Ruthenium Vinylidene and σ-Acetylide Complexes Containing 1,4,7-Trimethyl-1,4,7-triazacyclononane (Me_3tacn): Synthesis and Alkyne-Coupling Reactivity

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The ruthenium(II) complexes $[Ru(Me_3tacn)(L)_2X]PF_6$ (L = PMe_3, X = O_2CCF_3 (**1a**); L = PMe_3, X = Cl (**1b**); L = $^1/_2$ dmpe, X = O_2CCF_3 (**1c**)) are prepared. Only **1a** reacts with 1 equiv of RC≡CH (R = Ph and *p*-tolyl) to give the vinylidene complexes $[Ru(Me_3tacn)(PMe_3)(O_2CCF_3)\{C{=}CH(R)\}]PF_6$ (R = Ph (**2a**) and *p*-tolyl (**2b**)) in refluxing 1,2-dichloroethane. Reaction of **2a** and **2b** with PMe_3 in methanolic KOH solution give the corresponding σ-acetylide complexes $[Ru(Me_3tacn)(PMe_3)_2(C{\equiv}CR)]PF_6$ (R = Ph (**3a**) and *p*-tolyl (**3b**)). Similarly, treatment of **2a** with $P(OMe_3)_3$ affords $[Ru(Me_3tacn)(PMe_3)(P(OMe)_3)(C{\equiv}CPh)]PF_6$ (**3c**). Oxidative cleavage of the vinylidene ligand in **2a** by oxygen gives $[Ru(Me_3tacn)(PMe_3)(O_2CCF_3)(CO)]PF_6$ (**4**) and benzaldehyde. Complex **1b** reacts with 2.5 equiv of RC≡CH (R = Ph, *p*-tolyl) and 1.5 equiv of KOH in methanol to yield the η^3-butenynyl species $[Ru(Me_3tacn)(PMe_3)\{\eta^3\text{-}RC_3{=}CH(R)\}]PF_6$ (R = Ph (**5a**) and *p*-tolyl (**5b**)). In addition, **2a** and **2b** react with RC≡CH (R = Ph, *p*-tolyl) and KOH in methanol to give **5a** and **5b**, respectively. Treatment of **2a** with *p*-tolylC≡CH and KOH in methanol gives $[(Me_3tacn)Ru(PMe_3)\{\eta^3\text{-}PhC_3{=}CH(p\text{-tolyl})\}]PF_6$ (**5c**) and $[(Me_3tacn)Ru(PMe_3)\{\eta^3\text{-}(p\text{-tolyl})C_3{=}CH(Ph)\}]PF_6$ (**5c′**) in a 1:1 ratio. Reacting **2b** with PhC≡CH similarly gives **5c** and **5c′** in equal amounts. Structures of **3c**, **5a**, and **5c/5c′** are established by X-ray crystallography. Mechanistic insights from the isolated complexes suggest that hydrogen shift between vinylidene and acetylide moieties is an important process in the coupling of alkynes.

Reports on the reactivity of transition metal vinylidene and acetylide complexes demonstrate a close relationship between these organometallic interactions.[1] Their interconversions are important in the dimerization of alkynes[2] and condensation of alkynes with allylic alcohols[3] or carboxylic acids.[4] Many d^6 metal vinylidene complexes have been prepared by reaction of appropriate metal precursors with 1-alkynes.[5] Theoretical studies suggest that initial side-on coordination of the 1-alkyne is followed by a 1,2-hydrogen shift to give the metal vinylidene complex.[6,7] This usually spontaneous rearrangement is driven by a repulsive interaction between the filled $\pi_\perp$ orbital of the alkyne and the filled $d_\pi(t_{2g})$ metal orbital.[8] However, Selegue and Bullock reported that this rearrangement can require thermal initiation.[9] Recently, 1,2-hydrogen shift initiated by an electron transfer pathway was published.[10]

Ruthenium vinylidene complexes containing "soft" ligands[11] such as η-cyclopentadienyl,[12] η-benzene,[13] bis(diphenylphosphino)methane,[14] and $CH_3(CH_2)_2N(CH_2CH_2PPh_2)_2$[15] have been synthesized. However, since the unfavorable π-interaction between the d_π(Ru) and

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$\pi_\perp$(C≡C) orbitals is the driving force for the alkyne−vinylidene rearrangement, we anticipated that synthesis of vinylidene complexes may be achieved by utilizing "hard" amine ligand systems. However, reaction between $[Ru(NH_3)_5(H_2O)]^{2+}$ and phenylacetylene yielded the η^2-alkyne complex $[Ru(NH_3)_5(\eta^2\text{-PhC}{\equiv}CH)]^{2+}$.[16]

We have been studying the chemistry of organoruthenium complexes containing the saturated tertiary amine 1,4,7-trimethyl-1,4,7-triazacyclononane.[17,18] In this work, ruthenium vinylidene and σ-acetylide derivatives are prepared, and reactions of the former with base and oxygen are studied. Coupling reactions with 1-alkynes resulting in carbon−carbon bond formation are observed.

Experimental Section

All reactions were carried out in a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. $Ru(Me_3tacn)Cl_3$[19] and $[Ru(Me_3tacn)(OH_2)_2(O_2CCF_3)](OTf)_2$[20] (OTf = trifluoromethanesulfonate) were prepared according to the published methods. Trimethylphosphine and 1,2-bis(dimethylphosphino)ethane (dmpe) were purchased from Merck and used as received. PhC≡CH and *p*-tolylC≡CH were obtained from Aldrich and distilled before use. All solvents were reagent grade and used without further purification.

$^{13}C\{^1H\}$ and ^1H NMR spectra were recorded on a JEOL 270 FT-NMR, Bruker 300 DPX FT-NMR, or Bruker 500 DRX FT-NMR spectrometer operating at 270, 300, or 500 MHz (^1H) and 67.5, 75, or 125 MHz (^{13}C), respectively. Peak positions were calibrated with Me_4Si as internal standard. $^{31}P\{^1H\}$ NMR spectra were recorded on the Bruker 500 DRX FT-NMR spectrometer operating at 202.4 MHz, and chemical shifts were measured relative to external 85% H_3PO_4 with downfield values taken as positive. Fast atom bombardment (FAB) mass spectra were obtained on a Finnigan MAT 95 mass spectrometer with 3-nitrobenzyl alcohol matrix. Infrared spectra were recorded as Nujol mulls on a BIO RAD FT-IR spectrometer between KBr plates. Elemental analyses were performed by the Butterworth Laboratory Ltd, U.K.

$[Ru(Me_3tacn)(PMe_3)_2(O_2CCF_3)]PF_6$ (1a). PMe_3 (0.16 g, 2.1 mmol) and zinc powder (0.50 g) were mixed in acetone (20 cm^3). After 5 min, $[Ru(Me_3tacn)(H_2O)_2(O_2CCF_3)](OTf)_2$ (0.50 g, 0.69 mmol) was added to the stirred solution to give a yellow coloration instantaneously. The stirring was continued at room temperature for 1 h. After removal of zinc powder, the solvent was removed under reduced pressure and a saturated aqueous solution of NH_4PF_6 was added to give the titled compound as a yellow solid (yield = 0.22 g, 47%). Anal. Calcd for $C_{17}H_{39}N_3O_2F_9P_3Ru$: C, 30.02; H, 5.79; N, 6.11. Found: C, 29.86; H, 5.75; N, 6.15. ^1H NMR (300 MHz, $(CD_3)_2CO$): 1.43 (18H, virtual t, J_{PH} = 3.7 Hz, $P(CH_3)_3$), 2.76−3.53 (21H, m, Me_3tacn). IR (cm^{-1}): ν(CO) 1685. $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): −0.5. FAB mass spectrum: *m/z* 538 $[M^+ - PF_6]$, 462 $[M^+ - PF_6 - PMe_3]$, 386 $[M^+ - PF_6 - 2PMe_3]$.

$[Ru(Me_3tacn)(PMe_3)_2Cl]PF_6$ (1b). $Ru(Me_3tacn)Cl_3$ (0.10 g, 0.26 mmol) and zinc powder (0.50 g) were added to a stirred ethanolic solution (20 cm^3) of PMe_3 (0.05 g, 0.66 mmol). The mixture was refluxed for 18 h. The zinc powder was removed, and upon addition of NH_4PF_6, a yellow solid was formed. The solid was filtered, washed with ethanol, water, and diethyl ether, and air-dried (yield = 0.10 g, 63%). Anal. Calcd for $C_{15}H_{39}N_3ClF_6P_3Ru$: C, 29.78 ; H, 6.49; N, 6.95. Found: C, 29.95; H, 6.38; N, 6.85. ^1H NMR (500 MHz, CD_3CN): 1.49 (18H, virtual t, J_{PH} = 3.7 Hz, $P(CH_3)_3$), 2.66−3.13 (21H, m, Me_3tacn). $^{31}P\{^1H\}$ NMR (CD_3CN): −1.0. FAB mass spectrum: *m/z* 460 $[M^+ - PF_6]$, 384 $[M^+ - PF_6 - PMe_3]$.

$[Ru(Me_3tacn)(dmpe)(O_2CCF_3)]PF_6$ (1c). Compared to **1a**, the titled compound was prepared using dmpe instead of PMe_3 (yield = 0.19 g, 41%). Anal. Calcd for $C_{17}H_{37}N_3O_2F_9P_3Ru$: C, 30.00; H, 5.48; N, 6.18. Found: C, 30.05; H, 5.60; N, 6.15. ^1H NMR (300 MHz, $(CD_3)_2CO$): 1.42 (6H, d, *J* = 9 Hz, P-CH_3), 1.71 (6H, d, J_{PH} = 7.62 Hz, P-CH_3), 2.67 (3H, s, N-CH_3), 2.73−3.37 (22H, m, 2 × N-CH_3, N-CH_2, P-CH_2). IR (cm^{-1}): ν(CO) 1685. $^{31}P\{^1H\}$ NMR (CD_3CN): 42.9. FAB mass spectrum: *m/z* 536 $[M^+ - PF_6]$.

$[Ru(Me_3tacn)(PMe_3)(O_2CCF_3)\{C{=}CH(Ph)\}]PF_6$ (2a). Complex **1a** (0.20 g, 0.29 mmol) and PhC≡CH (0.03 g, 0.29 mmol) were mixed in 1,2-dichloroethane (20 cm^3). The solution was refluxed for 2 h to give a red solution. The solvent was removed, and a methanolic solution of NH_4PF_6 was added to afford a red crystalline solid (yield = 0.18 g, 87%). Anal. Calcd for $C_{22}H_{36}N_3O_2F_9P_2Ru$: C, 37.29; H, 5.12; N, 5.93. Found: C, 37.38; H, 5.12; N, 5.74. IR (cm^{-1}): ν(CO) 1710 (m); ν(C=C) 1621 (m). ^1H NMR (270 MHz, $(CD_3)_2CO$): 1.59 (9H, d, J_{PH} = 9.25 Hz, $P(CH_3)_3$), 3.25−3.65 (21H, m, Me_3tacn), 5.47 (1H, d, J_{PH} = 4.39 Hz, =C*H*(Ph)), 7.14−7.46 (m, 5H, C_6H_5). $^{13}C\{^1H\}$ NMR (270 MHz, CD_2Cl_2): 363.7 (d, J_{PC} = 22.3 Hz, Ru=*C*=C), 129.4, 128.3, 127.7, 126.9 (C_6H_5), 117.3, 112.9 (CF_3CO_2), 111.6 (Ru=C=*C*), 63.6, 63.2, 61.4, 60.3, 59.5, 58.2, 56.5, 52.0, 51.7 (Me_3tacn), 16.3 (d, J_{PC} = 30.9 Hz, $P(CH_3)_3$). $^{31}P\{^1H\}$ NMR (CD_3CN): −3.0. FAB mass spectrum: *m/z* 564 $[M^+ - PF_6]$, 462 $[M^+ - PF_6 - PhC{\equiv}CH]$.

$[Ru(Me_3tacn)(PMe_3)(O_2CCF_3)\{C{=}CH(p\text{-tolyl})\}]PF_6$ (2b). The procedure was similar to **2a** except *p*-tolylC≡CH was used instead of PhC≡CH (yield = 0.10 g, 50%). Anal. Calcd for $C_{23}H_{38}N_3O_2F_9P_2Ru$: C, 38.17; H, 5.26; N, 5.81. Found: C, 37.96, H, 5.52; N, 5.94. IR (cm^{-1}): ν(CO) 1715 (m); ν(C=C) 1635 (m). ^1H NMR (500 MHz, $(CD_3)_2CO$): 1.63 (9H, d, J_{PH} = 9.6 Hz, $P(CH_3)_3$), 2.30 (3H, s, $C_6H_4CH_3$), 3.02−3.87 (21H, m, Me_3tacn), 5.13 (1H, d, J_{PH} = 4.45 Hz, =C*H*(*p*-tolyl)), 7.04−7.13 (dd, 4H, C_6H_4). $^{13}C\{^1H\}$ NMR (125 MHz, $(CD_3)_2CO$): 362.9 (d, J_{PC} = 23.3 Hz, Ru=*C*=C), 130.2, 130.1, 127.9, 126.7 (C_6H_4), 110.8 (Ru=C=*C*), 63.8, 57.7, 58.7, 60.1, 61.2, 61.3, 63.2, 52.6 (Me_3tacn), 21.1 ($C_6H_4CH_3$), 17.1 (d, J_{PC} = 32.6 Hz, $P(CH_3)_3$). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): −3.8. FAB mass spectrum: *m/z* 578 $[M^+ - PF_6]$, 462 $[M^+ - PF_6 - p\text{-tolylC}{\equiv}CH]$.

$[Ru(Me_3tacn)(PMe_3)_2(C{\equiv}CPh)]PF_6$ (3a). PMe_3 (0.10 g, 1.3 mmol) and potassium hydroxide (0.10 g, 1.8 mmol) were dissolved in anhydrous methanol (10 cm^3). Complex **2a** (0.10 g, 0.14 mmol) was then added, and the mixture was stirred for 2 h to give a yellow solution. The methanol was removed under reduced pressure. The residue was then dissolved in acetone, and a saturated aqueous solution of NH_4PF_6 was added. Slow evaporation of acetone gave a yellow crystalline solid (yield = 0.05 g, 53%). Anal. Calcd for $C_{23}H_{44}N_3F_6P_3Ru$: C, 41.19: H, 6.61; N, 6.27. Found: C, 40.91; H, 6.53; N, 6.10. IR (cm^{-1}): ν(C≡C) 2065. ^1H NMR (500 MHz, $(CD_3)_2CO$): 1.64 (18H, virtual t, J_{PH} = 3.7 Hz, $P(CH_3)_3$), 2.75−3.34 (21H, m, Me_3tacn), 6.95−7.00 (1H, m, para H), 7.11−7.19 (4H, m, ortho and meta H). $^{13}C\{^1H\}$ NMR (125 MHz, $(CD_3)_2CO$): 131.3, 130.9, 128.7, 124.1 (C_6H_5), 131.0 (t, J_{PC} = 10 Hz, Ru-*C*≡C), 108.9 (Ru-C≡*C*), 62.5, 61.7, 60.1, 58.2, 55.4 (Me_3tacn), 21.9 (virtual t, J_{PC} = 14.5 Hz, $P(CH_3)_3$). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): 2.4. FAB mass spectrum: *m/z* 526 $[M^+ - PF_6]$, 450 $[M^+ - PF_6 - PMe_3]$.

$[Ru(Me_3tacn)(PMe_3)_2\{C{\equiv}C(p\text{-tolyl})\}]PF_6$ (3b). Compared to **3a**, **2b** was used instead of **2a** as starting material (yield = 0.04 g, 42%). Anal. Calcd for $C_{24}H_{46}N_3F_6P_3Ru$: C, 42.10; H, 6.77; N, 6.14. Found: C, 41.95; H, 6.41; N, 5.98. IR

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(cm^{-1}): ν(C≡C) 2065. ^{1}H NMR (270 MHz, CD_3CN): 1.51 (18H, virtual t, J_{PH} = 3.8 Hz, P(CH_3)$_3$), 2.24 (3H, s, $C_6H_4CH_3$), 2.66−3.19 (21H, m, Me$_3$tacn), 6.94−7.05 (4H, dd, C_6H_4). ^{13}C{^{1}H} NMR (67.5 MHz, CD_3CN): 133.9, 130.9, 129.7, 128.4 (C_6H_4), 108.5 (Ru-C≡*C*), 62.4, 61.7, 60.0, 58.3, 55.5 (Me$_3$tacn), 21.9 (virtual t, J_{PC} = 14.5 Hz, P(CH_3)$_3$), 21.2 ($C_6H_4CH_3$), Ru-*C*≡C not resolved. ^{31}P{^{1}H} NMR (CD_3CN): 2.4. FAB mass spectrum: *m*/*z* 540 [$M^+ - PF_6$], 464 [$M^+ - PF_6 - PMe_3$].

[Ru(Me$_3$tacn)(PMe$_3$)(P(OMe)$_3$)(C≡CPh)]PF$_6$ (3c). Compared to **2a**, P(OMe)$_3$ was used instead of PMe$_3$ (yield = 0.06 g, 55%). Anal. Calcd for $C_{23}H_{44}N_3O_3F_6P_3Ru$: C, 38.43; H, 6.17; N, 5.85. Found: C, 38.31; H, 6.16; N, 5.87. IR (cm^{-1}): ν(C≡C) 2056. ^{1}H NMR (270 MHz, $(CD_3)_2CO$): 1.57 (9H, d, J_{PH} = 8.6 Hz, P(CH_3)$_3$), 2.80−3.32 (21H, m, Me$_3$tacn), 3.98 (9H, d, J_{PH} = 10.0 Hz, P(OCH_3)$_3$), 7.01−7.20 (5H, m, phenyl). ^{13}C{^{1}H} NMR (270 MHz, $(CD_3)_2CO$): 130.9, 130.8, 128.8, 124.5 (C_6H_5), 110.1 (Ru-C≡*C*), 62.9, 62.2, 61.2, 60.6, 60.4, 59.5, 57.5, 55.6, 54.2 (Me$_3$tacn), 54.3 (d, J_{PC} = 10.4 Hz, P(O*C*H$_3$)$_3$), 20.8 (d, J_{PC} = 31.2 Hz, P(*C*H$_3$)$_3$), Ru-*C*≡C not resolved. ^{31}P{^{1}H} NMR ($(CD_3)_2CO$): 137.6 (d, J_{PP} = 70.5 Hz, *P*(OMe)$_3$), 3.2 (d, J_{PP} = 70.5 Hz, *P*Me$_3$). FAB mass spectrum: *m*/*z* 574 [$M^+ - PF_6$], 498 [$M^+ - PF_6 - PMe_3$].

[Ru(Me$_3$tacn)(PMe$_3$)(O$_2$CCF$_3$)(CO)]PF$_6$ (4). Oxygen gas was introduced into a 1,2-dichloroethane solution of **2a** (0.08 g, 0.11 mmol) for 8 h. The color of the solution changed from red-orange to yellow. The solution was then concentrated to *ca*. 5 cm^3 under reduced pressure. The titled compound was isolated as a yellow solid upon addition of diethyl ether and recrystallized from dichloromethane/diethyl ether (yield = 0.03 g, 52%). Anal. Calcd for $C_{15}H_{30}N_3O_3F_9P_2Ru$: C, 28.39; H, 4.77; N, 6.62. Found: C, 28.15; H, 4.62; N, 6.51. IR (cm^{-1}): ν(C≡O) 1964. ^{1}H NMR (500 MHz, $(CD_3)_2CO$): 1.60 (9H, d, J_{PH} = 9.2 Hz, P(CH_3)$_3$), 3.1−3.6 (21H, m, Me$_3$tacn). ^{13}C{^{1}H} NMR (125 MHz, $(CD_3)_2CO$): 204.8 (d, *J* = 18.4 Hz, *C*O), 63.8, 62.9, 61.4, 61.1, 59.9, 58.7, 58.1, 53.1, 52.7 (Me$_3$tacn), 16.4 (d, *J* = 10.9 Hz, P(*C*H$_3$)$_3$). ^{31}P{^{1}H} NMR ($(CD_3)_2CO$): −3.6. FAB mass spectrum: *m*/*z* 490 [$M^+ - PF_6$].

[Ru(Me$_3$tacn)(PMe$_3$){η^3-PhC$_3$=CH(Ph)}]PF$_6$ (5a). Method A. Complex **1b** (0.15 g, 0.24 mmol), PhC≡CH (0.06 g, 0.6 mmol), and KOH (0.02 g, 0.36 mmol) were refluxed in methanol (15 cm^3) for 18 h to give a clear red solution. After cooling, the solution was concentrated to *ca*. 5 cm^3 under reduced pressure. Upon addition of NH_4PF_6, a red microcrystalline solid was formed. The solid was filtered, washed with ice-cool ethanol and diethyl ether, and air-dried (yield = 0.11 g, 67%).

Method B. Complex **2a** (0.75 g, 1.0 mmol) was added slowly to a hot methanolic KOH (0.06 g, 1.1 mmol) solution (10 cm^3) over 15 min to give a clear yellow solution which was refluxed for a further 5 min. PhC≡CH (0.11 g, 1.1 mmol) in methanol (5 cm^3) was then added dropwise to the yellow solution to give a clear red solution which was refluxed for 5 h. The solution was then concentrated to *ca*. 5 cm^3, and upon addition of NH_4PF_6 a red microcrystalline solid formed. The solid was filtered, washed with ice-cool ethanol and diethyl ether, and then air-dried (yield = 0.10 g, 62%). Anal. Calcd for $C_{28}H_{41}N_3F_6P_2Ru$: C, 48.27; H, 5.93; N, 6.03. Found: C, 48.23; H, 5.96; N, 6.05. ^{1}H NMR (500 MHz, CD_2Cl_2) (the numbering scheme for the hydrogen and carbon resonances is given in ref 21): 0.94 (9H, d, J_{PH} = 7.9 Hz, P(CH_3)$_3$), 1.63 (3H, s, N-CH_3), 2.40−3.61 (15H, m, Me$_3$tacn), 3.81 (3H, s, N-CH_3), 6.94 (1H, s, *H4*), 7.21 (1H, t, *J* = 7.3 Hz, *H8′*), 7.33 (1H, t, *J* = 7.4 Hz, *H8*), 7.39 (2H, t, *J* = 7.6 Hz, *H7*), 7.44 (2H, t, *J* = 7.5 Hz, *H7′*), 7.77 (2H, d, *J* = 7.4 Hz, *H6′*), 7.82 (2H, d, *J* = 7.4 Hz, *H6*). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): 159.1 (d, *J* = 7.6 Hz, *C3*), 138.2, 132.4, 130.8, 129.6, 129.3, 127.8, 126.2, 125.3 (2 × C_6H_5), 124.6 (d, *J* = 6.1 Hz, *C1*), 123.2 (*C4*), 62.4, 61.6, 61.4, 59.8, 59.4, 58.9, 58.7, 58.4 (Me$_3$tacn), 57.2 (d, *J* = 1.5 Hz, *C2*), 47.8 (N-*C*H$_3$), 16.7 (d, *J* = 28.6 Hz, P(*C*H$_3$)$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): 4.8. FAB mass spectrum: *m*/*z* 553 [$M^+ - PF_6$], 477 [$M^+ - PF_6 - PMe_3$].

[Ru(Me$_3$tacn)(PMe$_3$){η^3-(*p*-tolyl)C$_3$=CH(*p*-tolyl)}]PF$_6$ (5b). Compared to **5a**, this complex was synthesized by method A using *p*-tolylC≡CH instead of PhC≡CH or by method B using complex **2b** and *p*-tolylC≡CH as the starting materials (yield = 0.09 g, 52%). Anal. Calcd for $C_{30}H_{45}N_3F_6P_2Ru$: C, 49.72; H, 6.22; N, 5.80. Found: C, 49.52; H, 6.46; N, 5.65. ^{1}H NMR (500 MHz, CD_2Cl_2): 0.93 (9H, d, J_{PH} = 7.9 Hz, P(CH_3)$_3$), 1.61 (3H, s, N-CH_3), 2.33 (3H, s, *H9*), 2.39 (3H, s, *H9′*), 2.41−3.61 (15H, m, Me$_3$tacn), 3.87 (3H, s, N-CH_3), 6.88 (1H, s, *H4*), 7.20 (2H, d, *J* = 7.9 Hz, *H7*), 7.26 (2H, d, *J* = 7.9 Hz, *H7′*), 7.66 (2H, d, *J* = 8.1 Hz, *H6′*), 7.72 (2H, d, *J* = 8.1 Hz, *H6*). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): 157.5 (d, *J* = 7.6 Hz, *C3*), 138.1 (*C8′*), 136.1 (*C8*), 135.7 (*C5*), 130.7 (*C6′*), 130.3 (*C7*), 129.9 (*C7′*), 129.5 (*C5′*), 125.2 (*C6*), 123.8 (d, *J* = 5.4 Hz, *C1*), 122.7 (*C4*), 62.4, 61.6, 61.4, 59.8, 59.4, 58.9, 58.7, 58.4 (Me$_3$tacn), 55.8 (d, *J* = 1.6 Hz, *C2*), 47.7(N-*C*H$_3$), 21.5(*C9′*), 21.3(*C9*), 16.7 (d, *J* = 28.5 Hz, P(*C*H$_3$)$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): 5.2. FAB mass spectrum: *m*/*z* 580 [$M^+ - PF_6$], 504 [$M^+ - PF_6 - PMe_3$].

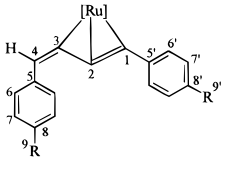
[Ru(Me$_3$tacn)(PMe$_3$){η^3-PhC$_3$=CH(*p*-tolyl)}]PF$_6$ (5c) and [Ru(Me$_3$tacn)(PMe$_3$){η^3-(*p*-tolyl)C$_3$=CH(Ph)}]PF$_6$ (5c′). *p*-TolylC≡CH was used in method B for **5a** (yield = 0.08 g, 48%). Anal. Calcd for $C_{29}H_{43}N_3F_6P_2Ru{\cdot}CH_3OH$: C, 48.51; H, 6.38; N, 5.66. Found: C, 48.22; H, 6.24; N, 5.57. ^{1}H NMR (500 MHz, CD_2Cl_2): 0.94 (18H, d, J_{PH} = 7.8 Hz, P(CH_3)$_3$), 1.62 (6H, s, N-CH_3), 2.39 (3H, s, CH_3 of *p*-tolyl), 2.45 (3H, s, CH_3 of *p*-tolyl), 2.50−3.59 (30H, m, Me$_3$tacn), 3.87 (6H, s, N-CH_3), 6.91 (1H, s, =C*H*), 6.93 (1H, s, =C*H*), 7.20−7.85 (18H, m, C_6H_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): 5.0. FAB mass spectrum: *m*/*z* 566 [$M^+ - PF_6$], 490 [$M^+ - PF_6 - PMe_3$].

Structural Determination. X-ray quality crystals were obtained by slow diffusion of diethyl ether into an acetone solution for **3c** and a dichloromethane solution for **5a**, respectively. Intensities and lattice parameters were measured on a Rigaku AFC7R or Enraf-Nonius CAD-4 diffractometer using the $\omega-2\theta$ scan mode. Crystal parameters and details of data collection and refinement are given in Table 1. Intensity data were corrected for Lorentz and polarization effects. Empirical absorptions were based on the ψ-scan of five strong reflections. The structures were solved by the heavy-atom Patterson method and refined by full-matrix least squares and Fourier-difference syntheses using the MSC-Crystal Structure Package TEXSAN on a Silicon Graphic Indy computer.[22] All non-H atoms were refined anisotropically. The H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Selected bond distances and angles of **3c** and **5a** are tabulated in Tables 2 and 3, respectively.

Results and Discussion

Zinc reduction of [Ru(Me$_3$tacn)(OH$_2$)$_2$(O$_2$CCF$_3$)]$^{2+}$ in acetone in the presence of PMe$_3$ and dmpe gives [Ru(Me$_3$tacn)(PMe$_3$)$_2$(O$_2$CCF$_3$)]PF$_6$ (**1a**) and [Ru(Me$_3$tacn)(dmpe)(O$_2$CCF$_3$)]PF$_6$ (**1c**), respectively. Similar

(21) Numbering scheme for hydrogen and carbon atoms in **5a** and **5b**:



R = H (**5a**), Me (**5b**)

(22) PATTY & DIRDIF92: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Grand, S.; Gould, R. O.; Smits, J. M. M.; Smykalla C.(1992). The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

Table 1. Crystal Data for 3c and 5a

	3c	5a
formula	$C_{23}H_{46}N_3O_3F_6P_3Ru$	$C_{28}H_{41}N_3F_6P_2Ru$
M_r	718.60	696.65
crystal dimensions/mm	0.30 × 0.20 × 0.20	0.25 × 0.35 × 0.50
space group	$P\bar{1}$	$P2_1/c$
a/Å	13.626(2)	19.366(4)
b/Å	13.772(3)	9.330(2)
c/Å	9.179(3)	17.240(8)
α/deg	109.06(2)	
β/deg	104.31(2)	100.73(3)
γ/deg	91.18(2)	
U/Å^3	1567.8(7)	3060.5(2)
Z	2	4
D_c/g cm^{-3}	1.522	1.512
μ/cm^{-1}	7.18	6.63
F(000)	740	1428
T/K	301	298
$2\theta_{max}$	48.0	45.0
no. of data measured	3937	3984
no. of data used	3435 ($I > 3\sigma(I)$)	2903 ($I > 2\sigma(I)$)
no. of variables	352	361
R, R_w[a]	0.053, 0.081	0.054, 0.055
GOF	2.94	1.13
$(\Delta\rho)_{max}$	−0.54, 1.15	−0.65, 0.91
$(\Delta/\sigma)_{max}$	0.01	0.05

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

Table 2. Selected Bond Distances (Å) and Angles (deg) for [Ru(Me$_3$tacn)(PMe$_3$)(P(OMe)$_3$)(C≡CPh)]PF$_6$ (3c)

Ru−P(1)	2.225(2)	Ru−P(2)	2.337(2)	Ru−N(1)	2.256(6)
Ru−N(2)	2.269(5)	Ru−N(3)	2.226(5)	Ru−C(1)	1.991(6)
C(1)−C(2)	1.235(8)	C(2)−C(3)	1.426(8)		
P(1)−Ru−P(2)	85.6(1)	P(1)−Ru−N(1)	98.1(2)		
P(1)−Ru−N(2)	174.9(1)	P(1)−Ru−N(3)	96.0(1)		
P(1)−Ru−C(1)	93.1(2)	P(2)−Ru−N(1)	104.1(2)		
P(2)−Ru−N(2)	99.6(1)	P(2)−Ru−N(3)	177.3(1)		
P(2)−Ru−C(1)	83.6(2)	N(1)−Ru−N(2)	79.7(2)		
N(1)−Ru−N(3)	77.8(2)	N(1)−Ru−C(1)	166.8(2)		
N(2)−Ru−N(3)	79.1(2)	N(2)−Ru−C(1)	88.5(2)		
N(3)−Ru−C(1)	94.1(2)	Ru−C(1)−C(2)	173.0(5)		
C(1)−C(2)−C(3)	176.6(6)				

Table 3. Selected Bond Distances (Å) and Angles (deg) for [Ru(Me$_3$tacn)(PMe$_3$)-{η^3-PhC$_3$=CH(Ph)}]PF$_6$ (5a)

Ru−P(1)	2.307(3)	Ru−N(1)	2.181(6)	Ru−N(2)	2.231(5)
Ru−N(3)	2.203(7)	Ru−C(16)	2.158(8)	Ru−C(17)	2.114(8)
Ru−C(18)	2.058(8)	C(15)−C(16)	1.47(1)	C(16)−C(17)	1.26(1)
C(17)−C(18)	1.37(1)	C(18)−C(19)	1.37(1)		
P(1)−Ru−N(1)	98.7(2)	P(1)−Ru−N(2)	177.9(2)		
P(1)−Ru−N(3)	98.5(2)	P(1)−Ru−C(16)	88.4(2)		
P(1)−Ru−C(17)	87.7(2)	P(1)−Ru−C(18)	88.2(2)		
N(1)−Ru−N(2)	82.8(3)	N(1)−Ru−N(3)	79.5(3)		
N(1)−Ru−C(16)	170.5(3)	N(1)−Ru−C(17)	139.1(3)		
N(1)−Ru−C(18)	101.2(3)	N(2)−Ru−N(3)	83.2(3)		
N(2)−Ru−C(16)	89.9(3)	N(2)−Ru−C(17)	90.2(3)		
N(2)−Ru−C(18)	90.1(3)	N(3)−Ru−C(16)	105.8(3)		
N(3)−Ru−C(17)	139.8(3)	N(3)−Ru−C(18)	173.1(3)		
C(16)−Ru−C(17)	34.3(3)	C(16)−Ru−C(18)	72.5(3)		
C(17)−Ru−C(18)	38.3(3)	Ru−C(16)−C(15)	152.7(6)		
Ru−C(16)−C(17)	70.9(5)	C(15)−C(16)−C(17)	136.1(8)		
Ru−C(17)−C(16)	74.8(5)	Ru−C(17)−C(18)	68.7(5)		
C(16)−C(17)−C(18)	143.4(8)	Ru−C(18)−C(17)	73.1(5)		
Ru−C(18)−C(19)	149.7(6)	C(17)−C(18)−C(19)	137.2(8)		
C(18)−C(19)−C(20)	126.3(7)				

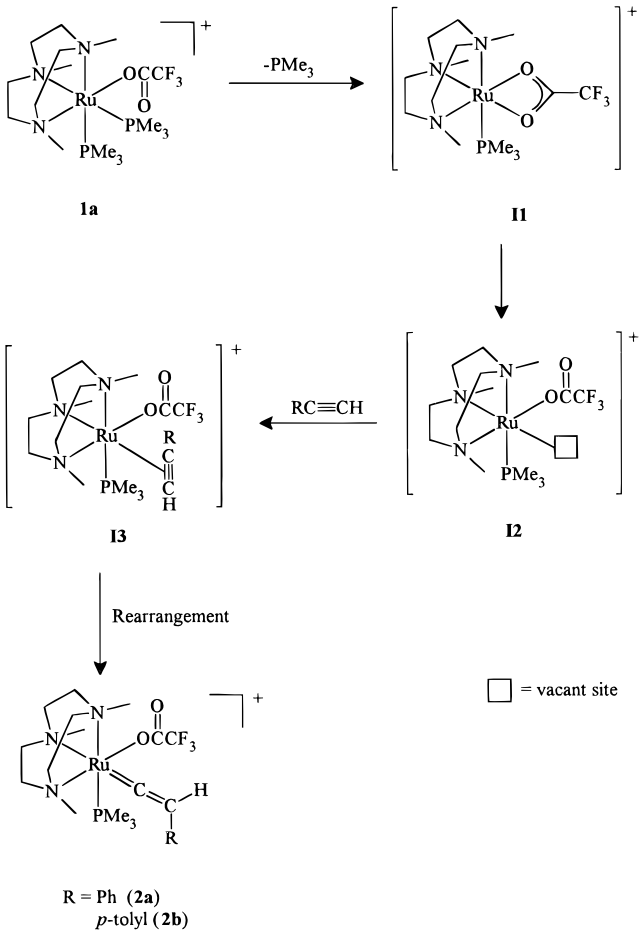
ruthenium complexes of Me$_3$tacn with π-acid ligands have been reported.[18] In addition, Ru(Me$_3$tacn)Cl$_3$ reacts with PMe$_3$ in ethanol in the presence of zinc to yield [Ru(Me$_3$tacn)(PMe$_3$)$_2$Cl]PF$_6$ (**1b**) in moderate yield. Attempts to prepare the bulkier PPh$_3$ analogues [Ru(Me$_3$tacn)(PPh$_3$)$_2$X]PF$_6$ (X = Cl or O$_2$CCF$_3$) were unsuccessful.

Preparation of Vinylidene Complexes [Ru(Me$_3$tacn)(PMe$_3$)(O$_2$CCF$_3$){C=CH(R)}]PF$_6$ (R = Ph (2a); R = *p*-tolyl (2b)) and σ-Acetylide Complexes [Ru(Me$_3$tacn)(L)(PMe$_3$)(C≡CR)]PF$_6$ (R = Ph, L = PMe$_3$ (3a); R = *p*-tolyl, L = PMe$_3$ (3b); R = Ph, L = P(OMe)$_3$ (3c)). [Ru(Me$_3$tacn)(PMe$_3$)$_2$(O$_2$CCF$_3$)]PF$_6$ (**1a**) reacts with PhC≡CH and *p*-tolylC≡CH in refluxing 1,2-dichloroethane to give the vinylidene complexes [Ru(Me$_3$tacn)(PMe$_3$)(O$_2$CCF$_3$){C=CH(R)}]PF$_6$ (R = Ph (**2a**) and *p*-tolyl (**2b**)) respectively. No desired products are obtained using alkylacetylenes such as 2-methyl-3-butyn-2-ol, *tert*-butylacetylene, (trimethylsilyl)acetylene, or 1-hexyne. Furthermore, no reaction was found between **1c** and PhC≡CH after refluxing in 1,2-dichloroethane or ethanol for 24 h. The chelating dmpe ligand in **1c** is expected to resist dissociation and prevent subsequent reaction with the 1-alkyne. Hence dissociation of PMe$_3$ to generate a coordination vacancy is presumably the first step in the formation of **2a**,**b**.

Reaction between **1b** and PhC≡CH in 1,2-dichloroethane gives impure [Ru(Me$_3$tacn)(PMe$_3$)(Cl){C=CH(Ph)}]PF$_6$ (identified by ^{1}H NMR) in very low yield (*ca.* 5%) after reflux for 10 h. The observation that the rate of formation for vinylidene complexes is faster for **1a** than for **1b** warrants further comment. Since **1a** and **1b** are coordinatively saturated 18-electron species, dissociation of PMe$_3$ is likely to be the most endothermic and hence the rate-determining step of vinylidene formation. In this system, ground state destabilization resulting in phosphine dissociation from [Ru(Me$_3$tacn)(PMe$_3$)$_2$X]$^+$ (X = O$_2$CCF$_3$ (**1a**), Cl (**1b**)) is negligible because the steric requirement of X is small. In addition, the rate of PMe$_3$ dissociation in CpRu(PMe$_3$)$_2$X (X = halide, alkyl, hydride, amide, and hydroxy) have been studied by Bercaw[23] and Caulton.[24] They suggested that π-donation from X can stabilize the 16-electron intermediate CpRu(PMe$_3$)X, which results in a faster dissociation rate. In both **1a** and **1b,** however, the ligand X has π-electrons which can stabilize the 16-electron species Ru(Me$_3$tacn)(PMe$_3$)X to a similar extent. Hence this factor cannot account for the large difference in the phosphine dissociation rate between **1a** and **1b**. We attribute this to neighboring group participation by the trifluoroacetate anion. This phenomenon has been invoked previously in the oxidative addition and reductive elimination of square-planar platinum[25] and iridium[26] complexes. Unlike in **1b**, the lone pair of the carboxylate group in **1a** can interact with the metal which lowers the activation energy for the dissociation of PMe$_3$ to form an 18-electron intermediate **I1** (Scheme 1). The η^2-trifluoroacetate anion in **I1** isomerizes to an η^1-mode (**I2**) to provide a vacant site for the coordination of RC≡CH. The conversion between η^1 and η^2 bonding modes for the carboxylate ligand is often observed in the generation of coordination vacancy.[27] It is likely that the RC≡CH is initially bound to the ruthenium center in a side-on fashion (**I3**), and 1,2-hydrogen shift subsequently occurs to give the vinylidene complex.

(23) Bryndza, H. E.; Domaille, P. J.; Paciello, R. A.; Bercaw, J. E. *Organometallics* **1989**, *8*, 379.
(24) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25.
(25) Constable, A. G.; Langrick, C. R.; Shabanzadeh, B.; Shaw, B. L. *Inorg. Chim. Acta* **1982**, *65*, L151.
(26) Miller, E. M.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1974**, 480.
(27) (a) Braun, T.; Gevert, O.; Werner, H. *J. Am. Chem. Soc.* **1995**, *117*, 7291. (b) Scher, M.; Wolf, J.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1991**, 1341.

Scheme 1



The vinylidene complexes **2a** and **2b** are air-stable solids. Their IR spectra each contain bands at *ca.* 1710 and 1620 cm^{-1} which are typical for the stretching frequencies of the C═O and C═C groups in η^1-O_2CCF_3 and vinylidene ligands, respectively. The $^{31}P\{^1H\}$ NMR spectra show a single resonance at −3.0 and −3.8 ppm for the coordinated PMe_3 in **2a** and **2b**, respectively. Their $^{13}C\{^1H\}$ NMR spectra each reveal a low-field doublet at *ca.* 363 ppm ($^2J_{PC} \approx 23$ Hz) for the metal-bonded vinylidene carbon while the resonance for the β-carbon is at *ca.* 110 ppm. The spectroscopic data confirm that **2a** is a vinylidene complex rather than a metallacyclic vinyl ester compound because the latter would display a lower ^{13}C resonance and ν(C═O) band for C_α and the CF_3CO_2 group, respectively.[28] In the ^1H NMR spectra, the chemical shifts of the vinylidene protons in **2a** and **2b** (5.47 and 5.13 ppm, respectively) are similar to the related complexes $[Ru(\eta\text{-}C_5H_5)(PPh_3)_2\{C{=}CH(Ph)\}]PF_6$ (5.43 ppm),[11a] $[Ru(\eta\text{-}C_6Me_6)(PMe_3)(Cl)\{C{=}CH(Ph)\}]PF_6$ (5.66 ppm),[12a] and $[Ru(P(OMe)_3)_4(C{\equiv}CPh)\{C{=}CH(Ph)\}]PF_6$ (5.98 ppm).[29]

Nucleophilic attack at the α-carbon of vinylidene complexes to give heteroatom-stabilized carbene species is well established and can be affected by the steric and electronic properties of the spectator ligands.[30] Complex **2a** and **2b** are stable in refluxing methanol, while only deprotonation of the vinylidene ligand is observed upon reaction with primary and secondary amines. Hence upon addition of *tert*-butylamine to an acetone-d_6 solution of **2a**, the vinylidene proton signal in the ^1H NMR spectrum vanishes and the σ-acetylide complex is formed (see below). This is in contrast to the report by Bianchini that primary and secondary amines react with ruthenium vinylidene derivatives to give amino-carbene and isocyanide complexes.[14a] We propose that complexes **2a**,**b** are resistant to nucleophilic addition as a result of electronic rather than steric factors: the auxiliary ligands in the present system do not appear to impart steric hindrance, while the high π-basicity of the $[Ru(Me_3tacn)]$ fragment is expected to lower the electrophilicity of the α-carbon atom.

Reaction of **2a** and **2b** with methanolic KOH in the presence of phosphine L (L = PMe_3 or $P(OMe)_3$) affords the σ-acetylide complexes $[Ru(Me_3tacn)(PMe_3)L(C{\equiv}CR)]^+$ (R = Ph, L = PMe_3 (**3a**), R = *p*-tolyl, L = PMe_3 (**3b**), R = Ph, L = $P(OMe)_3$ (**3c**)). It is noteworthy that the expected formation of the σ-acetylide species via direct substitution of **1b** with the appropriate Grignard reagent does not give the desired products. The use of amines, e.g. triethylamine, *tert*-butylamine, as base results in lower yields. The vinylidene derivative **2a** is first deprotonated by KOH to give the σ-acetylide intermediate; substitution of the CF_3CO_2 ligand by PMe_3 then proceeds to give **3a**. Complexes **3b** and **3c** are presumably formed via similar reaction pathways.

In the $^{13}C\{^1H\}$ NMR spectra for complexes **3a**−**c**, a singlet is observed at 108−110 ppm for the β-acetylide carbon (hence no phosphorus coupling). **3a** and **3b** both show five resonances in the range 55−63 ppm which correspond to the Me_3tacn ligand and suggest C_s symmetry. In complex **3c**, nine carbon resonances are assigned to Me_3tacn, and this implies the presence of C_i symmetry. Large coupling in the $^{31}P\{^1H\}$ NMR spectrum ($^2J_{PP} = 70.5$ Hz) between PMe_3 and $P(OMe)_3$ is evident. A triplet at *ca.* 131 ppm in the $^{13}C\{^1H\}$ NMR spectrum of **3a** is assigned to the α-carbon, but an analogous signal for **3b** and **3c** is obscured by phenyl resonances. The IR spectra for **3a**−**c** each show an intense absorption band at *ca.* 2060 cm^{-1} for the C≡C moiety.

Introduction of dioxygen into a 1,2-dichloroethane solution of **2a** affords $[Ru(Me_3tacn)(CO)(PMe_3)(O_2CCF_3)]^+$ (**4**) and benzaldehyde. Oxidative cleavage of vinylidene ligands have been previously reported.[31] We found that the incorporation of an electron-withdrawing group (e.g. NO_2, Cl) into the *para* position of the phenyl ring in **2a** leads to longer reaction times.[32] The stability of the vinylidene complexes toward oxidation therefore increases as the electron density at the C═C bond decreases. The FAB mass spectrum of **4** reveals a cluster at *m*/*z* 490 which corresponds to the parent cationic fragment $[Ru(Me_3tacn)(PMe_3)(O_2CCF_3)(CO)]^+$. A low-field doublet at 204.8 ppm ($^2J_{PC}$ = 28.6Hz) in the ^{13}C NMR spectrum and a strong absorption at 1964 cm^{-1} in the IR spectrum are characteristic of a terminal carbonyl ligand.

Synthesis of η^3-Butenynyl Complexes $[Ru(Me_3tacn)(PMe_3)\{\eta^3\text{-}RC_3{=}CH(R)\}]PF_6$ (R = Ph (5a),

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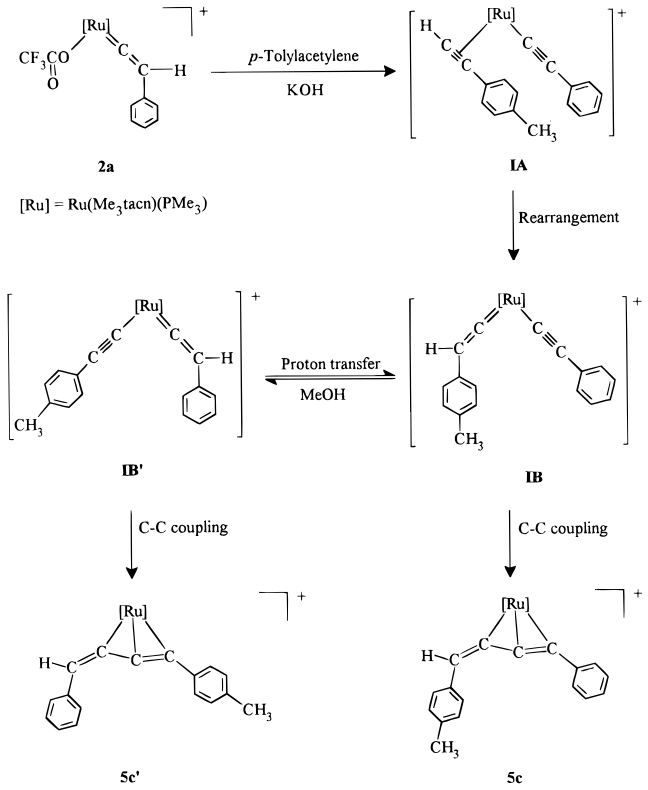
***p*-tolyl (5b)).** Reaction of excess PhC≡CH and KOH with $[Ru(Me_3tacn)(PMe_3)_2Cl]PF_6$ (**1b**) in refluxing methanol gives a orange-red solution from which red crystals of $[Ru(Me_3tacn)(PMe_3)\{\eta^3\text{-}PhC_3{=}CH(Ph)\}]PF_6$ (**5a)** are obtained (method A). Similarly, $[Ru(Me_3tacn)(PMe_3)\{\eta^3\text{-}(p\text{-tolyl})C_3{=}CH(p\text{-tolyl})\}]PF_6$ (**5b**) is formed using *p*-tolylC≡CH. Treatment of the vinylidene complexes **2a** and **2b** with KOH followed by RC≡CH in refluxing methanol also gives **5a** and **5b**, respectively (method B). Formation of η^3-butenynyl complexes from well-defined ruthenium[2b] and tungsten[33] precursors have been reported.

Using method A, we attempted to isolate the intermediate(s) of the reaction by adding diethyl ether to the mixture after reflux for 30 min to precipitate all ionic species present. A red solid and colorless solution were afforded, and the ^1H NMR spectrum of the solid consisted of three species: starting complex **1b** (PMe_3 protons at 1.49 ppm), a small amount of **5a** (characteristic vinyl proton at 6.94 ppm), and small amounts of an unknown species with a doublet at *ca*. 5.5 ppm. Due to the similarities between these resonances and that of **2a**, we suggest that this species is a vinylidene intermediate in the formation of **5a**. This assertion is further supported by the successful synthesis of **5a** from the vinylidene complex **2a** via method B.

The ^1H and $^{13}C\{^1H\}$ signals of the 1,4′-di(*p*-tolyl)-butenynyl ligand in complex **5b** have been assigned by DEPT-135, HMBC, and HSQC $^{13}C-^1H$ COSY NMR experiments. In the $^{13}C\{^1H\}$ NMR spectrum, three small doublets appearing at 55.8 ppm ($^2J_{PC}$ = 1.5 Hz), 123.8 ($^2J_{PC}$ = 5.4 Hz), and 157.5 ppm ($^2J_{PC}$ = 7.6 Hz) correlate to the ruthenium-bonded C2, C1, and C3 atoms respectively. The ^1H, $^{13}C\{^1H\}$, and $^{13}C-^1H$ COSY NMR spectra of **5a** are similar to those of **5b**, except the ^1H resonances in **5b** at 2.33 and 2.39 ppm are attributed to the *p*-tolyl methyl groups. The ^1H NMR spectra of **5a** and **5b** each contain a singlet at *ca*. 6.9 ppm which is assigned to the vinylic proton of the 1,4′-disubstituted η^3-butenynyl ligand. One Me_3tacn methyl group appears at a higher field in both the ^1H and $^{13}C\{^1H\}$ NMR spectra (*ca*. 1.6 and 48 ppm, respectively) than other signals for the ligand (2.4−3.6 ppm for ^1H and 58−63 ppm for ^{13}C). It is apparent from the X-ray structure of **5a** (*vide infra*) that this methyl substituent is located above one of the phenyl rings of the η^3-butenynyl moiety and is therefore shielded by the diamagnetic ring current.

$[Ru(Me_3tacn)(PMe_3)\{\eta^3\text{-}PhC_3{=}CH(p\text{-tolyl})\}]PF_6$ (5c) and $[Ru(Me_3tacn)(PMe_3)\{\eta^3\text{-}(p\text{-tolyl})C_3{=}CH(Ph)\}]PF_6$ (5c′): Synthesis and Mechanism. Reaction of **2a** with *p*-tolylC≡CH in methanolic KOH gives a red solid. The FAB mass spectrum shows a cluster around *m*/*z* 566 which can be assigned to the isomeric fragments $[Ru(Me_3tacn)(PMe_3)\{\eta^3\text{-}PhC_3{=}CH(p\text{-tolyl})\}]^+$ (**5c**) or $[Ru(Me_3tacn)(PMe_3)\{\eta^3\text{-}(p\text{-tolyl})C_3{=}CH(Ph)\}]^+$ (**5c′**). The $^{31}P\{^1H\}$ NMR spectrum shows a slightly broad signal at 5.0 ppm, while the ^1H and $^{13}C\{^1H\}$ NMR spectra are uninformative due to overlapping signals. Nevertheless, the ^1H NMR spectrum shows two signals of equal intensity at 6.91 and 6.93 ppm which are attributed to the vinylic protons of the η^3-butenynyl moieties in **5c** and **5c′**. In addition, two peaks of equal intensity at 2.39 and 2.45 ppm are assigned to the methyl hydrogens of the *p*-tolyl groups.

Scheme 2. Proposed Mechanism for the Formation of 5c/5c′



In order to eliminate the possibility that the isolated red solid is an equimolar mixture of **5a** and **5b**, we have also recorded the ^1H and $^{31}P\{^1H\}$ NMR spectra and the FAB mass spectrum of such a mixture. In the ^1H NMR spectrum, two signals at 6.94 and 6.88 ppm are visible for the vinylic protons of **5a** and **5b**, respectively, while the analogous resonances for **5c**/**5c′** are absent. The methyl hydrogens for the *p*-tolyl substituents appear at 2.33 and 2.39 ppm. Moreover, the $^{31}P\{^1H\}$ NMR spectrum shows two signals at 4.8 and 5.2 ppm which correspond to the PMe_3 ligand in **5a** and **5b**, respectively; again the corresponding peaks for **5c**/**5c′** are not observed. The FAB mass spectrum does not show a cluster at *m*/*z* 566. Hence there is no signals corresponding to the red product from the reaction of **2a** with *p*-tolylC≡CH, which is a 1:1 mixture of $[Ru(Me_3tacn)(PMe_3)\{\eta^3\text{-}PhC_3{=}CH(p\text{-tolyl})\}]PF_6$ (**5c**) and $[Ru(Me_3tacn)(PMe_3)\{\eta^3\text{-}(p\text{-tolyl})C_3{=}CH(Ph)\}]PF_6$ (**5c′**). Finally, the analogous reaction between complex **2b** with phenylacetylene also gives **5c**/**5c′** as a red solid with identical spectroscopic properties. The molecular structure of **5c**/**5c′** (see the Supporting Information) shows coordination of the η^3-butenynyl fragment to the metal center as in the structure of **5a**.

Scheme 2 depicts our proposed mechanism for the formation of the η^3-butenynylruthenium(II) complexes **5c** and **5c′**. The stepwise mechanism is related to others previously reported.[34] However, the location of the *p*-tolyl substituent in the final products provide interesting mechanistic information.

We have demonstrated that 1 molar equiv of KOH serves to deprotonate the vinylidene ligand in the preparation of **3a**−**c**. We propose that the reaction of

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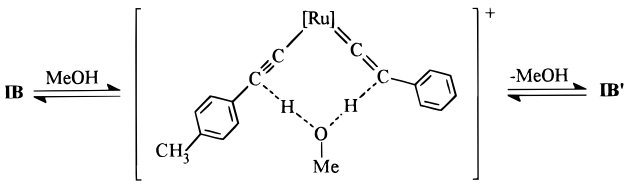
Scheme 3



[Ru] = Ru(Me_3tacn)(PMe_3)

2a with *p*-tolylacetylene in the presence of KOH yields the (η^2-*p*-tolylC≡CH)(σ-C≡CPh) intermediate **IA**. Rearrangement of *p*-tolylC≡CH results in formation of the (vinylidene)(σ-acetylide) intermediate **IB**, and subsequent 1,2-migratory insertion of the acetylide gives the observed complex **5c**. The formation of the **5c′** isomer gives greater insight into the reaction mechanism.[35] Complex **5c′** is derived from the (σ-*p*-tolylacetylide)-(phenylvinylidene) intermediate **IB′** which is generated by the isomerization of **IB** through proton transfer. From a thermodynamic viewpoint, the strong basicity at the β-carbon of the acetylide moiety and the high acidity of the vinylidene proton will favor the proton migration, and this is further facilitated by the electron-donating nature of the [Ru(Me_3tacn)] fragment. Such proton transfer processes have not been observed by Bianchini.[2b] We believe that the isomerization is kinetically unfavored in aprotic solvents, while in our system the proton transfer/isomerization can be assisted by the methanol solvent (Scheme 3). Moreover, we assume that the C−C coupling is slower than the rate of proton transfer partly because of the weak *trans* effect of the Me_3tacn ligand. Hence, the isomeric intermediates **IB** and **IB′** are generated in equilibrium, and this results in the formation of **5c** and **5c′** in equal proportions.

X-ray Crystal Structures of 3c and 5a. Figures 1 and 2 show perspective views of the cations in **3c** and **5a** respectively. Selected bond distances and angles are presented in Tables 2 and 3, respectively.

The coordination geometry around the ruthenium center in **3c** is a distorted octahedron with the metal atom surrounded by two phosphines, three nitrogen atoms of Me_3tacn, and a σ-acetylide ligand. The three Ru−N distances are comparable. The most evident distortion from idealized geometry is the bending of the acetylide moiety toward Me_3tacn and PMe_3 (N(2)−Ru−C(1) 88.5(2)°, P(2)−Ru−C(1) 83.6(2)°). The Ru−P distances are shorter for the more electron-accepting $P(OMe)_3$ (Ru−P(1) 2.225(2) Å) than for PMe_3 (Ru−P(2) 2.337(2) Å). Since the cone angles of $P(OMe_3)_3$ and

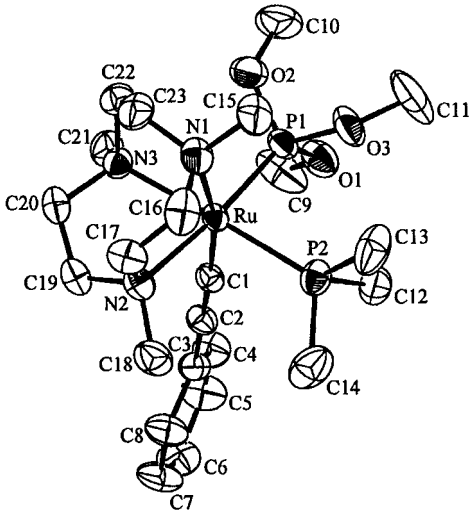


Figure 1. Perspective view of the cation in [Ru(Me_3tacn)-(PMe_3)($P(OMe)_3$)(C≡CPh)]PF_6 (**3c**).

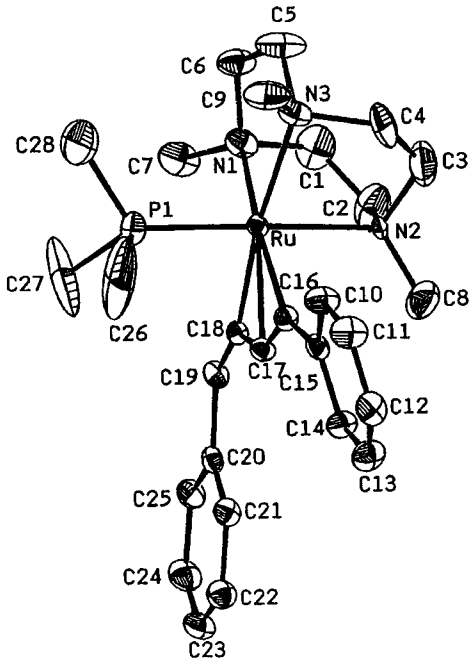


Figure 2. Perspective view of the cation in [Ru(Me_3tacn)-(PMe_3){η^3-PhC_3=CH(Ph)}]PF_6 (**5a**).

PMe_3 are similar (107° and 118°, respectively),[36] the strong π-basicity of the [Ru(Me_3tacn)] fragment apparently results in a stronger bond with $P(OMe_3)_3$. The ethynyl moiety is almost linear (Ru−C(1)−C(2) 173.0(5)°) and the Ru−C separation of 1.991(6) Å is within the range expected for ruthenium(II) σ-acetylide complexes.[37] The high-energy IR stretch (2065 cm^{-1}) of the C≡C bond is consistent with the C(1)−C(2) bond length of 1.235(8) Å, which is comparable to that in disubstituted organic alkynes (*ca.* 1.20 Å)[38] and organometallic alkynyl complexes (1.14−1.24 Å).[39]

The molecular structure of **5a** corresponds to that elucidated spectroscopically for the *p*-tolyl derivative **5b**. The ruthenium center is in a distorted octahedral environment assuming the η^3-butenynyl ligand is occupying two sites. The salient feature of **5a** is the

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(35) The possibility that **5c**/**5c′** are interconvertible by acid- or base-catalyzed isomerization was suggested by one reviewer. However, this is ruled out since no changes are observed by ^{1}H NMR spectroscopy for the treatment of **5b** with CF_3CO_2D or CD_3ONa in CD_3OD.

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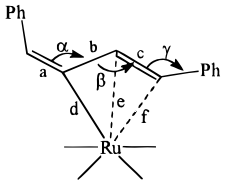
Table 4. Comparison of Structural Data for the Complexes $RuL_n\{\eta^3\text{-}PhC_3{=}CH(Ph)\}$



RuL_n	*a* (Å)	*b* (Å)	*c* (Å)	*d* (Å)	*e* (Å)	*f* (Å)	α (deg)	*β* (deg)	*γ* (deg)	ref
$[Ru(Me_3tacn)(PMe_3)]^+$ (**5a**)	1.366	1.368	1.260	2.058	2.114	2.158	137.2	143.4	136.1	this work
$[Ru(CO)_2(PPh_3)_2]^+$	1.319	1.371	1.244	2.170	2.233	2.320	138.1	147.4	148.7	41a
[RuCl(Cyttp)] (*syn-mer*)[a]	1.335	1.416	1.220	2.040	2.229	2.558	129.2	154.3	156.7	41b
[RuCl(Cyttp)] (*anti-mer*)[a]	1.343	1.396	1.248	2.084	2.169	2.319	130.4	148.2	147.0	41b
[Ru(C≡CPh)(Cyttp)][a]	1.339	1.379	1.249	2.200	2.191	2.258	133.1	148.7	144.6	41c
[Ru(PNP)(C≡CPh)] (*anti-mer*)[b]	1.34	1.41	1.23	2.06	2.19	2.39	130	150	154	2b
$[Ru(PMe_2Ph)_4]^+$	1.341	1.401	1.229	2.119	2.226	2.510	131.1	155.3	155.8	41d

[a] Cyttp = $PhP\{(CH_2)_3P(C_6H_{11})_2\}_2$. [b] PNP = $CH_3(CH_2)_3P(CH_2CH_2PPh_2)_2$.

$[RuC_3]$ unit of the η^3-butenynyl group. Structural parameters associated with this fragment for several related ruthenium complexes are collected in Table 4. The small bend-back angle γ for **5a** (136.1(8)°) falls in the range of metal−diphenylacetylene interactions (135−140°)[40] and suggests strong interaction between C(16)/C(17) and Ru. This is supported by the short corresponding bond distances *e* and *f*, while elongation of the C(16)−C(17) contact (distance *c*) to 1.260(1) Å is also observed. The greater interaction between the η^3-butenynyl unit and the ruthenium center in **5a** compared to other examples in Table 4 is believed to be a consequence of the strong π-basicity of the $[Ru(Me_3tacn)]$ moiety.

Conclusion

The rate of PMe_3 dissociation in $[Ru(Me_3tacn)(PMe_3)_2X]^+$ (X = O_2CCF_3 (**1a**), Cl (**1b**)) is enhanced by η^1/η^2 isomerization of the CF_3CO_2 ligand in **1a**. The vinylidene complexes $[Ru(Me_3tacn)(PMe_3)(O_2CCF_3)\{C{=}CH(R)\}]PF_6$ (R = Ph (**2a**) and *p*-tolyl (**2b**)) are prepared by the reaction of **1a** with the appropriate 1-alkyne. Due to the high π-basicity of the $[Ru(Me_3tacn)]$ moiety which lowers the electrophilicity of the vinylidene α-carbon, no nucleophilic addition across the C=C bond is observed. Alkyne coupling reactions to give η^3-butenynyl complexes **5a**, **5b**, and **5c/5c′** are studied. It is significant that, partly due to the weak *trans* effect of the saturated triamine, coupling of the σ-acetylide and vinylidene groups is slower than proton migration between these two ligands for **IB** and **IB′** (Scheme 2) in methanol. An equilibrium between these isomeric intermediates is thus established and yields an unprecedented mixture of **5c** and **5c′**.

Acknowledgment. We thank The University of Hong Kong and the Hong Kong Research Grants Council for support and S.-M.Y. is grateful for a Croucher Scholarship administrated by the Croucher Foundation of Hong Kong.

Supporting Information Available: Tables of final positional parameters, anisotropic displacement parameters and bond lengths and angles for **3c**, **5a**, and **5c**/**5c′** (27 pages). Ordering information and Internet access instructions are given on any current masthead page.

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