporting Information

ABSTRACT: On exposure to NaOMe (≥3 equiv) in CH_2Cl_2–MeOH at 23 °C, the first-generation Grubbs catalyst $RuCl_2(PCy_3)_2(=CHPh)$ (**1a**) is immediately transformed into the six-coordinate methoxyhydride complexes $RuH(OMe)(CO)_2(PCy_3)_2$ (**4a**) and $RuH(OMe)(CO)(H_2)(PCy_3)_2$ (**5a**). Complex **5a** can be recycled into **4a** under conditions conducive to removal of H_2. The second-generation catalyst $RuCl_2(IMes)(PCy_3)(=CHPh)$ (**1b**; IMes = *N*,*N*′-bis(mesityl)imidazol-2-ylidene) reacts more slowly, requiring several hours even at 20 equiv of NaOMe, and terminates at five-coordinate $RuH(OMe)(CO)(IMes)(PCy_3)$ (**3b**). Experiments in the presence of added PCy_3 reveal that consumption of **1a**, but not **1b**, proceeds via the four-coordinate intermediate formed by equilibrium loss of phosphine, a function of the lability of the PCy_3 ligand at ambient temperatures. The poor accessibility of such an intermediate for **1b** at 23 °C retards salt metathesis and inhibits further reaction of **3b**. For the bis(PCy_3) analogue **3a**, fast transformation into **4a** is proposed to involve reversible loss of PCy_3, coordination of methanol, σ-metathesis of methanol at the hydride site to liberate H_2, and β-elimination/decarbonylation of bound methoxide. Competitive uptake of H_2 by **3a** yields six-coordinate **5a** (the dihydrogen adduct of **3a**). Independent routes to $RuH(OMe)(CO)_2(L)(PCy_3)$ (**4a**/**b**; **a**, L = PCy_3; **b**, L = IMes) were developed: these involved sequential transformation of $RuHCl(CO)(L)(PCy_3)$ (**2a**/**b**) into the bis-carbonyl adducts $RuHCl(CO)_2(L)(PCy_3)$ (**7a**/**b**) under CO, conversion of **7a**/**b** into the more reactive triflates $RuH(OTf)(CO)_2(L)(PCy_3)$ (**8a**/**b**), and reaction of **8a**/**b** with equimolar NaOMe. Dihydride **6b** was also prepared, by reaction of **8b** with NaH.



INTRODUCTION

The Grubbs metathesis catalysts $RuCl_2(L)(PCy_3)(=CHPh)$ (e.g., **1a**: L = PCy_3; **1b**: L = IMes, *N*,*N*′-bis(mesityl)imidazol-2-ylidene) are now widely recognized as powerful agents for further, nonmetathetical transformations.[1,2] In some cases, this expanded reactivity is due to the action of **1** and its alkylidene and/or methylidene derivatives: in others, it reflects the operation of further ruthenium catalysts generated in situ, whether by chance or design.[3] While a greater understanding of the underlying inorganic transformations of these important complexes would clearly be advantageous, overwhelming interest in their organic applications has tended to overshadow their inorganic reaction chemistry. Many of their fundamental reactivity patterns thus remain obscure, studies of the transformation of **1** into the catalytically important hydrides $RuHCl(CO)(L)(PCy_3)$ (**2**) (particularly **2a**; L = PCy_3) notwithstanding.[4,5]

A potentially important example of this obscurity is found in the reactions of the Grubbs catalysts with alkoxides. Schmidt has demonstrated that postmetathesis treatment of **1a** with isopropanol and NaOH (5–10 equiv vs Ru) yields efficient catalysts for double-bond isomerization. Primary alcohols, however, were strikingly less effective.[6] While metal hydrides are formed in either case, one obvious difference lies in the resistance of *secondary* alkoxides to Ru-mediated decarbonylation. In contrast, Mol and co-workers[4a] have shown that treating **1a** with 1 equiv of methoxide at 70–75 °C yields the carbonyl adduct **2a**, among other Ru species (ca. 50% **2a**; we suspected that the unidentified coproducts might arise from thermolytic degradation of **1a**). Given that complexes **2a**/**b** are high-productivity catalysts in the mechanistically related context of olefin hydrogenation,[7] we hypothesized that the poor isomerization activity associated with primary alcohols might be due to formation of deactivated polycarbonyl species in the presence of excess alkoxide.

Within part of a broader program of study directed at evaluating the behavior of Ru-alkylidene complexes with reactive $[ER]^-$/HER species, we thus wished to clarify the reactivity of **1a** and **1b** toward *excess* methoxide (>2 equiv) in the presence of methanol. We chose to explore this chemistry at ambient temperatures, both to intercept the relevant Ru species (rather than "downstream" products arising from extraneous thermal decomposition pathways) and to gain a clearer picture of the minimum conditions required for loss of the benzylidene functionality. Here we report strikingly different outcomes for the first- and second-generation Grubbs catalysts. While **1a** is immediately converted into $RuH(OMe)(CO)_2(PCy_3)_2$ (**4a**) and $RuH(OMe)(CO)(H_2)(PCy_3)_2$ (**5a**) at 23 °C, complex **1b** undergoes much slower transformation into a rare, unexpectedly stable five-coordinate methoxyhydride species, $RuH(OMe)(CO)(IMes)(PCy_3)$ (**3b**), with no sign of

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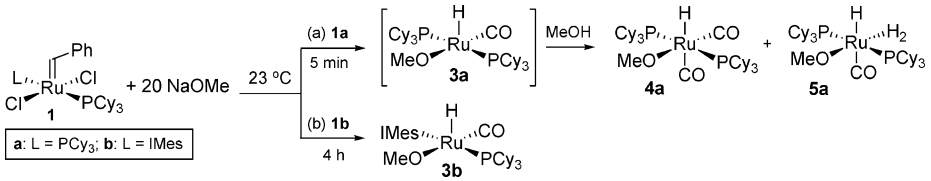
Scheme 1. Products Observed Following Reaction of Grubbs Catalysts with Excess Methoxide[a]



[a]Reactions at 23 °C in CH_2Cl_2–MeOH. PCy_3, toluene, and formaldehyde also observed; see text. The trans-disposition of the hydride and CO ligands in **5a** (favored by donor–acceptor push–pull interactions) is suggested by analogy to the structure of **4a**.

the expected **4b**/**5b**. Routes to the new complexes **3b** and **4a**/**b** from convenient hydride precursors were developed to confirm the identities of observed products (**3b**, **4a**) and the absence of expected products (**4b**).

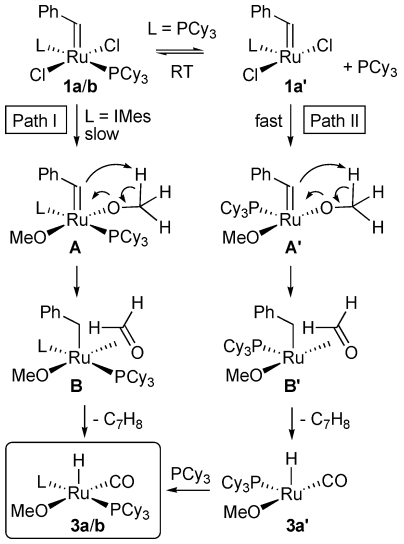
RESULTS AND DISCUSSION

Reactions of Grubbs Catalysts with Methoxide Ion. Addition of excess methanolic NaOMe to a solution of **1a** in CH_2Cl_2 (Scheme 1a) caused an instant color change from purple to pale yellow, evolution of small bubbles presumed to be H_2, and complete loss of the NMR signals for **1a** within 5 min, without need for elevated temperatures. No evidence was seen of methoxyhydride $RuH(OMe)(CO)(PCy_3)_2$ (**3a**), an intermediate inferred from the corresponding, slower reaction of **1b** discussed below (Scheme 1b). Instead, the sole Ru products observed were $RuH(OMe)(CO)_2(PCy_3)_2$ (**4a**) and $RuH(OMe)(CO)(H_2)(PCy_3)_2$ (**5a**), formed in ca. 2:1 ratio. Formaldehyde and free PCy_3 were also detected (ca. 10% each), as well as toluene, although quantification of the latter was hampered by interfering signals from the cyclohexyl groups or the internal standard Ph_3PO. Co-formation of ca. 25% paramagnetic material is indicated by integration against Ph_3PO, vide infra.

The distribution of Ru products did not change on longer reaction (4 h), but stripping off the solvent and redissolving the residue in C_6D_6 effected transformation of **5a** into **4a**, via uptake of a further equivalent of methanol (see mechanistic section). Traces of known[8] dihydride $RuH_2(CO)_2(PCy_3)_2$ (**6a**) (<5%) were also formed. The identity of **4a** was confirmed by independent synthesis from hydride precursors; dihydrogen adduct **5a** was characterized by in situ NMR analysis, including $T_{1(min)}$ measurements. Facile β-elimination from methoxide, discussed in more detail below, disfavors formation of stable bis(alkoxide) or deprotonated carbyne products, as formed in the corresponding reactions of **1a** with excess *tert*-butoxide[9] or phenoxides.[10−12]

Consumption of **1b**, in comparison, required several hours even at relatively high proportions of methoxide (4 h at 20 equiv). As shown in Scheme 1b, reaction also halted at an earlier stage, yielding five-coordinate $RuH(OMe)(CO)(IMes)(PCy_3)$ (**3b**) (a rare example of a coordinatively unsaturated alkoxyhydride complex),[13] rather than **4b** and/or **5b**. Addition of excess PCy_3 had no effect on the rate of transformation of **1b** into **3b**, although such treatment retarded consumption of the first-generation catalyst **1a**. We attribute the difference to the much higher lability of the PCy_3 ligand in **1a**, which gives equilibrium access to four-coordinate $RuCl_2(PCy_3)(=CHPh)$ (**1a′**) in solution. Salt metathesis via this sterically accessible species (see path II, Scheme 2) is sufficiently faster that the corresponding reaction of the parent **1a** (path I) does not compete. The slow salt metathesis of **1b**, as well as the resistance of **3b** to further reaction, is consistent with the very low room-temperature lability of the PCy_3 ligand in these IMes complexes,[16] which significantly increases the steric impediment to reaction. The strong binding characteristic of phosphine ligands trans to an NHC ligand is known to retard dissociative reaction pathways in catalysis, particularly at ambient temperatures. Such behavior has been documented in hydrogenation and isomerization via the hydride complex **2b**[14,15] and in metathesis via **1b**.[16,17]

Scheme 2. Proposed Mechanisms for Transformation of 1a/b into Five-Coordinate 3a/b[a]



[a]Product is isolable only for **3b** (L = IMes). For ensuing reactions of **3a**/**3a′**, see text. For L = PCy_3, both of the pathways depicted are feasible, but path II is kinetically dominant. For L = IMes, only path I is available, and reaction is slow.

A proposed mechanism for the transformation of **1** into **3** thus involves initial reaction of **1** via exchange of both chloride ligands, followed by proton transfer from bound methoxide to benzylidene (see **A**/**A′**; Scheme 2), and coordination of formaldehyde to give Ru-benzyl intermediate **B**/**B′**. Deinsertion of CO and liberation of the benzyl group as toluene (and recoordination of PCy_3, in the case of **3a′**) would then generate **3a**/**b**. Labeling evidence consistent with such a pathway was reported by Dinger and Mol[4a] in the transformation of **1a** into **2a** with a single equivalent of methoxide. More recently, Leung and co-workers invoked the analogous attack by bound methoxide on benzylidene on treatment of $RuCl[N(^iPr_2PS)_2](PCy_3)(=CHPh)$ with NaOMe.[18] These reactions fall into a broader class of proton migrations onto benzylidene from E-R groups on an adjacent ligand[19] (notwithstanding the moderately electrophilic character inferred computationally for $Ru=CH_2$ systems).[20] Migration need not be restricted to β- or α-E-H groups: Owen and co-workers recently reported attack on

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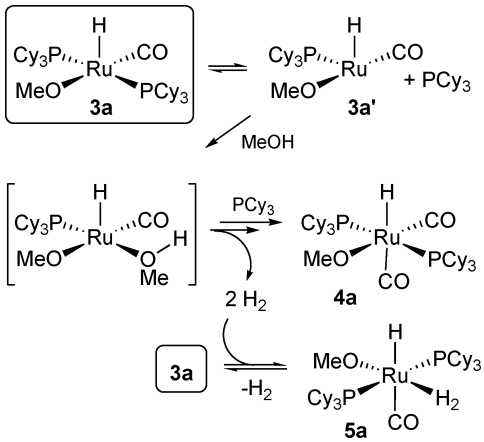
benzylidene by a γ-dihydroborate moiety in a scorpionate derivative of **1a**,[21] underscoring the point that ligand flexibility, in conjunction with a reactive E−H bond, can expand the scope of this alkylidene transformation pathway. Ru-NHC derivatives[22,23] show substantially higher tolerance toward adjacent N−H functionalities than first-generation complexes,[24] perhaps indicating that migration proceeds via a dissociative pathway (vide infra).

Conversion of the intermediate **3a** (or, more probably, **3a′**) into methoxydicarbonyl **4a** necessitates installation of a further equivalent of methoxide via reaction with methanol. The fact that **3b** does *not* evolve indicates that the associative pathway is not productive in this case. Scheme 3 depicts a plausible

Scheme 3. Proposed Mechanism for Transformation of 3a into Six-Coordinate 4a and 5a



pathway for **3a**, involving coordination of methanol and σ-metathesis[25] of the O−H and Ru−hydride bonds, followed by β-hydride elimination and CO deinsertion as before. Scavenging of H_2 by unreacted **3a** would account for the competitive formation of dihydrogen adduct **5a**. Reversible binding of dihydrogen enables release and recycling of **3a**, as indicated by the conversion of **5a** into **4a** on workup noted above. Transient signals assigned to **3a** are observed by in situ NMR analysis, at shifts very similar to those for **3b**, on freeze−pump−thaw degassing solutions of **5a**. Hydrogen-bonding interactions between incoming methanol and the hydride and/or methoxide ligands may account for the dramatically faster reaction of methanol with **3a**, vs the benzylidene complex **1a** (the latter reaction requires hours even at 60 °C).[5]

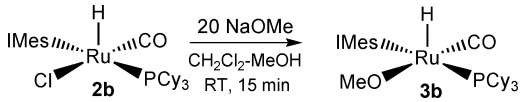
An anticipated competing pathway involves direct β-elimination and deinsertion from **3a**/**b** to afford dihydrides $RuH_2(CO)_2(L)(PCy_3)_2$ (**6a**/**b**). While traces of **6a** and **6b** form on workup, this pathway is clearly a minor one. The minimal formation of **6a** is probably due to the rapid conversion of **3a** into **4a** and **5a**, reflecting the abundance and noninnocence of the methanol cosolvent. Importantly, however, the resistance of **3b** to transformation into **6b** implies that β-elimination again requires phosphine loss, despite the formal coordinative unsaturation of **3b**.

Finally, it may be noted that the inhibited methanolysis of **3b**, relative to **3a**, contrasts with behavior earlier established for the corresponding dihydrogen complexes $RuHCl(H_2)(L)(PCy_3)$, in which the IMes derivative reacted only marginally slower with methanol and NEt_3 than did its PCy_3 analogue.[5] The difference may be due to the lability of the H_2 ligand (although this will be attenuated by the cis-hydride effect),[26] which circumvents the requirement for phosphine loss found in the present chemistry. Alternatively, an associative pathway involving outer-sphere, σ-bond metathesis of methanol may be enabled by the acidity of bound H_2.[27] Either is consistent with the reported $[PCy_3]$-independence of the reaction.[5]

Paramagnetic Byproducts. A common challenge in organometallic chemistry is the formation of paramagnetic products that go undetected by direct NMR methods. In the work above, observation of free PCy_3 led us to suspect the presence of such coproducts. We quantified the proportion of paramagnetic Ru by integration against Ph_3PO as an internal standard. A ca. 25% decrease in total integration was evident for the reactions of both **1a** and **1b**: we attribute this to the formation of paramagnetic species, rather than fluxional diamagnetic products, as low-temperature $^{31}P\{^1H\}$ NMR analysis revealed no additional signals. Notably, however, **4a** can be prepared in 85% isolated yield from a nonbenzylidene precursor (see below), tending to implicate the benzylidene functionality in the Ru(II) to Ru(III) oxidation. It is unclear whether C−H activation of the PCy_3 and/or IMes ligands also contributes: both are well precedented.[28,29] The four-coordinate species generated by phosphine loss is almost certainly a key vector for decomposition, as suggested by parallel experiments with the labile, phosphine-free "third-generation" Grubbs catalyst $RuCl_2(IMes)(py)_2(=CHPh)$. This complex was completely consumed within 15 min of treating with methoxide, but only ca. 15% of a hydride product was observed, which itself disappears within 1 h.

Synthetic Routes to Novel Complexes. Preparation of Five-Coordinate Methoxyhydride RuH(OMe)(CO)(IMes)(PCy$_3$) (3b). To confirm the identity of **3b**, we undertook its synthesis on a preparative scale from the well-behaved hydride precursor **2b**. Addition of methanolic NaOMe (20 equiv; Scheme 4) to a solution of **2b** in CH_2Cl_2 at 23 °C caused an

Scheme 4. Synthesis of Five-Coordinate Methoxyhydride Complex 3b



immediate color change from orange-yellow to red-orange. NMR analysis revealed complete conversion to the new methoxyhydride species $RuH(OMe)(CO)(IMes)(PCy_3)$ (**3b**) within 15 min. Quantitative conversion was confirmed in separate NMR-scale experiments by integration against Ph_3PO as internal standard, as noted above. Isolation of **3b** was frustrated by formation of traces of **4b** and **6b** on concentrating to dryness, but detailed NMR analysis supports the proposed structure. In particular, the upfield location and doublet multiplicity of the hydride signal (−23.61 ppm; $^2J_{HP}$ = 22 Hz; Table 1; cf. the very similar data for chloride analogue **2b**) provide unequivocal evidence for a square-pyramidal complex in which an apical hydride ligand lies cis to a single basal phosphine. The latter gives rise to a $^{31}P\{^1H\}$ singlet at 50.2 ppm. The hydride signal correlates (HMBC) with the IMes carbene carbon (δ_C 193.9 ppm, d, $^2J_{CP}$ = 103.2 Hz) and a single carbonyl ligand (δ_C 204.7 ppm, d, $^2J_{CP}$ = 8.7 Hz), although not with the broad OCH_3 signal (63.5 ppm, $\omega_{0.5}$ 25 Hz). Assignment of the latter was confirmed by a DEPT-135 experiment (−30 °C, C_7D_8) and HMQC correlation with the

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Table 1. Key NMR and IR Data for Hydride Complexes Discussed[a]

			δ_H (Ru−X)			IR (ν)	
complex	NMR solvent	δ_P	H ($^2J_{HP}$)	OCH_3	δ_{CO} ($^2J_{CP}$)	CO	Ru−H
$RuHCl(CO)(L)(PCy_3)$							
L = PCy_3, **2a**[33]	C_6D_6	46.9	−24.21 (t, 18 Hz)		202.1 (t, 14)	1905	1862
L = IMes, **2b**[15,33]	C_6D_6	47.8	−24.82 (d, 21 Hz)		202.3 (d, 14)	1894	1881
$RuH(OMe)(CO)(L)(PCy_3)$							
L = IMes, **3b**[b,c]	C_6D_6	50.2	−23.61 (d, 22 Hz)	4.22	204.7 (d, 9 Hz)[c]	1875	1890
$RuH(OMe)(CO)_2(L)(PCy_3)$							
L = PCy_3, **4a**[b]	C_6D_6	53.8	−4.25 (t, 20 Hz)	4.10	203.7 (t, 7 Hz)	2006	1939
					201.4 (t, 12 Hz)	1891	
L = IMes, **4b**[b]	C_6D_6	54.0	−4.18 (d, 25 Hz)	3.96	202.9 (d, 12 Hz)	2013	1948
					199.5 (d, 7 Hz)	1896	
$RuH(OMe)(CO)(H_2)(L)_2$							
L = PCy_3, **5a**[b]	CH_2Cl_2 MeOH	72.0	−7.45 (br s)	n.d.[d]	n.d.[d]	n.d.[d]	n.d.[d]
$Ru(H)_2(CO)_2(L)(PCy_3)$							
L = PCy_3, **6a**[8]	C_6D_6	68.3	−7.9 (t, 23 Hz)		206.2	2004	n.d.
						1994	
L = IMes, **6b**[b]	C_6D_6	68.9	−7.37 (d, 25 Hz)		204.7 (d, 8 Hz)	1995	1898
						1951	
$RuHCl(CO)_2(L)(PCy_3)$							
L = PCy_3, **7a**[8]	C_6D_6	49.8	−4.9 (t, 20 Hz)		201.6 (t, 7 Hz)	2016[b]	1869[b]
					200.7 (t, 12 Hz)	1942[b]	
L = IMes, **7b**[b]	C_6D_6	48.2	−4.77 (d, 23 Hz)		202.3 (d, 13 Hz)	2035	1954
					197.2 (d, 7 Hz)	1913	
$RuH(OTf)(CO)_2(L)(PCy_3)$							
L = PCy_3, **8a**[b]	C_6D_6	53.7	−4.02 (t, 19 Hz)		202.7 (t, 14 Hz)	2046	1917
					201.7 (t, 7 Hz)	1966	
L = IMes, **8b**[b]	C_6D_6	51.3	−4.07 (d, 23 Hz)		204.4 (d, 14 Hz)	2049	1972
					196.7 (d, 6 Hz)	1935	

[a]NMR chemical shifts in ppm; coupling constants in Hz; IR bands in cm^{-1}. Values at 23 °C unless otherwise noted. NMR samples in 10:1 CH_2Cl_2−MeOH were spiked with C_6D_6 as a deuterium lock. References are given to literature values in the solvents indicated. [b]This work. [c]Cf. values for transient species **3a** at −30 °C in C_7D_8: δ_P 47.8 ppm (s); δ_H −22.94 (d, 19 Hz). At 23 °C in C_6D_6, δ_H −22.81 (br t, $^2J_{HP}$ = 17.4 Hz). [d]Measurement of IR and ^{13}C NMR data was hampered by the low proportion of these species.

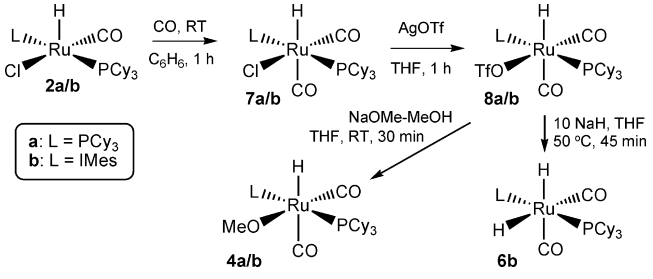
methoxy proton singlet (4.22 ppm). ^1H NOESY-NMR analysis reveals a through-space interaction between the methoxy protons and hydride. Rapid rotation about the Ru−C_{IMes} bond in **3b** is indicated by the equivalence of the IMes "backbone" protons, as well as the mesityl *p*-Me nuclei, despite the difference in environment above and below the basal plane of the square pyramid.[30]

Synthesis of Six-Coordinate $RuH(OMe)(CO)_2(L)(PCy_3)$ (4a/b) and $RuH_2(CO)_2(IMes)(PCy_3)$ (6b) from $RuH(OTf)(CO)_2(L)(PCy_3)$ (8a/b). High-yield routes to **4a/b** and **6b** were devised to support characterization of these previously unreported complexes (Scheme 5). We initially envisaged synthesis of **4** from the known[8] bis(carbonyl) complex $RuHCl(CO)_2(PCy_3)_2$ (**7a**) and its IMes analogue **7b**. Complexes **7** were conveniently prepared in ca. 85% isolated yield via reaction of **2a/b** with CO. As reactions of **7a** with methanolic NaOMe in THF proved slow (<20% in 4 h), we converted **7a/b** into their more reactive triflates $RuH(OTf)(CO)_2(L)(PCy_3)$ (**8a/b**) by reaction with AgOTf in THF (**8a**: 70%; **8b**: 83%). Treatment of **8a/b** with NaOMe−MeOH in THF effected complete conversion to yellow $RuH(OMe)(CO)_2(L)(PCy_3)$ (**4a/b**) within 30 min.[31] Sodium triflate was removed by stripping the reaction mixture to dryness, extracting with CH_2Cl_2, and filtering through Celite. Reprecipitation with hexanes afforded **4a/b** as light yellow powders in excellent yields (ca. 85% each).

A convenient route to $RuH_2(CO)_2(IMes)(PCy_3)$ (**6b**) from **8b** was also developed, via reaction with excess NaH at 50 °C in THF. Reaction was complete within 45 min. While high solubility in hexanes and diethyl ether frustrated reprecipitation, crude **6b** exhibits spectroscopic features closely similar to those reported for **6a** (originally prepared by the Chaudret group by treating $RuH_2(H_2)_2(PCy_3)_2$ with CO; data are provided in Table 1).[8]

The structures of the new complexes **4a/b**, **6b**, **7b**, and **8a/b** were established by one- and two-dimensional NMR experiments, supported by IR spectroscopy[32] and by elemental analysis for all but **6b**, which proved highly sensitive toward decomposition even in the solid state. Coordinative saturation

Scheme 5. Synthetic Routes to 4a/b and 6b from 2a/b



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in each is indicated by the downfield location of the hydride signal (between −4 and −8 ppm; Table 1), the triplet or doublet multiplicities of which indicate retention of the PCy_3 ligand(s) originally present. Trans-disposition of the two PCy_3 groups, or of the PCy_3 and IMes groups, is confirmed from the singlet multiplicity of the ^{31}P NMR signal (for **4a**, **8a**) or from the magnitude of $^2J_{CP}$ coupling to the carbene carbon (**4b**: 96 Hz; **6b**: 70 Hz; **7b**: 88 Hz; **8b**: 84 Hz). In contrast to **6b**, the symmetry of which results in equivalent carbonyl carbon (and hydride) signals, complexes **4a/b**, **7a/b**, and **8a/b** contain inequivalent carbonyl groups. Each appears as a $^{13}C\{^1H\}$ NMR doublet or triplet, the $^2J_{CP}$ values for which (6−15 Hz) confirm cis-disposition relative to the PCy_3 ligand(s). The expected HMBC correlations are seen between the hydride and the carbonyl and carbene ligands. For methoxides **4a/b**, assignment of the methoxy carbons (ca. 67 ppm) is confirmed by DEPT-135 analysis and HMQC correlation with the methoxy methyl singlet at ca. 4.0 ppm. A NOESY correlation between the latter and the hydride signal confirms the cis-disposition of these ligands. Finally, the triflate CF_3 groups in **8a/b** exhibit essentially identical NMR values (a $^{13}C\{^1H\}$ quartet at ca. 120 ppm ($^1J_{CF}$ = 319 Hz) and a $^{19}F\{^1H\}$ singlet at −77 ppm).

CONCLUSIONS

The foregoing describes the rapid reaction of the first-generation Grubbs catalyst **1a** with excess methoxide and methanol at room temperature. Major products are the coordinatively saturated methoxyhydride complexes $RuH(OMe)(CO)_2(PCy_3)_2$ (**4a**) and $RuH(OMe)(CO)(H_2)(PCy_3)_2$ (**5a**). Formation of such species may account for the poor isomerization activity found when an excess of primary alkoxides is used to trigger C═C isomerization following **1a**-mediated metathesis. Reaction of the second-generation catalyst **1b** with methanolic methoxide is much slower and terminates at the five-coordinate methoxyhydride complex $RuH(OMe)(CO)(IMes)(PCy_3)$ (**3b**). The identities of the new complexes **3b** and **4a/b** were confirmed by independent synthesis from $RuHCl(CO)(IMes)(PCy_3)$ (**2b**) or hydridotriflates $RuH(OTf)(CO)_2(L)(PCy_3)$ (**8a/b**), respectively; isolation of $RuH(OMe)(CO)(PCy_3)_2$ (**3a**) is hampered by its much higher reactivity. The slower rate of formation of **3b** at room temperature, and its stability once formed, reflect the low lability characteristic of phosphine ligands trans to an N-heterocyclic carbene. This constrains salt metathesis to a non-dissociative pathway for **1b**, rather than (as with **1a**) proceeding via a sterically accessible four-coordinate species formed by equilibrium loss of PCy_3. The stability of **3b** toward reaction with methanol indicates that for this subsequent reaction the associative pathway is either inaccessible or prohibitively slow. Precipitation of NaCl from solution (in which the proportion of CH_2Cl_2 dominates by 10:1 over MeOH) contributes to the greater driving force of the initial salt metathesis reaction.

Notable in this chemistry is the facility with which these "robust" benzylidene complexes decompose into hydride species under exceptionally mild conditions. Consumption of **1a** by alkoxide occurs within minutes at room temperature; loss of **1b**, while slower, is complete within a few hours. Reaction conditions that can give rise to adventitious alkoxides, particularly in the presence of methanol cosolvent (a favored reaction medium for olefin metathesis reactions of biologically relevant substrates),[34] should thus be recognized as profoundly detrimental to catalytic performance.

EXPERIMENTAL SECTION

General Procedures. Reactions were carried out at room temperature (23 °C) under argon using standard Schlenk or glovebox techniques, unless otherwise stated. Dry, oxygen-free solvents were obtained using a Glass Contour solvent purification system and stored over Linde 4 Å molecular sieves. C_6D_6 was degassed by consecutive freeze/pump/thaw cycles and dried over molecular sieves (Linde 4 Å). Methanol was distilled from $Mg(OMe)_2$ under Ar and stored over molecular sieves (Linde 3 Å). Sodium methoxide solutions were prepared by digesting Na metal in methanol immediately before use. $RuCl_2(PCy_3)_2(═CHPh)$ (**1a**),[35] $RuCl_2(IMes)(PCy_3)(═CHPh)$ (**1b**),[36,37] and $RuHCl(CO)(L)(PCy_3)$ (**2a**: L = PCy_3, **2b**: L = IMes)[33] were prepared according to literature procedures. NMR spectra were recorded on a Bruker Avance 300 or Avance 500 spectrometer, at 298 K unless otherwise specified. Chemical shifts are reported relative to TMS (^{13}C, ^1H), 85% external H_3PO_4 (^{31}P), or $CFCl_3$ (^{19}F) at 0 ppm. ^1H and ^{13}C NMR spectra were referenced to the carbon or residual proton signal of the deuterated solvent; ^{19}F spectra, to CF_3CO_2H at −76.55 ppm. In the NMR assignments of IMes derivatives given below, *a/b* labels indicate corresponding, inequivalent nuclei on the same mesityl ring, as indicated by HMQC or HMBC correlations. IR spectra were measured as Nujol mulls between NaCl plates using a Bomem MB100 spectrometer or as powders using a Varian 640-IR reflectance IR spectrometer. Microanalyses were carried out by Guelph Chemical Laboratories Ltd., Guelph, Ontario.

NMR-Scale Reactions of Grubbs Catalysts with Methoxide. In a representative reaction, a solution of **1a** (10 mg, 0.012 mmol) was dissolved in CH_2Cl_2 (0.7 mL, with a 50 μL spike of C_6D_6) in a J. Young NMR tube. To this was added NaOMe as a solution in MeOH (9.7 μL of a 3.75 M solution, 3 equiv), and the reactions were monitored by NMR analysis (in some cases with Ph_3PO added as an internal standard for integration). No solvent suppression was used for the ^1H NMR spectra, as the alkylidene and hydride regions (10 to 30 ppm and 0 to −30 ppm, respectively) could be viewed without interference.

$RuCl_2(PCy_3)_2(═CHPh)$ (1a) + Methoxide: Observation of 4a and 5a. The solution changed color from deep purple to pale yellow over 5 min. $^{31}P\{^1H\}$ NMR (CH_2Cl_2−MeOH−C_6D_6): δ 52.1 (s, **4a**, 48%), 72.0 (s, **5a**, 19%); 11.1 (s, PCy_3, 13%); the deficit is attributed to paramagnetic material (see text). ^1H NMR (CH_2Cl_2−MeOH−C_6D_6; hydride region): δ −4.59 (**4a**), −7.45 (**5a**). For the synthesis and full characterization of **4a**, see below.

$RuCl_2(IMes)(PCy_3)(═CHPh)$ (1b) + Methoxide: Observation of 3b. A color change from red to pale orange-yellow occurred over 4 h. $^{31}P\{^1H\}$ NMR (CH_2Cl_2−MeOH−C_6D_6): δ 49.6 (**3b**, 73%), 11.1 (s, PCy_3, 10%); the deficit is attributed to paramagnetic material (see text). ^1H NMR (CH_2Cl_2−MeOH−C_6D_6; hydride region): δ −25.02 ppm (**3b**). For the synthesis of **3b** using 20 equiv of NaOMe, with full details of NMR characterization, see below.

In Situ Observation of 5a. Complex **5a** was generated in situ (as a 2:1 mixture of **4a** and **5a**) as described above. Sweeping the atmosphere with Ar resulted in partial transformation of **5a** into **3a** (ca. 15% vs the original **1a**). This was readily reversed by freeze−pump−thaw degassing (3×) and backfilling with H_2. NMR data for **5a**: $^{31}P\{^1H\}$ NMR (121.5 MHz, 10:1 CH_2Cl_2−MeOH): δ 72.0 (s). ^1H NMR (300.1 MHz, 10:1 CH_2Cl_2−MeOH): δ −7.45 (br s). Hydride $T_{1(min)}$ (C_7D_8, H_2, 263 K, 500.1 MHz): 37.5 ms (d_{H-H} = 0.95 Å for fast-spinning H_2).[26,38] Decoalescence was not observed down to −90 °C in C_7D_8.

Synthesis of $RuH(OMe)(CO)(IMes)(PCy_3)$, 3b. Adding a solution of NaOMe in methanol (300 μL, 2.75 M, 0.83 mmol, 20 equiv) to a vigorously stirred solution of $RuHCl(CO)(IMes)(PCy_3)$ (**2b**) (31 mg, 0.041 mmol) in 3 mL of CH_2Cl_2 caused a color change from orange-yellow to red-orange over 15 min. In situ $^{31}P\{^1H\}$ NMR analysis indicated solely **3b**. The solvent was stripped off, and the residue was redissolved in benzene, filtered through Celite, and stripped to dryness. Yield: 24 mg (78%). $^{31}P\{^1H\}$ NMR analysis of the residue revealed, in addition to **3b**, small amounts of $Ru(H)_2(CO)_2(IMes)$-

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(PCy_3) (**6b**) (5%), $RuH(OMe)(CO)_2(IMes)(PCy_3)$ (**4b**) (2%), and free PCy_3 (5%), which impede microanalysis. Data for **3b**: $^{31}P\{^1H\}$ NMR (121.5 MHz, C_7D_8): δ 50.2 (s). ^1H NMR (300.1 MHz, C_6D_6): δ 6.85 (s, 2H, Mes *m*-CH^b) 6.83 (s, 2H, Mes *m*-CH^a), 6.26 (s, 2H, =C*H*N), 4.22 (s, 3H, OCH_3), 2.42−2.38 (two overlapping s, 12H, Mes *o*-CH_3), 2.14 (s, 6H, Mes *p*-CH_3), 2.2−1.1 (m, Cy; accurate integration impeded by overlap with Cy signals for **6b**, **4b**), −23.61 (d, $^2J_{HP}$ = 22.2 Hz, 1H, Ru*H*). $^{13}C\{^1H\}$ NMR (125.8 MHz, C_7D_8, 243 K): δ 204.7 (d, $^2J_{CP}$ = 8.7 Hz, *C*O), 193.9 (d, $^2J_{CP}$ = 103.2 Hz, *N*CN), 138.3 (s, Mes *p*-*C*), 138.0 (br, Mes *o*-*C*), 137.3 (br, Mes *o*-*C*), 136.4 (s, Mes *i*-*C*), 129.0 (s, Mes *m*-*C*H), 122.1 (s, =*C*HN), 63.5 (br s, $\omega_{0.5}$ 25 Hz, OCH_3), 34.2 (d, $^1J_{CP}$ = 16.6 Hz, C1 of Cy), 31.1 (s, Cy), 30.2 (s, Cy) 28.6 (m, Cy), 27.4 (s, Cy), 21.5 (s, Mes *p*-CH_3), 19.3 (s, Mes *o*-CH_3). IR (Nujol, cm^{-1}): ν(CO) 1875 (s); ν(Ru−H) 1890 (w).

Preparation of $RuH(OMe)(CO)_2(L)(PCy_3)$, 4a/b. *L = PCy₃, **4a**.* Addition of NaOMe as a solution in methanol (49 μL, 3.58 M, 0.18 mmol) to $RuH(OSO_2CF_3)(CO)_2(PCy_3)_2$ (**8a**) (150 mg, 0.173 mmol) in THF (5 mL), with stirring, caused a color change from pale brown to yellow over 30 min and deposition of a white precipitate. The reaction mixture was stripped to dryness, and the residue was taken up in CH_2Cl_2 (15 mL). The mixture was filtered through Celite, concentrated to ca. 0.5 mL, treated with hexanes (5 mL), and chilled to −35 °C. A light yellow powder deposited, which was filtered off, washed with cold hexanes (3 × 2 mL), and dried under vacuum. Yield: 110 mg (85%). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ 53.8 (s). ^1H NMR (300.1 MHz, C_6D_6): δ 4.10 (s, 3H, OCH_3), 2.3−1.2 (m, 66H, Cy), −4.25 (t, $^2J_{HP}$ = 20.2 Hz, 1H, Ru*H*). $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6): δ 203.7 (t, $^2J_{CP}$ = 6.6 Hz, *C*O), 201.4 (t, $^2J_{CP}$ = 11.6 Hz, *C*O), 66.4 (s, OCH_3), 34.4 (vt, $^1J_{CP}$ = 10 Hz, C1 of Cy), 29.8 (d, J_{CP} = 2.6 Hz (or two overlapping s), Cy), 28.3 (overlapping m, Cy), 27.1 (s, C4 of Cy). IR (Nujol, cm^{-1}): ν(CO) 2006 (s), 1891 (s); ν(Ru−H) 1939 (w). Anal. Calcd for $C_{39}H_{70}O_3P_2Ru$: C, 62.46; H, 9.41. Found: C, 62.07; H, 9.77.

*L = IMes, **4b**.* The light yellow powder was prepared as for **4a**, from $RuH(OSO_2CF_3)(CO)_2(IMes)(PCy_3)$ (**8b**) (154 mg, 0.173 mmol). Yield: 115 mg (86%). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ 54.0 (s). ^1H NMR (300.1 MHz, C_6D_6): δ 6.91 (s, 2H, Mes *m*-CH^a), 6.89 (s, 2H, Mes *m*-CH^b), 6.32 (s, 2H, =C*H*N), 3.96 (s, 3H, OCH_3), 2.37 (s, 6H, Mes *o*-C$H_3{}^b$), 2.30 (s, 6H, Mes *o*-C$H_3{}^a$), 2.20 (s, 6H, Mes *p*-CH_3), 2.2−1.0 (m, 33H, Cy), −4.18 (d, $^2J_{HP}$ = 25.3 Hz, 1H, Ru*H*). $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6): δ 202.9 (d, $^2J_{CP}$ = 12.4 Hz, *C*O), 199.5 (d, $^2J_{CP}$ = 6.9 Hz, *C*O), 187.5 (d, $^2J_{CP}$ = 95.6 Hz, *N*CN), 139.4 (s, Mes *i*-*C*), 138.2 (s, Mes *p*-*C*), 137.4 (s, Mes *o*-*C*^{a}), 136.2 (s, Mes *o*-*C*^{b}), 129.2 (s, Mes *m*-*C*H^b), 128.9 (s, Mes *m*-*C*H^a), 122.3 (m, =*C*HN), 67.4 (s, OCH_3), 34.1 (d, $^1J_{CP}$ = 18.8 Hz, C1 of Cy), 29.4 (d, J_{CP} = 6.9 Hz (or two overlapping s), Cy), 28.3 (d, $^3J_{CP}$ = 9.9 Hz, Cy), 28.3 (d, $^3J_{CP}$ = 10.1 Hz, Cy), 27.0 (s, C4 of Cy), 21.2 (s, Mes *p*-CH_3), 18.4 (overlapping s, Mes *o*-CH_3). IR (powder, cm^{-1}): ν(CO) 2013 (s), 1896 (s); ν(Ru−H) 1948 (w). Anal. Calcd for $C_{42}H_{62}N_2O_3PRu$: C, 65.09; H, 8.06; N, 3.61. Found: C, 64.76; H, 7.96; N, 3.67.

Preparation of $Ru(H)_2(CO)_2(IMes)(PCy_3)$, 6b. Solid NaH (30 mg, 1.3 mmol) was added to a solution of $RuH(OSO_2CF_3)(CO)_2(IMes)(PCy_3)$ (**8b**) (110 mg, 0.123 mmol) in THF (1.0 mL), and the reaction mixture was heated to 50 °C. A color change from pale brown to light yellow occurred over 45 min, accompanied by complete transformation to **6b**. The solvent was stripped off, and the residue taken up in benzene (5 mL) and filtered through Celite. Additional, unassigned NMR signals (<5% total integration) were observed when the filtrate was stripped to dryness and redissolved in C_6D_6. Attempts to obtain pure **6b** by reprecipitation from benzene−hexanes, benzene−diethyl ether, or neat hexanes were frustrated by high solubility, and satisfactory microanalysis could not be obtained. $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ 68.9 (s). ^1H NMR (300.1 MHz, C_6D_6): δ 6.88 (s, 4H, Mes *m*-C*H*), 6.28 (s, 2H, =C*H*N), 2.24 (s, 12H, Mes *o*-CH_3), 2.19 (s, 6H, Mes *p*-CH_3), 2.0−1.1 (m, 33H, Cy), −7.37 (d, $^2J_{HP}$ = 24.9 Hz, 2H, Ru*H*). $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6): δ 204.7 (d, $^2J_{CP}$ = 7.7 Hz, *C*O), 190.1 (d, $^2J_{CP}$ = 69.8 Hz, *N*CN), 139.6 (s, Mes *i*-*C*), 138.0 (s, Mes *p*-*C*), 136.1 (s, Mes *o*-*C*), 129.2 (s, Mes *m*-*C*H), 121.5 (s, =*C*HN), 37.9 (d, $^1J_{CP}$ = 20.9 Hz, C1 of Cy), 30.1 (s, Cy), 28.1 (d, J_{CP} = 10.1 Hz, Cy), 27.0 (s, C4 of Cy), 21.2 (s, Mes *p*-CH_3), 18.6 (s, Mes *o*-CH_3). IR (Nujol, cm^{-1}): ν(CO) 1995 (s), 1951 (s); ν(Ru−H) 1898 (w).

Preparation of $RuHCl(CO)_2(IMes)(PCy_3)$, 7b. (Known[8] **7a** was prepared similarly, in 84% yield.) An orange-yellow solution of $RuHCl(CO)(IMes)(PCy_3)$ (**2b**) (320 mg, 0.546 mmol) in benzene (5 mL) was stirred under 1 atm of CO for 1 h, after which the colorless solution was concentrated (ca. 0.5 mL) and hexanes were added to precipitate the white product. This was reprecipitated from benzene−hexanes, filtered off, washed with cold hexanes (3 × 2 mL), and dried under vacuum. Yield: 270 mg (81%). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ 48.2 (s). ^1H NMR (300.1 MHz, C_6D_6): δ 6.87 (s, 2H, Mes *m*-C*H*), 6.84 (s, 2H, Mes *m*-C*H*), 6.28 (s, 2H, =C*H*N), 2.36 (s, 6H, Mes *o*-CH_3), 2.34 (s, 6H, Mes *o*-CH_3), 2.21 (s, 6H, Mes *p*-CH_3), 2.3−1.1 (m, 33H, Cy), −4.77 (d, $^2J_{HP}$ = 22.8 Hz, 1H, Ru*H*). $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6): δ 202.3 (d, $^2J_{CP}$ = 12.6 Hz, *C*O), 197.2 (d, $^2J_{CP}$ = 6.6 Hz, *C*O), 184.6 (d, $^2J_{CP}$ = 88.4 Hz, *N*CN), 139.4 (m, Mes *i*-*C*), 138.5 (s, Mes *p*-*C*), 136.9 (m, Mes *o*-*C*), 136.6 (m, Mes *o*-*C*), 129.4 (m, Mes *m*-*C*H), 122.7 (overlapping s, =*C*HN), 34.5 (d, $^1J_{CP}$ = 20.0 Hz, C1 of Cy), 29.3 (d, J = 12.4 Hz (or overlapping s), Cy), 28.0 (d, J_{CP} = 9.0 Hz, Cy), 27.9 (d, J_{CP} = 9.0 Hz, Cy), 26.8 (s, C4 of Cy), 21.2 (s, Mes *p*-CH_3), 18.8 (s, Mes *o*-CH_3), 18.7 (s, Mes *o*-CH_3). IR (powder, cm^{-1}): ν(CO) 2035 (s), 1913 (s); ν(Ru−H) 1954 (w). Anal. Calcd for $C_{41}H_{59}ClN_2O_2PRu$: C, 63.18; H, 7.63; N, 3.59. Found: C, 63.09; H, 7.53; N, 3.63.

Preparation of $RuH(OSO_2CF_3)(CO)_2(L)(PCy_3)$, 8a/b. *L = PCy₃, **8a**.* Solid $AgOSO_2CF_3$ (90 mg, 0.35 mmol) was added to $RuHCl(CO)_2(PCy_3)_2$ (**7a**) (250 mg, 0.35 mmol) in THF (15 mL) in a foil-wrapped vessel and stirred for 1 h. The solvent was stripped off under vacuum, and the residue extracted with CH_2Cl_2 (3 × 5 mL). The combined extracts were filtered through Celite, concentrated (ca. 0.5 mL), and treated with hexanes to precipitate the pale beige powder. This was chilled (−35 °C), filtered off, washed with cold hexanes (3 × 2 mL), and dried under vacuum. Yield: 200 mg (70%). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ 53.7 (s). ^1H NMR (300.1 MHz, C_6D_6): δ 2.4−1.0 (m, 66H, Cy), −4.02 (t, $^2J_{HP}$ = 18.8 Hz, 1H, Ru*H*). $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6): δ 202.7 (t, $^2J_{CP}$ = 13.5 Hz, *C*O), 201.7 (t, $^2J_{CP}$ = 7.0 Hz, *C*O), 119.8 (q, $^1J_{CF}$ = 319.2 Hz, OSO_2CF_3), 34.7 (br s, C1 of Cy), 29.7 (d, J_{CP} = 12.2 Hz (or overlapping s), Cy), 27.7 (m, Cy), 26.8 (s, C4 of Cy). $^{19}F\{^1H\}$ NMR (282.4 MHz, C_6D_6): δ −77.2 (s, CF_3). IR (powder, cm^{-1}): ν(CO) 2046 (s), 1966 (s); ν(Ru−H) 1917 (w). Anal. Calcd for $C_{39}H_{67}F_3O_5P_2RuS$: C, 53.96; H, 7.78. Found: C, 54.22; H, 8.20.

*L = IMes, **8b**.* Reaction was as for **8a**, using $RuHCl(CO)_2(IMes)(PCy_3)$ (**7b**) (250 mg, 0.321 mmol) as precursor. Yield of the pale beige powder: 190 mg (83%). In the NMR assignments, *a*/*b* labels indicate corresponding, inequivalent nuclei on the same mesityl ring, as indicated by HMQC or HMBC correlations; a prime label is used to differentiate the two Mes rings. $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ 51.3 (s). ^1H NMR (300.1 MHz, C_6D_6): δ 6.94 (s, 1H, Mes *m*-C$H^{a\prime}$), 6.89 (s, 1H, Mes *m*-CH^a), 6.84 (s, 1H, Mes *m*-CH^b), 6.73 (s, 1H, Mes *m*-C$H^{b\prime}$), 6.32 (s, 1H, =C*H*N), 6.22 (s, 1H, =C*H*N), 2.57 (s, 3H, Mes *o*-C$H_3{}^{a\prime}$), 2.34 (s, 3H, Mes *o*-C$H_3{}^a$), 2.19 (s, 3H, Mes *p*-CH_3), 2.12 (s, 3H, Mes *p*-C$H_3{}'$), 2.02 (overlapping s; 6H, Mes *o*-C$H_3{}^b$, *o*-C$H_3{}^{b\prime}$), 2.2−1.0 (m, 33H, Cy), −4.07 (d, $^2J_{HP}$ = 23.1 Hz, 1H, Ru*H*). $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6): δ 204.4 (d, $^2J_{CP}$ = 13.9 Hz, *C*O), 196.7 (d, $^2J_{CP}$ = 5.5 Hz, *C*O), 182.3 (d, $^2J_{CP}$ = 83.8 Hz, *N*CN), 139.9 (s, Mes *i*-*C*), 139.7 (s, Mes *p*-*C*$'$), 138.3 (s, Mes *p*-*C*), 138.1 (s, Mes *o*-*C*$^{a\prime}$), 137.5 (s, Mes *o*-*C*^{a}), 137.3 (s, Mes *i*-*C*$'$), 135.3−135.2 (overlapping s, Mes *o*-*C*^{b}, *o*-*C*$^{b\prime}$), 130.4 (s, Mes *m*-C$H^{a\prime}$), 129.4 (s, Mes *m*-CH^a), 129.1 (s, Mes *m*-C$H^{b\prime}$), 128.5 (s, Mes *m*-CH^b), 123.5 (s, =*C*HN), 119.9 (q, $^1J_{CF}$ = 320.4 Hz, OSO_2CF_3), 34.2 (d, $^1J_{CP}$ = 15.7 Hz, C1 of Cy), 29.3 (overlapping s, Cy), 27.8 (d, J_{CP} = 10.2 Hz, Cy), 27.7 (d, J_{CP} = 10.4 Hz, Cy), 26.7 (s, C4 of Cy), 21.0 (coincident s, Mes *p*-CH_3, *p*-C$H_3{}'$), 19.1 (s, Mes *o*-CH_3), 18.4−18.3 (overlapping s, Mes *o*-CH_3). $^{19}F\{^1H\}$ NMR (282.4 MHz, C_6D_6): δ −77.1 (s, CF_3). IR (powder, cm^{-1}): ν(CO) 2049 (s), 1935 (s); ν(Ru−H) 1972 (w).

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Anal. Calcd for $C_{42}H_{59}F_3N_2O_5PRuS$: C, 56.49; H, 6.66; N, 3.14. Found: C, 56.65; H, 6.68; N, 3.10.

■ ASSOCIATED CONTENT

Supporting Information

Kinetics plots showing phosphine-dependence studies, and NMR spectra for the new complexes **3b**, **4a**/**b**, **6b**, **7b**, and **8a**/**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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