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Synthesis of Cyclopentadienyl(1,4-diisopropyl-1,3-diazabutadiene)(L)ruthenium Trifluoromethanesulfonate (L = Alkene, Alkyne, CO, Pyridine, PPh_3). X-ray Structure of $[(\eta^5\text{-}C_5H_5)Ru(iPr\text{-}DAB)(\eta^2\text{-propene})][CF_3SO_3]$[†]

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Reaction of CpRuCl(iPr-DAB) (**1**) with AgOTf ($AgCF_3SO_3$) in THF and subsequent addition of L (L = ethene (**a**), propene (**b**), *cis*-2-butene (**c**), dimethyl maleate (**d**), dimethyl fumarate (**e**), fumaronitrile (**f**), acetylene (**i**), dimethyl acetylenedicarboxylate (DMAC) (**j**), CO (**l**), pyridine (**m**), triphenylphosphine (**n**)) led to the ionic complexes [CpRu(iPr-DAB)(L)][OTf] **2a−f,i,j,l−n**, respectively. For *trans*-2-butene (**g**) and 2-methylpropene (**h**), no coordination complex was formed. Addition of methyl propiolate ($HC{\equiv}CC(O)OCH_3$, **k**) to [CpRu(iPr-DAB)][OTf] resulted in $[CpRu(iPr\text{-}DAB)(\eta^2\text{-}HC{\equiv}CC(O)OCH_3)][OTf]$ (**2k**) and **2l** in a 4:1 ratio. An X-ray structure determination on **2b** was carried out. Crystal data for **2b**: triclinic, space group $P\bar{1}$ with $a = 9.0649(6)$ Å, $b = 9.6151(6)$ Å, $c = 13.0099(6)$ Å, $\alpha = 94.322(6)°$, $\beta = 104.258(8)°$, $\gamma = 98.977(6)°$, $Z = 2$, final $R = 0.033$. Surprisingly, the structure shows the propene η^2-coordinated to the metal center with the methyl group pointing toward the cyclopentadienyl ring. Nucleophilic attack of OCH_3^- on $[CpRu(iPr\text{-}DAB)(\eta^2\text{-dimethyl maleate})][OTf]$ (**2d**) at 20 °C led to two diastereomers of $CpRu(iPr\text{-}DAB)CH(C(O)OCH_3)CH(OCH_3)(C(O)OCH_3)$ (**3**) in a 97:3 ratio. Reaction of $[CpRu(iPr\text{-}DAB)(\eta^2\text{-DMAC})][OTf]$ (**2j**) with $^-OCH_3$ at 20 °C yielded $CpRu(iPr\text{-}DAB)OCH_3$ (**6**), whereas reaction at −40 °C gave **6** (30%) and $CpRu(iPr\text{-}DAB)C(C(O)OCH_3){=}C(OCH_3)(C(O)OCH_3)$ (**4**; 70%). Reaction of **2d** with NH_2iPr and $NHiPr_2$ as the nucleophiles yielded the substitution products $[CpRu(iPr\text{-}DAB)(NH_2iPr)][OTf]$ (**2p**) and $[CpRu(iPr\text{-}DAB)(NHiPr_2)][OTf]$ (**2q**), respectively. Complex **2j** reacted with NH_2iPr to form **2p**, whereas **2j** was inert to substitution with $NHiPr_2$.

Introduction

Complexes of the type $[CpML_2(\eta^2\text{-}un)][X]$ (*un* = alkene, alkyne; Cp = cyclopentadienyl) are well-known for M = Fe and provide useful starting complexes for C−C coupling reactions *via* nucleophilic attack on the activated substrate.[1,2] Whereas the iron complexes have attracted much attention,[2] little is known about the synthesis and reactions of the ruthenium analogues.[3] The complexes $[CpRu(CO)_2(\eta^2\text{-ethene})]$,[4] $[CpRu(PPh_3)_2(\eta^2\text{-ethene})]$,[5] $[CpRu(PPh_3)_2(\eta^2\text{-styrene})]$,[5] $[CpRu(PMe_2Ph)_2(HC{\equiv}CH)]$,[6] $[CpRu(dppe)(\eta^2\text{-alkene})]$,[7] and the chiral $[CpRu\{(S,S)\text{-}Ph_2PCH(CH_3)CH(CH_3)PPh_2\}(\eta^2\text{-alkene})]$[8] all feature an electron-donating alkene in combination with π-accepting phosphine or carbonyl ligands. An exception is $[CpRu(PMe_3)_2(\eta^2\text{-}un)]$, which not only coordinates the electron-donating alkenes and alkynes (*un*) $CH_2{=}CHPh$, $CH_2{=}CHCN$, $CH_2{=}CHCH_3$, *trans*-$ClHC{=}CClH$, $PhC{\equiv}CPh$, and $EtC{\equiv}CEt$ but also diethyl maleate and dimethyl acetylenedicarboxylate (DMAC).[9] Recently several complexes $[Cp^*Ru(bpy)(\eta^2\text{-}un)]$ were described (Cp* = pentamethylcyclopentadienyl, bpy 2,2′-bipyridine), in which alkenes and alkynes (*un*) with electron-withdrawing substituents such as diethyl maleate, ethyl maleate, and DMAC are coordinated.[10] The X-ray structure of $[Cp^*Ru(bpy)(\eta^2\text{-diethyl maleate})][PF_6]$ (Figure 1) shows the alkene in the η^2 coordination mode, with both ester groups pointing away from the Cp*

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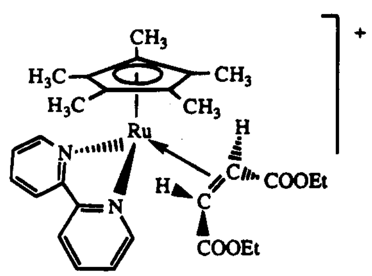

Figure 1. Schematic presentation of [Cp*Ru(bpy)(η^2-diethyl maleate)].[10]

ring.[10] However, it was reported that it was not possible to coordinate unsaturated hydrocarbons bearing no electron-withdrawing groups, such as ethene, cyclohexene, stilbene or diphenylacetylene, most probably because of an insufficient π back-bonding interaction from the electron-rich [Cp*Ru(bpy)] fragment into the high-lying π^* orbital of the electron-rich alkenes or alkynes.[10]

Apart from [Cp*Ru(bpy)(*un*)], there are no precedents in the literature for cyclopentadienylruthenium complexes with alkenes or alkynes stabilized by σN,σN′ donor ligands.[10] Here we wish to report complexes of this type with the α-diimine ligand 1,4-diisopropyl-1,3-diazabutadiene (iPr-DAB), which is a strong σ donor and a better π acceptor than bipyridine,[11] and Cp instead of Cp*, since replacement of Cp* by Cp is expected to diminish the electron density on the metal center. It will be shown that the combination of the iPr-DAB ligand and the Cp ligand makes the ruthenium complex very flexible in its electronic properties, since it has been possible to coordinate both alkenes with electron-donating and with electron-withdrawing substituents to the same metal fragment. Furthermore, the reactivity of the complexes [CpRu(iPr-DAB)(η^2-dimethyl maleate)][OTf] **(2d)** and [CpRu(iPr-DAB)(η^2-DMAC)][OTf] **(2j)** toward $^-OCH_3$, NH_2iPr, and $NHiPr_2$ was investigated.

Experimental Section

$RuCl_3{\cdot}3H_2O$ was obtained as a loan from Johnson Matthey, Inc., and CpRuCl(iPr-DAB) was prepared according to the literature.[12] Alkenes were obtained from commercial suppliers and used as received. Unless stated otherwise, all syntheses were carried out under an atmosphere of dry nitrogen, using standard Schlenk techniques. Solvents were dried by refluxing over sodium metal or calcium carbonate. Column chromatography was performed using dried and activated silica gel (Kieselgel 60, E. Merck, 70–238 mesh) as the stationary phase. ^1H and ^{13}C NMR measurements were carried out on Bruker AMX 300 or AC 100 spectrometers at 293 K unless stated otherwise. ^{19}F NMR measurements were performed on an Bruker AC 100 spectrometer (94.22 MHz) at 293 K. Chemical shifts (δ, ppm) are given relative to $SiMe_4$. IR spectra were recorded on KBr pellets with a Perkin-Elmer 283 spectrometer. Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr 1, Germany. The products were identified by elemental analysis and ^1H, ^{13}C, and ^{19}F NMR and IR spectroscopy.

[CpRu(iPr-DAB)][OTf]. Solid CpRuCl(iPr-DAB) (10 mg, 0.03 mmol) and AgOTf (8.26 mg, 0.03 mmol) were placed in an NMR tube under an N_2 atmosphere. After addition of 0.3 mL of acetone-d_6 the NMR spectra were recorded. ^1H NMR (100.13 MHz, 213 K, acetone-d_6): δ 1.54 (d, 6H, $CH(CH_3)_2$) and 1.59 (d, 6H, $CH(CH_3)_2$), 4.86 (s, 5H, C_5H_5), 4.7–4.9 (m, $CH(CH_3)_2$), 8.92 (s, 2H, $CH{=}N$). ^{13}C NMR (75.46 MHz, acetone-d_6): δ 24.7 and 25.3 ($CH(CH_3)_2$), 50.6 ($H_2C{=}C$), 69.3 ($CH(CH_3)_2$), 85.7 (C_5H_5), 159.7 ($CH{=}N$). ^{19}F NMR (acetone-d_6): δ −77.8 ($CF_3SO_3^-$). Except for signals of the added solvents, no change was observed in the ^1H and ^{19}F NMR spectra upon addition of CH_3CN or THF.

[CpRu(iPr-DAB)(η^2-ethene)][OTf] (2a). CpRuCl(iPr-DAB) (100 mg, 0.29 mmol) and AgOTf (83 mg, 0.32 mmol) were dissolved in 30 mL of THF. After 15 min of stirring at room temperature, the suspension was filtered, and the red-brown solution was cooled to 0 °C in an ice bath. A stream of ethene was slowly passed through the solution. Within 1–2 min the solution turned yellow, indicating that the reaction was complete. Addition of diethyl ether to this solution yielded **2a** as a red-brown solid (172 mg/ yield 99%). Recrystallization by diffusion of hexane into a THF solution of **2a** gave small red block-shaped crystals. IR (cm^{-1} in KBr): ν(SO) 1370 (m), 1260–1280 (vs), 1160 (s), 1030 (m). Anal. Calcd for $C_{16}H_{25}N_2O_3SF_3Ru$: C, 39.74; H, 5.21; N, 5.79. Found: C, 39.71; H, 5.14; N, 5.72. ^1H NMR (300.13 MHz, acetone-d_6): δ 1.65 (d, J = 6.6 Hz, 6H, $CH(CH_3)_2$) and 1.67 (d, J = 6.6 Hz, 6H, $CH(CH_3)_2$), 3.28 (s, 4H, $H_2C{=}C$), 5.26 (sept, J = 6.6 Hz, 2H, $CH(CH_3)_2$), 5.48 (s, 5H, C_5H_5), 8.50 (s, 2H, $CH{=}N$). ^{13}C NMR (75.46 MHz, acetone-d_6): δ 24.7 and 25.3 ($CH(CH_3)_2$), 50.6 ($H_2C{=}C$), 69.3 ($CH(CH_3)_2$), 85.7 (C_5H_5), 159.7 ($CH{=}N$). ^{19}F NMR (acetone-d_6): δ −77.9 ($CF_3SO_3^-$).

[CpRu(iPr-DAB)(η^2-propene)][OTf] (2b). The same procedure as for **2a** with CpRuCl(iPr-DAB) (61 mg, 0.18 mmol), AgOTf (46 mg, 0.18 mmol), and propene as starting materials yielded **2b** (90 mg/ 99% yield). Recrystallization by diffusion of hexane into THF gave red block-shaped crystals. IR (cm^{-1} in KBr): ν(SO) 1275–1260 (broad, s), 1223 (w), 1165 (broad, s), 1028 (m). Anal. Calcd for $C_{17}H_{27}N_2O_3SF_3Ru$: C, 41.03; H, 5.47; N, 5.63. Found: C, 40.06; H, 5.43; N, 5.25. ^1H NMR (300.13 MHz, acetone-d_6): δ 1.55, 1.58, 1.69, and 1.72 (4 d, J = 6.6 Hz, 3H, $CH(CH_3)_2$), 1.95 (d, J = 7.0 Hz, 3H, $C{=}CH(CH_3)$), 2.70 (m, 1H, $H_2C{=}CH$), 2.85 (d, J = 8.1 Hz, 1H, $H_aH_bC{=}C$), 4.11 (d, J = 12.6 Hz, 1H, $H_aH_bC{=}C$), 5.11 and 5.35 (sept, J = 6.6 Hz, 1H, $CH(CH_3)_2$), 5.39 (s, 5H, C_5H_5), 8.47 and 8.53 (d, J = 0.8 Hz, 1H, $CH{=}N$). ^1H NMR (300.13 MHz, 190 K, acetone-d_6): δ 1.53–1.78 (m, 12H, $CH(CH_3)_2$), 2.02 (d, J = 7.0 Hz, 3H, $C{=}CH(CH_3)$), 2.39 (m, 1H, $H_aH_bC{=}CH_c$), 2.69 (dd, $J(H_bH_c)$ = 7.8 Hz, 1H, $H_aH_bC{=}C$), 4.20 (dd, $J(H_aH_c)$ = 12.6 Hz, 1H, $H_aH_bC{=}C$), 5.09 and 5.38 (m, 1H, $CH(CH_3)_2$), 5.54 (s, 5H, C_5H_5), 8.58 and 8.67 (s, 1H, $CH{=}N$). ^{13}C NMR (75.46 MHz, acetone-d_6): δ 23.9, 24.4, 24.7, and 25.4 ($CH(CH_3)_2$), 26.5 ($CH_3C(H){=}C$), 53.4 ($H_2C{=}C$), 68.7 and 68.8 ($CH(CH_3)_2$), 73.3 ($CH_3CH{=}C$), 86.1 (C_5H_5), 159.6 and 159.7 ($CH{=}N$). ^{19}F NMR (acetone-d_6): δ −77.8 ($CF_3SO_3^-$).

[CpRu(iPr-DAB)(η^2-*cis*-2-butene)][OTf] (2c). The same procedure as for **2a** but with CpRuCl(iPr-DAB) (18.1 mg, 0.06 mmol), AgOTf (15 mg, 0.06 mmol), and *cis*-2-butene as starting materials gave **2c** as a yellow solid (30 mg; yield 99%). ^1H NMR (300.13 MHz, acetone-d_6): δ 1.68 (d, J = 6.6 Hz, 6H, $CH(CH_3)_2$) and 1.72 (d, J = 6.6 Hz, 6H, $CH(CH_3)_2$), 2.04 (d, J = 5.8 Hz, 6H, $CH_3C(H){=}C$), 3.03 (q, J = 5.8 Hz, 2H, $CH_3C(H){=}C$), 5.30 (sept, J = 6.6 Hz, 2H, $CH(CH_3)_2$), 5.30 (s, 5H, C_5H_5), 8.53 (s, 2H, $CH{=}N$). ^{13}C NMR (75.46 MHz, acetone-d_6): δ 18.9 ($CH_3C(H){=}C$), 24.7 and 25.6 ($CH(CH_3)_2$), 68.7 ($CH(CH_3)_2$), 73.2 ($CH_3C(H){=}C$), 86.7 (C_5H_5), 159.4 ($CH{=}N$).

[CpRu(iPr-DAB)(η^2-dimethyl maleate)][OTf] (2d). The same procedure as for **2a** (CpRuCl(iPr-DAB) (88 mg, 0.26 mmol), AgOTf (70 mg, 0.27 mmol)) but with addition of dimethyl maleate (41 mg, 28 mmol) yielded within 15 min a yellow solid precipitate. After filtration **2d** was obtained in pure form (154 mg; yield 99%). IR (cm^{-1} in KBr): ν(CO) 1740 (s); ν(SO) 1265–1280 (s), 1225 (w), 1160 (m), 1057 (m) cm^{-1}. Anal. Calcd for $C_{20}H_{29}N_2O_7SF_3Ru$: C, 40.06; H, 4.87; N, 4.67.

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Found: C, 39.97; H, 4.82; N, 4.70. ^{1}H NMR (300.13 MHz, acetone-d_6): δ 1.64 (d, J = 6.6 Hz, 6H, CH(CH_3)$_2$) and 1.66 (d, J = 6.6 Hz, 6H, CH(CH_3)$_2$), 3.58 (s, 2H, CH$_3$O(O)CC(H)=C), 3.84 (s, 6H, CH_3O(O)CC(H)=C), 5.14 (sept, J = 6.6 Hz, 2H, CH(CH$_3$)$_2$), 5.61 (s, 5H, C$_5H_5$), 8.59 (s, 2H, CH=N). ^{13}C NMR (75.46 MHz, acetone-d_6): δ 24.7 and 25.0 (CH(CH$_3$)$_2$), 52.7 (CH$_3$O(O)CCH=C), 55.0 (CH$_3$O(O)CC(H)=C), 69.0 (CH(CH$_3$)$_2$), 91.7 (C_5H$_5$), 164.5 (CH=N), 172.7 (CH$_3$O(O)CC(H)=C). ^{19}F NMR (acetone-d_6): δ −77.8 (CF$_3$SO$_3^-$).

[CpRu(iPr-DAB)(η^2-dimethyl fumarate)][OTf] (2e). With CpRuCl(iPr-DAB) (36 mg, 0.11 mmol) and AgOTf (27 mg, 0.11 mmol) as starting materials and with addition of dimethyl fumarate (14 mg, 0.10 mmol), the same procedure as for **2a** yielded a brown solution. The solution was stirred at 22 °C for 3 h, during which time the solution turned yellow. Addition of diethyl ether to this solution gave **2e** as a yellow solid (63 mg; yield 99%). IR (cm^{-1} in KBr): ν(CO) 1710−1720 (m); ν(SO) 1275−1265 (s), 1225 (w), 1160(m), 1057 (m). Anal. Calcd for C$_{20}$H$_{29}$N$_2$O$_7$SF$_3$Ru: C, 40.06; H, 4.88; N, 4.67. Found: C, 39.96; H, 4.90; N, 4.57. ^{1}H NMR (300.13 MHz, acetone-d_6, 255 K): δ 1.61 (d, J = 6.6 Hz, 6H, CH(CH_3)$_2$) and 1.69 (d, J = 6.6 Hz, 6H, CH(CH_3)$_2$), 3.65 and 3.78 (s, 3H, CH_3O(O)CC(H)=C), 3.96 and 4.88 (d, J = 10.5 Hz, 1H, CH$_3$O(O)CC(H)=C), 4.93 and 5.08 (sept, J = 6.6 Hz, 1H, CH(CH$_3$)$_2$), 5.66 (s, 5H, C$_5H_5$), 8.55 and 8.67 (d, J = 0.8 Hz, 1H, CH=N). ^{13}C NMR (75.46 MHz, acetone-d_6, 255 K): δ 24.9, 25.1, 25.2, 26.1 (CH(CH$_3$)$_2$), 48.4 and 52.3 (CH$_3$O(O)CC(H)=C), 52.5 and 53.2 (CH$_3$O(O)-CCH=C), 69.0 and 69.8 (CH(CH$_3$)$_2$), 91.8 (C_5H$_5$), 164.5 and 164.8 (CH=N), 173.5 and 175.0 (CH$_3$O(O)CC(H)=C). ^{19}F NMR (acetone-d_6): δ −77.8 (CF$_3$SO$_3^-$).

[CpRu(iPr-DAB)(η^2-fumaronitrile)][OTf] (2f). CpRuCl-(iPr-DAB) (69 mg, 0.20 mmol) and AgOTf (62 mg, 0.24 mmol) were dissolved in 20 mL of THF. After 30 min the red-brown suspension was filtered and fumaronitrile (31 mg, 0.40 mmol) was added. The brown solution was refluxed for 4 h, after which time the solvent was evaporated in vacuo. The solid was washed three times with 20 mL of diethyl ether and recrystallized from a CH$_2$Cl$_2$/hexane (5/1) mixture (85 mg; yield 80%). IR (cm^{-1} in KBr): ν(CN) 2217 (w); ν(SO) 1260 (vs), 1222 (m), 1155 (s), 1112 (w), 1027 (m). Anal. Calcd for C$_{18}$H$_{23}$-N$_4$O$_3$SF$_3$Ru·$^1/_2$CH$_2$Cl$_2$: C, 38.57; H, 4.20; N, 9.72. Found: C, 39.17; H, 4.40; N, 9.45. ^{1}H NMR (300.13 MHz, acetone-d_6): δ 1.60, 1.66, 1.71, 1.77 (4 d, J = 6.6 Hz, 3H, CH(CH_3)$_2$), 3.62 (d, J = 9.9 Hz, 1H, CH=), 4.90−5.09 (m, 2H, CH(CH$_3$)$_2$), 5.10 (d, J = 9.9 Hz, 1H, CH=), 5.96 (s, 5H, C$_5H_5$), 8.78 and 8.85 (s, 1H, CH=N). ^{13}C NMR (75.46 MHz, acetone-d_6, 293 K): δ 29.2, 29.3, 29.7, and 29.8 (CH(CH$_3$)$_2$), 70.9 (C=C), 73.3 and 74.5 (CH-(CH$_3$)$_2$), 98.6 (C_5H$_5$), 125.4 (CN), 170.8 and 171.9 (C(H)=N). ^{19}F NMR (acetone-d_6): δ −77.8 (CF$_3$SO$_3$).

Attempts To Synthesize [CpRu(iPr-DAB)(η^2-*trans*-2-butene)][OTf]. CpRuCl(iPr-DAB) (38.2 mg, 0.11 mmol) and AgOTf (30 mg, 0.12 mmol) were dissolved in 30 mL of THF. After 15 min of stirring at 20 °C, the suspension was filtered, and the red-brown solution was cooled to 0 °C in an ice bath. A stream of *trans*-2-butene was slowly passed through the solution. After evaporation of the solvent *in vacuo* a red-brown solid resulted. However, NMR showed that the desired product [CpRu(iPr-DAB)(η^2-*trans*-2-butene)][OTf] had not been formed; rather, [CpRu(iPr-DAB)][OTf] was isolated. The same reaction carried out in CH$_2$Cl$_2$ at 20 °C yielded [CpRu(iPr-DAB)][OTf] also. When a solution of [CpRu(iPr-DAB)][OTf] was placed under an ethene atmosphere, product **2a** was formed in quantitative yield.

When **2a** was placed under a *trans*-2-butene atmosphere for several days, ^{1}H NMR revealed that no [CpRu(iPr-DAB)(η^2-*trans*-2-butene)][OTf] was formed.

Attempt To Synthesize [CpRu(iPr-DAB)(η^2-2-methyl-propene)][OTf]. CpRuCl(iPr-DAB) (72.6 mg, 0.21 mmol) and AgOTf (55 mg, 0.22 mmol) was dissolved in 30 mL of THF. After 15 min of stirring at 20 °C, the suspension was filtered, and the red-brown solution was cooled to 0 °C in an ice bath. A stream of 2-methylpropene was slowly passed through the solution. After 15 min the solution turned brown-yellow and the solvent was evaporated *in vacuo*. NMR revealed that only [CpRu(iPr-DAB)][OTf] was formed.

[CpRu(iPr-DAB)(η^2-HC≡CH)][OTf] (2i). CpRuCl(iPr-DAB) (45 mg, 0.13 mmol) and AgOTf (37 mg, 0.14 mmol) were dissolved in 20 mL of CH$_2$Cl$_2$. After 15 min of stirring at 20 °C, the suspension was filtered and placed under an atmosphere of acetylene. Adding 10 mL of hexane and cooling the solution to −20 °C resulted in a brown precipitate of **2i** (80% yield). ^{1}H NMR (300.13 MHz, acetone-d_6): δ 1.59 (d, J = 6.6 Hz, 6H, CH(CH_3)$_2$) and 1.64 (d, J = 6.6 Hz, 6H, CH(CH_3)$_2$), 2.96 (s, 2H, HC≡C), 4.65 (s, 5H, C$_5H_5$), 4.78 (sept, J = 6.6 Hz, 2H, CH(CH$_3$)$_2$), 8.59 (s, 2H, CH=N). ^{13}C NMR (75.46 MHz, acetone-d_6): δ 24.4 and 24.8 (CH(CH$_3$)$_2$), 69.2 (CH(CH$_3$)$_2$), 77.1 (C_5H$_5$), 156.3 (CH=N) (CH≡C not observed).

[CpRu(iPr-DAB)(η^2-DMAC)][OTf] (2j). CpRuCl(iPr-DAB) (316 mg, 0.93 mmol) and AgOTf (296 mg, 1.15 mmol) were dissolved in 30 mL of THF. After 15 min of stirring at 22 °C, the suspension was filtered and cooled to 0 °C. Carefully, DMAC (0.2 μL, 1.41 mmol) was added to the solution. The brown solution was stirred, first at 0 °C and then at 20 °C for 2 h. Adding diethyl ether to the orange solution and cooling to −20 °C gave orange crystals of [CpRu(iPr-DAB)(η^2-DMAC)]-[OTf] (**2j**; 440 mg, 80% yield). IR (cm^{-1} in KBr): ν(C≡C) 1896 (m); ν(CO) 1712 (vs); ν(SO) 1220−1280 (s), 1154 (m), 1030 (s). Anal. Calcd for C$_{22}$H$_{27}$N$_2$O$_7$SF$_3$Ru: C, 42.50; H, 4.38; N, 4.50. Found: C, 39.98; H, 4.46; N, 4.95. ^{1}H NMR (300.13 MHz, acetone-d_6): δ 1.50 (d, J = 6.6 Hz, 6H, CH(CH_3)$_2$) and 1.63 (d, J = 6.6 Hz, 6H, CH(CH_3)$_2$), 4.00 (s, 6H, CH_3O(O)C≡C), 5.27 (sept, J = 6.6 Hz, 2H, CH(CH$_3$)$_2$), 5.95 (s, 5H, C$_5H_5$), 8.61 (d, J = 0.8 Hz, 2H, CH=N). ^{13}C NMR (75.46 MHz, acetone-d_6): δ 23.9 and 25.3 (CH(CH$_3$)$_2$), 54.2 (CH$_3$O(O)CC≡C), 69.6 (CH-(CH$_3$)$_2$), 84.4 (C≡CC(O)CH$_3$), 91.2 (C_5H$_5$), 161.9 (C≡CC(O)-CH$_3$), 162.9 (CH=N).

[CpRu(iPr-DAB)(η^2-methyl propiolate)][OTf] (2k). CpRuCl(iPr-DAB) (89.3 mg, 0.26 mmol) and AgOTf (73.8 mg, 0.29 mmol) were dissolved in 30 mL of THF. After 15 min of stirring at room temperature, the suspension was filtered, and methyl propiolate (25 μL, 0.29 mmol) was added to the solution. The brown solution was stirred at room temperature for 45 min, during which time the solution turned orange. Addition of diethyl ether gave a yellow solid which contained **2k** (80% yield) together with [CpRu(iPr-DAB)(CO)][OTf] (**2l**; 20% yield).

Carrying out the reaction at 0 °C, at 20 °C with a 3-fold excess of MCA (MCA = methyl propiolate), or at 20 °C in the presence of H$_2$O (0.1 mL) or O$_2$ did not change the ratio **2k**:**2l**.

Selected data for **2k** from a mixture of **2k** and **2l** are as follows. IR (cm^{-1} in KBr): ν(CO) (**2l**) 1970; ν(CO) (**2k**) 1820; ν(C≡C) 1695 (s); ν(SO) 1240−1280 (s), 1225 (w), 1160 (broad, m), 1032 (s). No satisfactory elemental analysis could be obtained because of decomposition of the product. Selected data for **2k**: ^{1}H NMR (300.13 MHz, acetone-d_6, 255 K): δ 1.46 (d, J = 6.6 Hz, 6H, CH(CH_3)$_2$) and 1.58 (d, J = 6.6 Hz, 6H, CH(CH_3)$_2$), 3.69 (s, 3H, CH_3O(O)C≡C), 5.43 (sept, J = 6.6 Hz, 2H, CH(CH$_3$)$_2$), 5.71 (s, 5H, C$_5H_5$), 7.03 (s, 1H, HC≡C), 8.50 (d, J = 0.8 Hz, 2H, CH=N). ^{13}C NMR (75.46 MHz, acetone-d_6, 255 K): δ 24.2 and 25.3 (CH(CH$_3$)$_2$), 53.9 (CH$_3$O(O)CC≡C), 68.3 (CH≡C), 69.5 (CH(CH$_3$)$_2$), 82.8 (HC≡CC(O)CH$_3$), 89.3 (C_5H$_5$), 160.3 (CH=N), 161.8 (CH$_3$O(O)CC≡C). ^{19}F NMR (acetone-d_6): δ −77.8 (CF$_3$SO$_3$).

[CpRu(iPr-DAB)(CO)][OTf] (2l). CpRuCl(iPr-DAB) (80 mg, 0.23 mmol) and AgOTf (67 mg, 0.24 mmol) were dissolved in 30 mL of THF. After 15 min of stirring at 20 °C, the suspension was filtered, and the red-brown solution was cooled to 0 °C in an ice bath. A stream of carbon monoxide was slowly passed through the solution. Within 2 min the solution turned bright yellow. Crystallization from a saturated THF solution at −20 °C gave **2l** in almost quantitative yield (110 mg; yield 99%). IR (cm^{-1} in KBr): ν(CO) 1970; ν(SO) 1260−1270 (vs), 1221 (m), 1140−1160 (vs), 1028 (s). Anal. Calcd for C$_{15}$H$_{21}$-N$_2$O$_4$SF$_3$Ru: C, 37.26; H, 4.38; N, 5.79. Found: C, 37.24; H, 4.36; N, 5.85. ^{1}H NMR (300.13 MHz, acetone-d_6): δ 1.55 and 1.64 (two d, J = 6.6 Hz, 6H, CH(CH_3)$_2$), 4.62 (sept, J = 6.6 Hz, 2H, CH(CH$_3$)$_2$), 5.64 (s, 5H, C_5H_5), 8.76 (s, 2H, CH=N). ^{13}C NMR (75.46 MHz, acetone-d_6): δ 23.6 and 25.1 (CH(CH_3)$_2$), 68.4 (CH(CH$_3$)$_2$), 85.0 (C_5H$_5$), 165.0 (CH=N), 196.4 (CO). ^{19}F NMR (acetone-d_6): δ −77.6 ($CF_3SO_3^-$).

[CpRu(iPr-DAB)(σ-pyridine-*N*)][OTf] (2m). CpRuCl(iPr-DAB) (30 mg, 0.08 mmol) and AgOTf (22.5 mg, 0.09 mmol) were dissolved in 30 mL of THF. After 15 min of stirring at 20 °C, the suspension was filtered, and 10 μL (0.13 mmol) of pyridine was added to the red-brown solution after cooling to 0 °C in an ice bath. Within 5 min the solution turned yellow, and after evaporation of the solvent **2m** was obtained as a brownish powder (42.3 mg/ yield 99%). IR (cm^{-1} in KBr): ν(SO) 1260–1280 (vs), 1224 (m), 1153 (broad, vs), 1030 (vs). Anal. Calcd for $C_{19}H_{26}N_3O_3SF_3Ru\cdot{}^1/_3H_2O$: C, 42.21; H, 4.97; N, 7.77. Found: C, 42.32; H, 4.47; N, 7.69. ^{1}H NMR (300.13 MHz, acetone-d_6): δ 1.57 (d, J = 6.6 Hz, 6H, CH(CH_3)$_2$) and 1.61 (d, J = 6.6 Hz, 6H, CH(CH_3)$_2$), 4.98 (sept, J = 6.6 Hz, 2H, CH(CH$_3$)$_2$), 5.02 (s, 5H, C$_5H_5$), 7.46 (m, 2H, H(2-py)), 7.99 (m, 1H, H(4-py)), 8.30 (m, 2H, H(3-py)), 8.93 (s, 2H, CH=N). ^{13}C NMR (75.46 MHz, acetone-d_6): δ 24.0 and 24.5 (CH(CH_3)$_2$), 67.5 (CH(CH$_3$)$_2$), 79.0 (C_5H$_5$), 126.8 (C(3-py)), 138.8 (C(4-py)), 155.8 (C(2-py)), 160.8 (CH=N). ^{19}F NMR (acetone-d_6): δ −77.8 ($CF_3SO_3^-$).

[CpRu(iPr-DAB)(PPh$_3$)][OTf] (2n). CpRuCl(iPr-DAB) (28 mg, 0.08 mmol) and AgOTf (24 mg, 0.09 mmol) were dissolved in 15 mL of CH$_2$Cl$_2$. After 15 min of stirring at 20 °C, the suspension was filtered, and triphenyl phosphine (25 mg, 0.1 mmol) was added to the solution. The brown solution was stirred at 20 °C for 45 min, during which time the solution turned orange. Evaporation of the solvent gave **2n** (100% yield). ^{1}H NMR (300.13 MHz, acetone-d_6, 255 K): δ 0.69 (d, J = 6.6 Hz, 6H, CH(CH_3)$_2$) and 1.45 (d, J = 6.6 Hz, 6H, CH(CH_3)$_2$), 4.51 (sept, J = 6.6 Hz, 2H, CH(CH$_3$)$_2$), 4.73 (s, 5H, C$_5H_5$), 6.8–7.6 (m, P–Ph), 8.86 (d, J(P–H) = 3.12 Hz, 2H, CH=N). ^{13}C NMR (75.46 MHz, acetone-d_6, 255 K): δ 22.4 and 26.1 (CH(CH_3)$_2$), 68.3 (CH(CH$_3$)$_2$), 81.1 (C_5H$_5$), 129–135 (P–Ph). ^{31}P NMR (acetone-d_6, 255 K): δ 40.22.

Reaction of [CpRu(iPr-DAB)(η^2-dimethyl maleate)]-[OTf] (2d) with NaOCH$_3$. To **2d** (54 mg, 0.09 mmol) in 20 mL of dichloromethane was added a 0.46 M solution of NaOCH$_3$ (in CH$_3$OH; 0.3 mL, 0.14 mmol) at 20 °C. After 2 h of stirring at room temperature, the solvent was evaporated and the brown solid digested with diethyl ether (2 × 15 mL). The brown residue contained unreacted **2d**. Evaporation of the diethyl ether solution in vacuo resulted in a yellow solid, containing the two products **I** and **II** (two diastereomers of CpRu(iPr-DAB)(CH$_3$OC(O)CHCH(OCH$_3$)(C(O)OCH$_3$) (**3**)) in a 97:3 ratio, according to ^{1}H NMR. Recrystallization of **I** and **II** from diethyl ether or by diffusion of hexane into THF did not succeed. ^{1}H NMR data selected from a mixture of **I** and **II** (300.13 MHz, acetone-d_6): complex **I**, δ 1.35 (d, J = 6.6 Hz, 6H, CH(CH_3)$_2$) and 1.39 (d, J = 6.6 Hz, 6H, CH(CH_3)$_2$), 3.46 (s, 3H, OCH_3), 3.52 and 3.81 (s, 3H, C(O)OCH_3), 4.40 (sept, J = 6.6 Hz, 2H, CH(CH$_3$)$_2$), 4.75 (s, 5H, C$_5H_5$), 8.26 (s, 2H, CH=N); complex **II**, δ 1.5–1.6 (d, J = 6.6 Hz, 12H, CH(CH_3)$_2$), 3.71 (s, 3H, OCH_3), 3.78 and 3.80 (s, 3H, C(O)OCH_3), 4.74 (s, 5H, C$_5H_5$), 8.40 (s, 2H, CH=N).

Reaction of [CpRu(iPr-DAB)(η^2-DMAC)][OTf] (2j) with NaOCH$_3$. (i) To **2j** (51 mg, 0.08 mmol) in 20 mL of dichloromethane at −40 °C was slowly added an 0.46 M solution of NaOCH$_3$ (in CH$_3$OH; 0.25 mL, 0.11 mmol). While it was warmed to −10 °C (1 h) the solution slowly turned from orange to brown. After evaporation of the solvent, the brown residue was digested with diethyl ether (2 × 15 mL). Removal of the diethyl ether in vacuo resulted in a yellow solid, containing the products CpRu(iPr-DAB)C(C(O)OCH$_3$)=C(OCH$_3$)(C(O)-OCH$_3$) (**4**) and CpRu(iPr-DAB)OCH$_3$ (**6**) in a 2:1 ratio, according to ^{1}H NMR. Recrystallization of **4** and **6** from diethyl ether did not succeed, and attempts to separate the two products by column chromatography (silica) resulted in the decomposition of **4** and **6**. ^{1}H NMR data selected from a mixture of **4** and **6** (300.13 Mhz, acetone-d_6): CpRu(iPr-DAB)C(C(O)CH$_3$)=C-(OCH$_3$)C(O)OCH$_3$ (**4**), δ 1.39 (m, 12H, CH(CH_3)$_2$), 3.37 (s, 3H, OCH_3), 3.52 and 3.76 (s, 3H, C(O)OCH_3), 4.47 (sept, J = 6.6 Hz, 2H, CH(CH$_3$)$_2$), 4.68 (s, 5H, C$_5H_5$), 8.02 (s, 2H, CH=N); complex **6**, δ 1.49 (pseudotriplet, J = 6.6 Hz, 12H, CH(CH_3)$_2$), 3.56 (s, 3H, OCH_3), 4.47 (sept, J = 6.6 Hz, 2H, CH(CH$_3$)$_2$), 4.86 (s, 5H, C$_5H_5$), 8.19 (s, 2H, CH=N).

(ii) The same procedure as for (i) at 20 °C yielded only product **6**, according to ^{1}H NMR.

Reaction of [CpRu(iPr-DAB)(η^2-dimethyl maleate)]-[OTf] (2d) with NH$_2$iPr. (i) To **2d** (16 mg, 0.03 mmol) in 20 mL of refluxing THF was slowly added a solution of NH$_2$iPr (0.01 mL, 0.11 mmol) in 15 mL of THF. The yellow solution turned to dark orange. The solvent was evaporated, and [CpRu(iPr-DAB)(NH$_2$iPr)][OTf] (**2p**) was obtained in 100% yield according to ^{1}H NMR (300.13 MHz, acetone-d_6).

(ii) The reaction carried out in an NMR tube at 20 °C ([CpRu(iPr-DAB)(η^2-dimethyl maleate)][OTf] (9 mg, 0.016 mmol); NH$_2$iPr (1.5 mL, 0.018 mmol); 0.5 mL of CDCl$_3$) showed 8% conversion in 20 h to **2p**.

Reaction of [CpRu(iPr-DAB)(η^2-DMAC)][OTf] (2j) with NH$_2$iPr. (i) To **2j** (27 mg, 0.045 mmol) in 10 mL of dichloromethane was slowly added a solution of NH$_2$iPr (4 mL, 0.047 mmol) in 10 mL of dichloromethane. The orange solution turned to dark orange in 20 h with stirring at 20 °C. After evaporation of the solvent a mixture of **2p** and CH$_3$OC(O)C-(H)=C(C(O)CH$_3$)NH(iPr) (Z:E = 1:3) was obtained.

(ii) The reaction carried out in an NMR tube at 20 °C (**2j** (6 mg, 0.01 mmol); NH$_2$iPr (1.0 mL, 0.01 mmol); 0.5 mL of CDCl$_3$) showed 100% conversion to **2p** and CH$_3$OC(O)C(H)=C(C(O)-CH$_3$)NH(iPr) (100% E) in 2 h. No intermediates were observed by NMR. Prolonged standing resulted in the isomerization of the organic product to the Z isomer.

Reaction of [CpRu(iPr-DAB)(η^2-dimethyl maleate)]-[OTf] (2d) with NHiPr$_2$. To [CpRu(iPr-DAB)(η^2-dimethyl maleate)][OTf] (6 mg, 0.01 mmol) in 0.05 mL of CDCl$_3$ was added NHiPr$_2$ (1.5 mL, 0.02 mmol) at 20 °C. Immediately after addition of NHiPr$_2$ no reaction was observed in ^{1}H NMR. After 2 days at 20 °C a mixture of **2d**, free dimethyl maleate, and [CpRu(iPr-DAB)(NHiPr$_2$)][OTf] was formed (2:5:2), as revealed by ^{1}H NMR. By visual inspection some decomposition products were observed on the bottom of the NMR tube. Selected ^{1}H NMR data for [CpRu(iPr-DAB)(NHiPr$_2$)][OTf]: δ 1.10–1.20 (broad, NH(CH(CH_3)$_2$), 1.50–1.55 (m, 12H, C=NCH(CH_3)$_2$), 2.65 (broad, NH(CH(CH$_3$)$_2$), 4.57 (s, 5H, C$_5H_5$), 4.61 (m, CH(CH$_3$)$_2$), 8.39 (s, 2H, CH=N).

Reaction of [CpRu(iPr-DAB)(η^2-DMAC)][OTf] (2j) with NHiPr$_2$. (i) To [CpRu(iPr-DAB)(η^2-DMAC)][OTf] (6 mg, 0.01 mmol) in 0.05 mL of CDCl$_3$ was added NHiPr$_2$ (1.5 mL, 0.02 mmol) at 20 °C. No reaction took place.

(ii) Stirring the above solution at 50 °C for 2 h also did not result in a reaction.

Synthesis of [CpRu(iPr-DAB)(NH$_2$iPr)][OTf] (2p). CpRuCl(iPr-DAB) (60 mg, 0.18 mmol) and AgOTf (50 mg, 0.19 mmol) were dissolved in 30 mL of CH$_2$Cl$_2$. After 15 min of stirring at room temperature, the suspension was filtered and NH$_2$iPr (1 mL, 12 mmol) was added to the solution. The brown solution turned orange within 2 h. Addition of hexane gave a brown precipitate of [CpRu(iPr-DAB)(NH$_2$iPr)][OTf] (**2p**). IR (cm^{-1} in KBr): ν(NH) 3276 (m), 3240 (m); ν(SO) 1280–1290 (s), 1160 (m), 1030 (s). Anal. Calcd for $C_{19}H_{30}N_3O_3SF_3Ru$: C, 42.37; H, 5.62; N, 7.80. Found: C, 38.54; H, 5.95; N, 7.96. Mass (m/z): found 366, calcd for M − CF$_3$SO$_3$ 366 (exact isotopic pattern for [CpRu(iPr-DAB)(NH$_2$iPr)] was found). ^{1}H NMR (300.13 MHz, acetone-d_6): δ 1.16 (d, J = 6.5 Hz, 6H, NCH(CH_3)$_2$), 1.52 (d, J = 6.6 Hz, 12H, CH(CH_3)$_2$), 2.19 (d, broad, J = 5.4 Hz, 2H, NH$_2$), 2.66 (sept, J = 6.5 Hz, 1H, NCH(CH$_3$)$_2$), 4.58 (m and s, 7H, CH(CH$_3$)$_2$ and C$_5H_5$), 8.52 (s, 2H, CH=N). ^{13}C NMR (75.46 MHz, acetone-d_6): δ 24.1, 24.4, 24.8, 24.9 (CH(CH_3)$_2$ and NCH(CH_3)$_2$), 52.1 (NCH(CH$_3$)$_2$), 66.8 (CH(CH$_3$)$_2$), 77.0 (C_5H$_5$), 159.5 (broad, CH=N).

Table 1. Crystal and Refinement data for [CpRu(iPr-DAB)(η^2-propene)][OTf] (2b)

formula	$C_{17}H_{27}N_2O_3SF_3Ru$	$F(000)$	508
mol wt	497.5	V (Å^3)	1077.9(2)
cryst syst	triclinic	Z	2
space group	P-1	T (K)	293
a (Å)	9.0649(6)	D_{calc} (g/cm^{-3})	1.53
b (Å)	9.6151(6)	λ(Cu Kα) (Å)	1.5418
c (Å)	13.0099(6)	μ(Cu Kα) (cm^{-1})	73.2
α (deg)	94.322(6)	$(\sin\theta)/\lambda$ (Å^{-1})	0.61
β (deg)	104.258(8)	no. of data collected[a]	4071
γ (deg)	98.977(6)	no. of data used in rfmt	3785 ($I > 2.5\sigma(I)$)

[a] *hkl* ranges: $-11 \le h \le 11$; $-11 \le k \le 0$, $-15 \le l \le 15$.

X-ray Structure Determination of Complex 2b. A crystal with approximate dimensions 0.10 × 0.20 × 0.40 mm was used for data collection on an Enraf-Nonius CAD-4 diffractometer with Cu Kα radiation and ω–2θ scan. Two reference reflections (1–20, 0–12) were measured hourly and showed no decrease during the 46-h collecting time. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with $80 < 2\theta < 86°$. Corrections for Lorentz and polarization effects were applied. The positions of Ru and S were found by direct methods. The remainder of the non-hydrogen atoms were found in a subsequent ΔF synthesis. The hydrogen atoms were calculated. Full-matrix least-squares refinement of F, anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms, the latter restrained in such a way that the distance to their carrier remained constant at approximately 1.09 Å, converged to $R = 0.033$, $R_w = 0.043$, and $(\Delta/\sigma)_{max} = 0.44$. The weighting scheme $w = (7.2 + F_o + 0.0071F_o^2)^{-1}$ was used. An empirical absorption correction (DIFABS)[13] was applied, with coefficients in the range of 0.80–1.35. A final difference Fourier map revealed a residual electron density between −0.8 and +0.5 e Å^{-3}. The anomalous scattering of Ru and S was taken into account.[14,15] All calculations were performed with XTAL.[16] Table 1 presents the crystal and refinement data and Table 2 the fractional coordinates. In Figure 2 the PLUTO presentation of **2b** is depicted.[17]

Results and Discussion

Syntheses of [CpRu(iPr-DAB)(L)][OTf]. The reaction of AgOTf with CpRuCl(iPr-DAB) (**1**) in CH_2Cl_2 or THF and subsequent addition of L (**a**–**n**) at 0 °C results in the formation of the ionic complexes **2a**–**f**,**i**,**j**,**l**–**n** in quantitative yeild (Scheme 1). The structures of these complexes have been proven by ^{1}H, ^{13}C, and ^{19}F NMR and IR spectroscopy and elemental analysis. The spectroscopic data of the complexes are reported in the Experimental Section. The counterion $[CF_3SO_3^-]$ shows one resonance between −77.5 and −77.8 ppm in ^{19}F NMR for all complexes, which is indicative of uncoordinated triflate anion.[18] From variable-temperature ^{1}H NMR it appears that fast rotation around the M–alkene bond takes place for **2a**,**e**,**f**.[20]

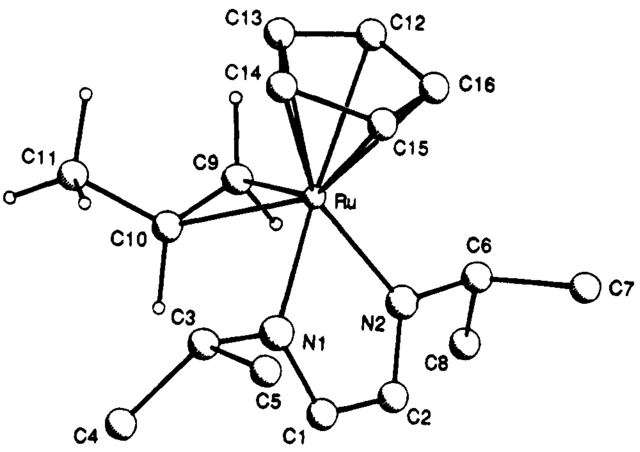

Figure 2. PLUTO drawing of [CpRu(iPr-DAB)(η^2-propene)][OTf] (**2b**).

Table 2. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for [CpRu(iPr-DAB)(η^2-propene)][OTf] (2b)

	x	y	z	U_{eq} (Å^2)
Ru	0.38399(3)	0.77323(2)	0.25214(2)	0.0348(1)
S	−0.0447(1)	0.1776(1)	0.2452(1)	0.0691(7)
C(1)	0.1236(4)	0.5506(4)	0.1680(4)	0.058(2)
C(2)	0.2532(5)	0.4801(4)	0.1857(4)	0.056(2)
C(3)	0.0250(4)	0.7656(5)	0.1833(4)	0.057(2)
C(4)	−0.0831(7)	0.7382(8)	0.0708(5)	0.085(4)
C(5)	−0.0611(7)	0.7261(8)	0.2670(6)	0.086(4)
C(6)	0.5276(5)	0.4959(4)	0.2482(3)	0.055(2)
C(7)	0.5298(9)	0.4184(8)	0.3470(6)	0.097(5)
C(8)	0.5376(8)	0.3983(7)	0.1547(5)	0.089(4)
C(9)	0.5019(5)	0.7945(5)	0.1232(3)	0.055(2)
C(10)	0.3540(5)	0.8250(5)	0.0844(3)	0.056(2)
C(11)	0.3233(8)	0.9700(7)	0.0630(5)	0.083(4)
C(12)	0.5970(6)	0.8945(6)	0.3685(4)	0.077(3)
C(13)	0.5108(8)	0.9857(6)	0.3244(4)	0.086(4)
C(14)	0.3724(8)	0.9632(9)	0.3494(6)	0.114(5)
C(15)	0.3741(9)	0.848(1)	0.4119(5)	0.116(5)
C(16)	0.5194(9)	0.8099(6)	0.4216(4)	0.090(4)
C(17)	0.0067(8)	0.241(1)	0.3825(6)	0.124(6)
N(1)	0.1552(3)	0.6859(3)	0.1938(2)	0.044(2)
N(2)	0.3853(3)	0.5618(3)	0.2241(2)	0.042(1)
O(1)	0.0996(5)	0.1575(5)	0.2261(4)	0.103(3)
O(2)	−0.1548(6)	0.0518(5)	0.2365(4)	0.118(3)
O(3)	−0.1048(5)	0.2881(5)	0.1931(4)	0.112(3)
F(1)	−0.1109(7)	0.2666(9)	0.4181(5)	0.190(6)
F(2)	0.1105(8)	0.3615(9)	0.4034(5)	0.212(6)
F(3)	0.0692(9)	0.151(1)	0.4435(5)	0.228(8)

Coordination of Alkenes L = a–h in [CpRu(iPr-DAB)(L)][OTf]. For alkenes in **2a**–**f** the shifts of the vinylic hydrogen and carbon atoms upon coordination are large, which indicates that there is strong π back-bonding from the ruthenium center to the alkene (Table 3).[19]

The resonances of the vinylic hydrogen and carbon atoms of **2d** are almost identical with those of [Cp*Ru(bpy)(EtOOCCH=CHCOOEt)][PF_6],[10] which suggests that the π back-bonding to dimethyl maleate in both complexes is of the same order of magnitude. According

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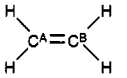
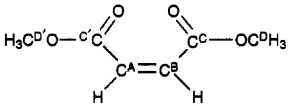
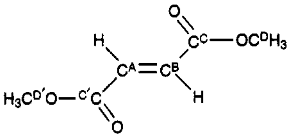
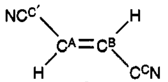
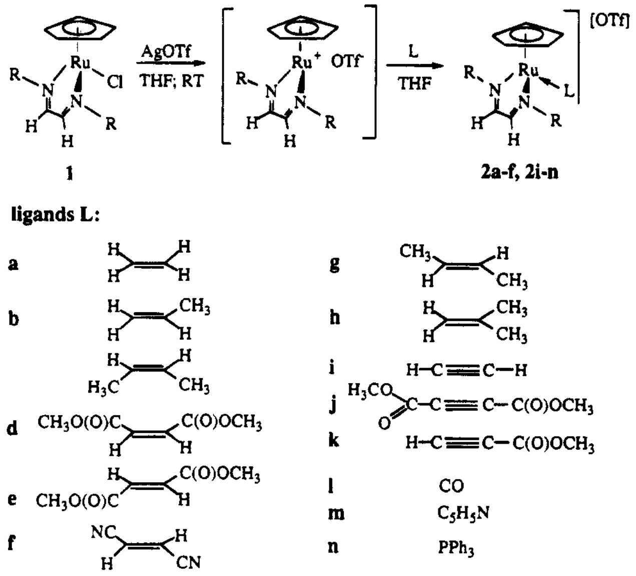
Table 3. ^{1}H and ^{13}C NMR Data (ppm) for Free and Coordinated Alkenes in [CpRu(iPr-DAB)(η^2-alkene)][OTf]

atom labeling of alkene	NMR	free alkene	coordinated alkene in [CpRu(iPr-DAB)(η^2-alkene)][OTf]	Δδ
 **a**	^{1}H	5.48 (all H's)	3.28 (all H's)	2.30
	^{13}C	123.8 (A, B)	50.6 (A, B)	73.2
 **d**	^{1}H	3.83 (D, D′), 6.60 (A, B)	3.84 (D, D′), 3.58 (A, B)	3.02
	^{13}C	52.4 (D, D′), 130.9 (A,B), 166.5 (C, C′)	52.7 (D, D′), 55.0 (A,B), 172.7 (C, C′)	75.9
 **e**	^{1}H	3.89 (D, D′), 6.60 (A, B)	3.65 (D), 3.78 (D′), 3.96 (A), 4.88 (B)	3.18 (mean)
	^{13}C	53.4 (D, D′), 134.4 (A,B)	48.4 (D), 52.3 (D′), 52.5 (A), 53.2 (B), 173.5(C), 175.0 (C′)	81.6 (mean)
 **f**	^{1}H	6.95 (A,B)	3.62 (A), 5.10 (B)	2.59 (mean)
	^{13}C	116.0 (A,B), 120.9 (C, C′)	70.9 (A, B), 125.4 (C, C′)	45.1 (mean)

Scheme 1. Synthesis of [CpRu(iPr-DAB)(L)][OTf] (L = a−n)



to the chemical shift values of the vinylic carbon atoms, it can be deduced that the metal−alkene bond strength decreases in the order **1b**, **1a**, and **1c**.[21,22a]

The electron density needed for the π back-bonding of the ruthenium center to the alkene is obtained from both the α-diimine and Cp ligand, as can be seen from their ^{1}H and ^{13}C NMR resonances shifting to lower field. The signals of the Cp and imine protons of [CpRu(iPr-DAB)(η^2-fumaronitrile)][OTf] (**2f**) show the largest shift to lower field, which indicates that there is much π back-bonding to the fumaronitrile. For the imine protons a single resonance is seen at ca. 8.5 ppm for the symmetric compounds **2a**,**c**,**d**, while for complexes **2b**,**e**,**f** two doublets are observed as a result of the asymmetric chemical environment of the alkene.[22]

It has been reported that the electron-rich [Cp*Ru(bpy)] moiety does not bind diethyl fumarate, which has the same electronic properties as, but is far more sterically demanding than, diethyl maleate.[10] However, dimethyl fumarate coordinates to [CpRu(iPr-DAB)][OTf] to form [CpRu(iPr-DAB)(η^2-dimethyl fumarate)][OTf] (**2e**), which indicates that the steric hindrance in [CpRu(iPr-DAB)][OTf] is less pronounced than in the Cp*Ru(bpy) complex. This is not unexpected, since the Cp* ligand is far more bulky than the Cp ligand. On the other hand, it should be noted that molecular models suggest that the iPr-DAB ligand is sterically more demanding that the bipyridine ligand because of the isopropyl groups on the imine nitrogen atoms (*vide infra*).

Reaction of [CpRu(iPr-DAB)][OTf] with *trans*-2-butene (**g**) or 2-methylpropene (**h**) did not result in the coordination of the alkene: after workup [CpRu(iPr-DAB)][OTf] was isolated unchanged. When these syntheses were carried out *in situ* in an NMR tube, it was shown that the alkenes **g** and **h** do not coordinate to [CpRu(iPr-DAB)][OTf] at all, which shows that the

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(22) (a) The difference between the ^{13}C NMR shifts (Δδ(^{13}C) (ppm))[21] of the alkene carbon atoms of free alkene and coordinated alkenes can be used as a measure of the metal−alkene bond strength.[21] The values of Δδ(^{13}C) are 81.6, 73.2, and 45.1 ppm for dimethyl fumarate (**b**), ethene (**a**), and fumaronitrile (**c**), respectively. (b) The small (J = 0.8 Hz in **2e**) or negligible (**2f**) coupling constant of the inequivalent imine protons is most probably caused by the large angle between the two adjacent carbon−proton bonds. See: Barfield, M.; Smith, W. B. *J. Am. Chem. Soc.* **1992**, *114*, 1574.

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Table 4. Selected Bond Distances (Å) and Angles (deg) for [CpRu(iPr-DAB)(η^2-propene)][OTf] (2b)

Ru—C(9)	2.206(5)	C(3)—C(5)	1.525(9)
Ru—C(10)	2.236(4)	C(3)—N(1)	1.489(6)
Ru—N(1)	2.042(3)	C(6)—C(7)	1.530(9)
Ru—N(2)	2.041(3)	C(6)—C(8)	1.509(8)
C(1)—C(2)	1.426(6)	C(6)—N(2)	1.499(6)
C(1)—N(1)	1.287(5)	C(9)—C(10)	1.396(6)
C(2)—N(2)	1.286(4)	C(10)—C(11)	1.497(8)
C(3)—C(4)	1.526(7)		

C(9)—Ru—C(10)	36.6(2)	C(7)—C(6)—N(2)	108.4(5)
C(9)—Ru—N(1)	111.6(1)	C(8)—C(6)—N(2)	112.6(4)
C(9)—Ru—N(2)	84.9(1)	Ru—C(9)—C(10)	72.9(3)
C(10)—Ru—N(1)	81.8(1)	Ru—C(10)—C(9)	70.5(2)
C(10)—Ru—N(2)	98.1(1)	Ru—C(10)—C(11)	117.2(3)
N(1)—Ru—N(2)	76.4(1)	C(9)—C(10)—C(11)	123.7(4)
C(2)—C(1)—N(1)	115.7(3)	Ru—N(1)—C(1)	116.2(3)
C(1)—C(2)—N(2)	114.9(3)	Ru—N(1)—C(3)	125.0(2)
C(4)—C(3)—C(5)	111.6(4)	C(1)—N(1)—C(3)	118.7(3)
C(4)—C(3)—N(1)	111.9(4)	Ru—N(2)—C(2)	116.8(3)
C(5)—C(3)—N(1)	108.7(4)	Ru—N(2)—C(6)	124.8(2)
C(7)—C(6)—C(8)	111.5(5)	C(2)—N(2)—C(6)	118.4(3)

failure to isolate the desired complexes is not due to dissociation of the alkene during workup, as has been reported for some other alkene complexes.[28] The fact that **g** and **h** do not coordinate is most probably caused by steric interactions between the methyl groups of the butene and the iPr groups of the α-diimine on the one hand, and the Cp ring on the other hand, since for ligands **g** and **h** it is not possible to minimize this interaction as in the case of propene **(b)** (*vide supra*), or *cis*-2-butene **(c)**, which form complexes **2b** and **2c**. That the electronic properties of the alkenes **g** and **h** play a role is less probable, since **g** and **h** have electronic properties similar to those of both propene **(b)** and *cis*-2-butene **(c)**.[29]

Structure Determination of [CpRu(iPr-DAB)(η^2-propene)][OTf] (2b). A single-crystal structure determination was carried out for **2b**. In Figure 2 the PLUTO representation is depicted, which shows the ruthenium complex in a piano-stool configuration with the cyclopentadienyl ligand in a η^5, the α-diimine ligand in a four-electron-donating σN,σN′, and the propene in a η^2 coordination mode. Selected bond distances and angles are shown in Table 4.

The C(9)—C(10) bond length of the η^2-coordinated propene (1.396(6) Å) is longer than that in free alkene (ca. 1.35(1) Å), as a result of π back-bonding of the ruthenium in the π^* orbital of propene,[20] which is antibonding between C(9) and C(10). The γ and δ torsion angles defined by Ittel and Ibers,[19e] which are a measurement for the sp^3 character of the coordinated alkene, cannot be used for the structure of **2b**, since the alkene hydrogen atoms were not found but calculated. The Ru—N(1) and Ru—N(2) bond distances (2.042(3) and 2.041(3) Å, respectively) are in the range observed for σN,σN′-coordinating diazabutadienes.[23]

The most striking feature of the structure is that the methyl group of the η^2-coordinating propene points toward the cyclopentadienyl ring; the torsion angle between the plane of the Cp ring and the C(9)—C(10) vector is 13.1(0.2)°. The ideal configuration of an alkene in (η^5-cyclopentadienyl)ML_2(η^2-alkene) complexes is thought to have the C═C vector of the double bond

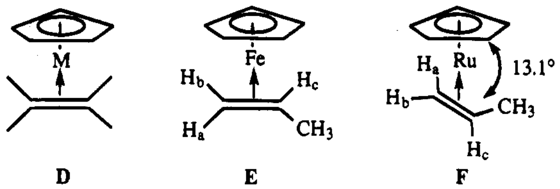

Figure 3. Angle between the η^2-coordinated alkene and Cp ring in CpML_2(η^2-alkene).

coplanar with the Cp or Cp* ring,[24] with the R groups on the alkene pointing away from the cyclopentadienyl ring (configurations **D** and **E**, Figure 3).

There are, however, not many examples of X-ray structures of CpML_2(η^2-alkene) complexes with asymmetrically substituted alkenes. Examples are CpMn(CO)$_2$(η^2-CH_2═CHCOCH$_3$),[25] which shows the double bond of the alkene almost coplanar with the Cp ring (2.8(0.3)°), and Cp*Re(CO)$_2$(η^2-Me_2C═CHCOCH$_3$),[26] in which the angle between the Cp* ring and the double bond is 17.9(0.7)°. In both structures the methyl ketone group points away from the ring.[25,26] Extensive study of the preferred configuration(s) of alkenes in the asymmetric rhenium complexes CpRe(NO)(PPh$_3$)(η^2-L′) shows that there are several preferred orientations for substituted alkenes, which are determined mainly by the steric interaction between the R group on the alkene and the phenyl groups of the PPh$_3$ ligand.[27]

It should be noted that until now only complexes of the type CpML_2(η^2-L′) (M = Mn, Re, Fe, Ru) with less sterically demanding spectator ligands (L) have been examined.[24] In **2b**, apparently steric interactions of the methyl group of the propene ligand with the isopropyl groups on the DAB ligand outweigh those with the Cp ring, as the methyl group of the propene points toward the Cp ring. Nevertheless, it seems that steric interactions of the methyl group with the cyclopentadienyl ring induce the alkene to make an angle (13.1(0.2)°) with the cyclopentadienyl plane (**F** in Figure 3). Cutler et al. suggested that the methyl group in [CpFe(CO)$_2$(η^2-1-butene)][BF$_4$] was pointing away from the cyclopentadienyl ring, on the basis of the close correspondence of the terminal vinyl proton resonances of the η^2-coordinating 1-butene in this complex (^{1}H NMR: δ 3.59 ppm, $J(H_aH_c)$ = 15 Hz for H$_a$; δ 4.0 ppm, $J(H_bH_c)$ = 8 Hz for H$_b$) (**E**, Figure 3).[24c,d] For **2b** the chemical shifts of the vinyl protons H$_a$ and H$_b$ differ considerably at both 293 and 190 K (^{1}H NMR (293 K): δ 2.39, H$_c$; δ 2.69, $J(H_bH_c)$ = 7.8 Hz, H$_b$; δ 4.20 ppm, $J(H_aH_c)$ = 12.6 Hz, H$_a$) (**F**, Figure 3), which suggests that the solid-state configuration, with the methyl group pointing towards the cyclopentadienyl ring, is also present in solution.

Synthesis and Characterization of [CpRu(iPr-DAB)(L)][OTf] with the Alkynes i–k. The reaction of [CpRu(iPr-DAB)][OTf] with acetylene **(i)** and DMAC **(j)** yielded the expected complexes **2i**,**j** in 100% yield. These complexes are stable in solution under a nitrogen atmosphere at 20 °C. The fact that the resonances of the acetylene protons in **2i** are drastically shifted toward higher field (δ 2.96 ppm) compared to those in the complexes [CpRu(PMe$_3$)$_2$(η^2-HC≡CH)] (δ 4.98 ppm) and [CpRu(PMe$_2$Ph)$_2$(η^2-HC≡CH)] (δ 5.57 ppm)[6] indicates that acetylene **(i)** acts as a σ donor, and not as a π acceptor, in the case of **2i**. The σ-bonding nature of **i** in **2i** is confirmed by the UV/vis data of **2i**[20c] and by the low chemical shift of the Cp ring. The resonances of

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the Cp ligand in [CpRu(iPr-DAB)(η^2-alkyne)][OTf] (**2i–k**; **k** = MCA) drastically shifts to lower field when more electron-withdrawing alkynes are coordinated, while the resonances of the imine proton and carbon atom do not shift significantly. This indicates that the Cp ring compensates the electron density at the ruthenium center when alkynes with electron-withdrawing substituents are coordinated, which is in contrast to complexes [CpRu(iPr-DAB)(η^2-alkene)][OTf], where both the iPr-DAB ligand and the Cp ring are affected when alkenes with electron-withdrawing substituents are used (*vide supra*).

In the reaction of [CpRu(iPr-DAB)][OTf] with alkynes, no formation of vinylidene complexes are observed, in contrast to most complexes [CpRu(PR$_3$)$_2$], which form CpRu(PR$_3$)$_2$=C=CH$_2$ on reacting with acetylene.[6,30] Lomprey and Selegue argue that the isolation of the kinetic products [CpRu(PR$_3$)$_2$(η^2-alkyne)] (PR$_3$ = PMe$_3$, PMe$_2$Ph) is made possible by small alkyne substituents and small ancillary ligands on the metal,[6] since with larger ancillary ligands (PR$_3$ = PPh$_3$, $^1/_2$ dppm or dppe) the η^2- acetylene complex could not even be isolated.[6] It is very well possible that the η^2-alkyne complexes **2i–k** (*vide infra*) are stable because of steric reasons, since CPK models show that iPr-DAB is less bulky than two PPh$_3$ ligands.

Another important difference between the iPr-DAB ligand and PPh$_3$ is the ease of dissociation of PPh$_3$. Bruce et al. reported the di-, tri-, and tetramerization of DMAC on reaction of DMAC with CpRuCl(PPh$_3$)$_2$ and NH$_4$PF$_6$ in refluxing methanol, reactions in which [CpRu(PPh$_3$)(η^2-DMAC)][PF$_6$] was not observed.[31] Obviously the lability of the PPh$_3$ ligands makes CpRuCl(PPh$_3$)$_2$ more reactive than [CpRu(iPr-DAB)][OTf].

The reaction of [CpRu(iPr-DAB)][OTf] with methyl propiolate (**k**) yielded [CpRu(iPr-DAB)($HC\equiv CC(O)OCH_3$)][OTf] (**2k**) and [CpRu(iPr-DAB)(CO)][OTf] (**2l**) in a 4:1 ratio. Attempts to avoid the formation of **2l** by changing the reaction temperature or the complex:alkyne ratio did not lead to a change in product ratios. Addition of H$_2$O to [CpRu(iPr-DAB)][OTf] before or after addition of MCA did not alter the ratio **2k**:**2l** formed, which suggests that the formation of **2l** is not due to conversion of **2k** to [CpRu(iPr-DAB)(=C=C(H)C(O)OCH$_3$)] and subsequent reaction with water to form **2l**, a reaction which has been reported for CpFe(CO)$_2$($HC\equiv CCH_3$).[32]

For [CpRu(prophos)(=C=C(H)Ph)][PF$_6$] (prophos = Ph$_2$PPh(CH$_3$)CH$_2$PPh$_2$) the reaction with O$_2$ (1 atm) in CH$_2$Cl$_2$ led to complete conversion to [CpRu(prophos)(CO)][PF$_6$] within 24 h.[33] However, the possibility that traces of dioxygen cause the formation of **2l** can be excluded, since carrying out the reaction of [CpRu(iPr-DAB)][OTf] with MCA under dioxygen led to also to a **2k**:**2l** ratio of 4:1.

Complex **2k** decomposes slowly in solution, but this does not result in the formation of **2l**. The reaction of methyl propiolate to form **2l** clearly takes place during the formation of **2k**, not when **2k** has been formed already. Thus, the formation of **2k** and **2l** (4:1) most probably proceeds via decarbonylation of $HC\equiv CC(O)OCH_3$ (**k**). The abstraction of CO from aldehydes and acyl halides by several organometallic complexes has been reported, but the mechanism of the decarbonylation is still unclear.[33–35] For the decarbonylation of benzaldehyde by CpRuCH$_2$(CH$_3$)$_3$(PMe$_3$)$_2$ to form CpRuC$_6$H$_5$(PMe$_3$)(CO) and free PMe first C–H activation took place to form CpRuC(O)C$_6$H$_5$(PMe$_3$)$_2$, and subsequent dissociation of PMe$_3$ and carbonyl deinsertion led to CpRuC$_6$H$_5$(PMe$_3$)(CO) (no other intermediates were observed in the NMR spectra).[33] The reaction of [CpRu(iPr-DAB)][OTf] with benzaldehyde in THF (5 days; 60 °C) did not lead to any [CpRu(iPr-DAB)(CO)][OTf] (**2l**). Notwithstanding extensive investigations, we have been unable to establish which reaction is responsible for the formation of **2l** in the reaction of [CpRu(iPr-DAB)][OTf] with **j**.

Synthesis and Characterization of [CpRu(iPr-DAB)(L)][OTf] with L = l–n. Addition of L = CO (**l**), pyridine (**m**), and PPh$_3$ (**n**) to [CpRu(iPr-DAB)][OTf] at 20 °C yielded the ionic complexes [CpRu(iPr-DAB)(CO)][OTf] (**2l**), [CpRu(iPr-DAB)(σ-pyridine-*N*)][OTf] (**2m**), and [CpRu(iPr-DAB)(PPh$_3$)][OTf] (**2n**), respectively, in quantitative yields. The coordination of CO in **2l** is shown by a ^{13}C NMR resonance at 196.4 ppm and a single CO stretching frequency at 1970 cm^{-1}. The CO frequency of the analogous [CpRu(bpy)(CO)][PF$_6$][10] and [CpRu(1,10-phen)(CO)][BPh$_4$][36] complexes were reported to be 1963 (Nujol) and 1948 (Nujol) cm^{-1}, respectively. The decrease in the CO frequency for [CpRu(N–N)(CO)]$^+$ as one goes from N–N = iPr-DAB to bipyridine and phenanthroline can be assigned to a decreasing π-acceptor capacity and increasing σ-donor properties of the N–N ligand, resulting in a stronger π back-bonding from the metal center to the carbonyl, in going from iPr-DAB to phenanthroline.[11]

The fact that [CpRu(iPr-DAB)][OTf] coordinates CO, PPh$_3$, pyridine, and alkenes with electron-donating and electron-withdrawing groups as well as acetylene, DMAC, and MCA, while [Cp*Ru(bpy)(L)][PF$_6$] does not coordinate ethene or propene, most probably can be attributed to the combined effect of the α-diimine ligand and Cp ligand. The spectroscopic data indicate that the Cp ring and iPr-DAB ligand compensate the electron density at the ruthenium center; i.e., the α-diimine tunes the electron density on the metal center by both σN-donor or π-accepting properties, while the Cp ligand is a good electron donor, which enables the metal atom to cope with alkenes with different electronic properties.

Nucleophilic Attack of $^-$OCH$_3$, NH$_2$iPr, and NHiPr$_2$ on 2d,j. [CpRu(iPr-DAB)(η^2-dimethyl maleate)][OTf] (**2d**) and [CpRu(iPr-DAB)(η^2-dimethyl acetylenedicarboxylate)][OTf] (**2j**) were tested for their reactivity toward nucleophiles. The substrates $^-$OCH$_3$, NH$_2$iPr, and NHiPr$_2$ were chosen in view of the recently reported results involving reactions of these nucleophiles with the complex [CpFe(CO)$_2$(diphenylacetylene)].[1]

Reaction of 2d,j with $^-$OCH$_3$. The reaction of [CpRu(iPr-DAB)(η^2-dimethyl maleate)][OTf] (**2d**) in CH$_2$-

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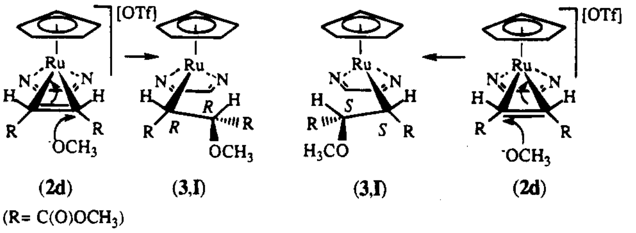
Scheme 2. Formation of the *RR* and *SS* Enantiomers of $CpRu(iPr\text{-}DAB)CH(C(O)OCH_3)CH(OCH_3)(C(O)OCH_3)$ (3; Diastereomer I) by *anti* Addition of $^-OCH_3$ on $[CpRu(iPr\text{-}DAB)(\eta^2\text{-dimethyl maleate})][OTf]$ (2d)



Cl_2 with sodium methoxide (MeOH solution, 1 equiv) at 20 °C resulted in the formation of two diastereomers of the neutral compound $CpRu(iPr\text{-}DAB)CH(C(O)OCH_3)CH(OCH_3)(C(O)OCH_3)$ (**3**; diastereomers I and II) in a 97:3 ratio. These diastereomers most probably result from the *anti* and *syn* attack[37] of the methoxy group on the double bond, respectively, as it is known that the anti nucleophilic attack is favored in these types of complexes since the nucleophile attacks the alkene on the less hindered side.[38]

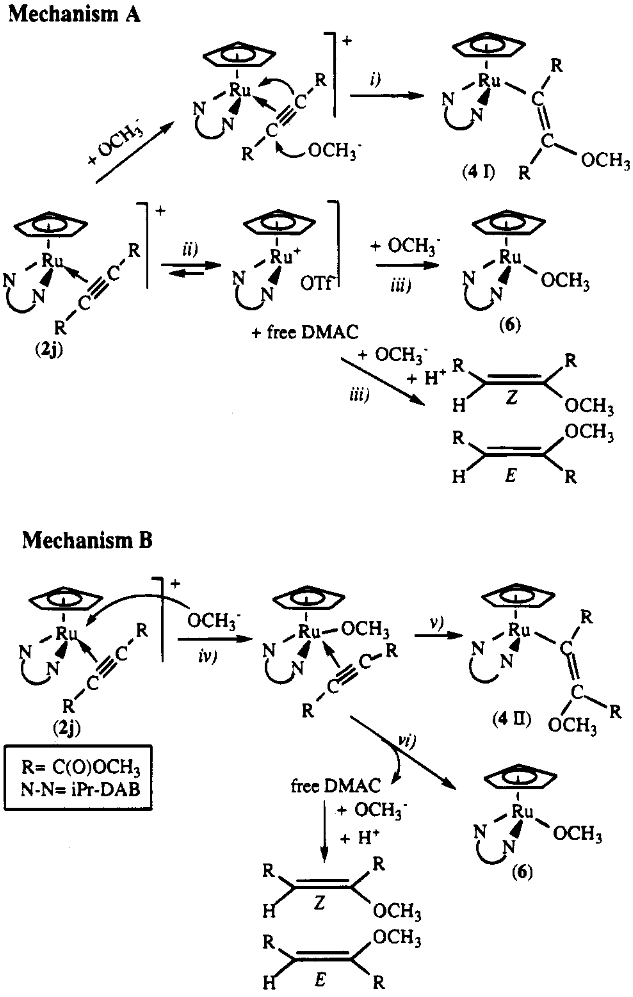
Since the formation of the two chiral centers is coupled (Scheme 2), *anti* attack results in the formation of the *RR*/*SS* diastereomer (I) and *syn* attack results in the *SR*/*RS* diastereomer (**II**).

Sodium methoxide in MeOH solution also reacts with free dimethyl maleate under these conditions, to form $CH_3OC(O)CH(OCH_3)CH_2(C(O)OCH_3)$.[29] This organic compound was not observed in the reaction with the complex, which indicates that sodium methoxide reacts quickly with the coordinated dimethyl maleate and also that complexes **3** (I and II) are inert toward sodium methoxide.

The reaction of the analogous alkyne complex **2j** with $NaOCH_3$ (MeOH solution, 1 equiv) at 20 °C resulted in $CpRu(iPr\text{-}DAB)OCH_3$ (**6**; Scheme 3). When this reaction was carried out at −40 °C, only one stereoisomer of $CpRu(iPr\text{-}DAB)C(C(O)OCH_3){=}C(OCH_3)C(O)OCH_3$ was formed (70%) either isomer **4I** or **4II** besides 30% of **6**. It was not possible to separate the products **4** and **6**, nor was it possible to determine whether isomer **I** or **II** was formed, as crystallization was not successful, while chromatography led to decomposition.

There are several possibilities to rationalize the formation of **4** and **6** in the reaction of $^-OCH_3$ with **2j**. For reactions of nucleophiles with coordinated alkynes, trans addition is generally favored, since the nucleophile approaches the alkyne from the less hindered side (mechanism A, step *i*, in Scheme 3),[38] which would lead to isomer **I** of complex **4**. The formation of complex **6** can be rationalized by assuming an equilibrium between complex **2j** and [CpRu(iPr-DAB)][OTf] and free DMAC (A, step *ii*, in Scheme 3), while $^-OCH_3$ attacks the unsaturated metal complex and the free ligand separately (mechanism A, step *iii*, in Scheme 3), to form **6** and the organic products (*Z*)- and (*E*)-$CH_3OC(O)CH{=}C(OCH_3)C(O)OCH_3$. In a separate experiment we checked that free DMAC reacts very quickly with $NaOCH_3$ in MeOH under these circumstances to give a mixture of (*Z*)- and (*E*)-$CH_3OC(O)CH{=}C(OCH_3)C(O)OCH_3$.[40]

Scheme 3. Different Reaction Pathways for the Reaction of $[CpRu(iPr\text{-}DAB)(\eta^2\text{-}DMAC)][OTf]$ (2j) with $^-OCH_3$



Recently, the cis instead of trans addition of $^-OCH_3$ to diphenylacetylene in $[CpFe(CO)_2(PhC{\equiv}CPh)]$ was reported.[1] In this complex the nucleophile attacks one of the carbonyl ligands prior to reaction with the acetylene. This reaction is not feasible for complex **2j**, since no carbonyl ligand is present. However, an alternative pathway for nucleophilic attack is, first, attack at the metal atom (mechanism B, step *iv*, in Scheme 3 and then either subsequent transfer of the nucleophilic group to the alkyne (mechanism B, step *v*, in Scheme 3), which results in isomer **II** of complex **4**,

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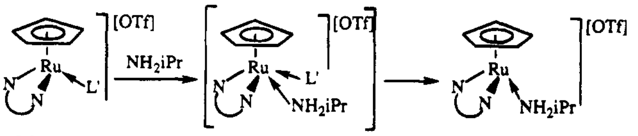
Scheme 4. Reaction of [CpRu(iPr-DAB)(η^2-dimethyl maleate)][OTf] (2d) and [CpRu(iPr-DAB)(η^2-DMAC)][OTf] (2j) with NH_2iPr



2d (L'= dimethyl maleate)
2j (L'= dimethylacetylenedicarboxylate; DMAC)

(2p)
and free L'

or dissociation of the alkyne to form **6** (mechanism B, step *vi*, in Scheme 3). The formation of the organic products (*Z*)- and (*E*)-$CH_3OC(O)CH{=}C(OCH_3)C(O)OCH_3$ can be rationalized by the reaction of free DMAC with $^-OCH_3$.[40] On the basis of these observations it is not possible to distinguish between mechanisms A and B, and no intermediates have been observed to elucidate this problem. However, the fact that complex **2d** does not react with $NHiPr_2$ (*vide infra*) indicates that the dissociation of the alkyne (step *ii* in mechanism A, Scheme 3) does not occur under these circumstances, which renders mechanism A improbable.

Reaction of 2d,j with NH_2iPr. The reaction of [CpRu(iPr-DAB)(η^2-dimethyl maleate)][OTf] (**2d**) with NH_2iPr in $CDCl_3$ or CH_2Cl_2 at 20 °C gave a new product in 8% yield after 20 h, together with some free dimethyl maleate and 92% of unreacted **2d**. When the same reaction was carried out by slow addition of the amine to a refluxing solution of **2d** in THF, [CpRu(iPr-DAB)-(NH_2iPr)][OTf] **(2p)** was formed in quantitative yield (Scheme 4), while **2p** could alternatively be synthesized by addition of NH_2iPr to [CpRu(iPr-DAB)][OTf] in CH_2Cl_2 at 20 °C. The substitution of dimethyl maleate in **2d** was also achieved by addition of $NHiPr_2$, resulting in formation of [CpRu(iPr-DAB)($NHiPr_2$][OTf] **(2q)** within 2 days at 20 °C in CH_2Cl_2.

Reaction of [CpRu(iPr-DAB)(DMAC)][OTf] **(2j)** with NH_2iPr at 20 °C also led to the formation of **2p** (Scheme 4), together with the alkenes (*E*)- and (*Z*)-$CH_3C(O)OCH{=}C(NHiPr)C(O)OCH_3$[40d] in a 1:3 ratio after 20 h at 20 °C. Monitoring the reaction with ^1H NMR revealed that first only the *Z* isomer of the alkene is formed as a result of trans attack, which isomerizes to the *E* form. It was determined that free DMAC reacts with NH_2iPr to form (*Z*)-$CH_3C(O)OCH{=}C(NHiPr)C(O)OCH_3$ as a kinetic product under these conditions.[40d] Since no other intermediates were observed in the ^1H NMR spectrum during the reaction of **2j** with NH_2iPr, the alkenes are most probably formed from free DMAC, not as a result of nucleophilic attack of NH_2iPr at coordinated DMAC followed by protonation and substitution. Complex **2j** does not react with $NHiPr_2$ in $CDCl_3$ both at 20 °C and at reflux temperature, which points to an associative substitution pathway (Scheme 4), since [CpRu(iPr-DAB)($NHiPr_2$)][OTf] **(2q)** is easily formed from [CpRu(iPr-DAB)][OTf] and $NHiPr_2$.[42] Most probably, the four-legged piano-stool intermediate (Scheme 4) in the associative pathway is too crowded when diisopropylamine is used.

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Supplementary Material Available: Tables of fractional coordinates and isotropic thermal parameters for the hydrogen atoms, anisotropic thermal parameters for the non-hydrogen atoms, and complete tables of bond distances and angles for **2b** (8 pages). Ordering information is given on any current masthead page.

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