[Ru(η\(^3\)-2-C\(_3\)H\(_4\)Me)(CO)(dppf)][SbF\(_6\)]: A mononuclear 16\(^\circ\) ruthenium(II) catalyst for propargylic substitution and isomerization of HC≡CCPh\(_2\)(OH)

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**Experimental Section**

**General methods.** The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers and used without further purification with the exception of compound [RuCl(η\(^3\)-2-C\(_3\)H\(_4\)Me)(CO)(dppf)] (1) which was prepared by following the method reported in the literature. Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. The C, H and N analyses were carried out with a Perkin-Elmer 2400 microanalyzer. The conductivities were measured at room temperature, in ca. 10\(^{-3}\) mol dm\(^{-3}\) acetone solutions, with a Jenway PCM3 conductimeter. NMR spectra were recorded on a Bruker DPX300 instrument at 300 MHz (\(^1\)H), 121.5 MHz (\(^{31}\)P) or 75.4 MHz (\(^{13}\)C) using SiMe\(_4\) or 85% H\(_3\)PO\(_4\) as standards. DEPT experiments have been carried out for all the compounds reported in this paper. GC measurements were made on a Hewlett-Packard HP6890 equipment using a HP-INNOWAX cross-linked polyethyleneglycol (30 m, 250 μm) or Supelco Beta-Dex™ 120 (30 m, 250 μm) column. GC/MS measurements were performed on a Agilent 6890N equipment coupled to a 5973 mass detector (70eV electron impact ionization) using a HP-1MS column.

**Synthesis of [Ru(η\(^3\)-2-C\(_3\)H\(_4\)Me)(CO)(dppf)][SbF\(_6\)] (2).** A solution of complex [RuCl(η\(^3\)-2-C\(_3\)H\(_4\)Me)(CO)(dppf)] (1) (0.774 g, 1 mmol) in dichloromethane (50 cm\(^3\)) was treated with AgSbF\(_6\) (351 mg, 1 mmol) and stirred for 15 min at room temperature in the absence of light. The AgCl formed was then filtered off (Kieselguhr) and the resulting solution evaporated to dryness to afford a yellow solid which was washed with diethyl ether (3 x 50 cm\(^3\)) and vacuum-dried. Yield: 0.945 g, 97% (Found: C, 47.92; H, 3.71. RuFeC\(_3\)H\(_3\)F\(_6\)P\(_2\)OSb requires C, 48.08; H, 3.62%). Conductivity (acetone, 20°C) 113.4 Ω\(^{-1}\) cm\(^2\) mol\(^{-1}\). \(\nu\)cm\(^{-1}\) (CO) 1944s (KBr). \(\delta\) (CD\(_2\)Cl\(_2\)) 39.79 (s); \(\delta\)\(_h\) (CD\(_2\)Cl\(_2\)) 1.26 (s, 2 H, CH\(_H\)\(_{anti}\)), 2.21 (s, 3 H, CH\(_3\)), 3.79 (s, 2 H, CH\(_H\)\(_{syn}\)), 4.31, 4.51, 4.69 and 4.93 (br, 2 H each, C\(_3\)H\(_4\)), 7.10-7.70 (m, 20 H, Ph); \(\delta\)\(_c\) (CD\(_2\)Cl\(_2\)) 26.07 (s, CH\(_3\)), 60.87 (m, CH\(_3\)), 72.96, 73.18, 75.16 and 75.47 (br, CH of C\(_3\)H\(_4\)), 81.24 (d, \(^1\)J(C,P) = 48.8 Hz, C of C\(_3\)H\(_4\)), 121.72 (s, C), 127.80-135.50 (m, Ph), 205.01 (t, \(^2\)J(C,P) = 16.8 Hz, CO); MS (FAB) \(m/z\) 739 [M\(^+\)], 655 [M\(^+\) - CO - C\(_3\)H\(_4\)Me].
Synthesis of [Ru(η^3-2-C₃H₄Me)(CO)(NCMe)(dppf)][SbF₆] (3). A solution of complex [Ru(η^3-2-C₃H₄Me)(CO)(dppf)][SbF₆] (2) (0.974 g, 1 mmol) in a dichloromethane/acetonitrile mixture (50 cm^3; 1:1 v/v) was stirred at room temperature for 4 h. The resulting solution was then evaporated to dryness to afford a yellow solid which was washed with diethyl ether (3 x 50 cm^3) and vacuum-dried. Yield: 0.924 g, 91% (Found: C, 48.31; H, 3.42; N, 1.31. RuFeC₄₁H₃₈F₆P₂NOSb requires C, 48.50; H, 3.77; N, 1.38%). Conductivity (acetone, 20°C) 120.4 Ω⁻¹ cm² mol⁻¹. ν/cm⁻¹ (CO) 1959s, (CN) 2291w (KBr). δ_p (CD₂Cl₂) 39.30 (s); δ_H (CD₂Cl₂) 1.25 (s, 3 H, NCCH₃), 1.66 (s, 2 H, CHH(anti)), 2.28 (s, 3 H, CH₃), 3.58 (s, 2 H, CHH(syn)), 4.38, 4.55, 4.73 and 4.86 (br, 2 H each, C₅H₄), 7.40-7.70 (m, 20 H, Ph); δ_C (CD₂Cl₂) 2.19 (s, NCCH₃), 25.39 (s, CH₃), 55.58 (m, CH₂), 72.73, 72.92, 74.87 and 75.04 (br, CH of C₅H₄), 81.36 (d, J(C,P) = 48.5 Hz, C of C₅H₄), 119.59 (s, C), 124.26 (s, NCCH₃), 128.65-135.95 (m, Ph), 205.02 (t, J(C,P) = 16.2 Hz, CO).

Synthesis of [Ru(η^3-2-C₃H₄Me)(CO)₂(dppf)][SbF₆] (4). Carbon monoxide was bubbled at room temperature through a solution of [Ru(η^3-2-C₃H₄Me)(CO)(dppf)][SbF₆] (2) (0.974 g, 1 mmol) in dichloromethane (50 cm^3) for 1.5 h. The resulting solution was then evaporated to dryness to afford a yellow solid which was washed with diethyl ether (3 x 50 cm^3) and vacuum-dried. Yield: 0.952 g, 95% (Found: C, 47.57; H, 3.31. RuFeC₄₀H₃₅F₆O₂P₂Sb requires C, 47.93; H, 3.52%). Conductivity (acetone, 20°C) 115.7 Ω⁻¹ cm² mol⁻¹. ν/cm⁻¹ (CO) 1998s and 2058s (KBr). δ_p (CD₂Cl₂) 33.82 (s); δ_H (CD₂Cl₂) 2.26 (s, 2 H, CHH(anti)), 2.38 (s, 3 H, CH₃), 3.31 (s, 2 H, CHH(syn)), 4.59, 4.79, 4.83 and 4.86 (br, 2 H each, C₅H₄), 7.25-7.70 (m, 20 H, Ph); δ_C (CD₂Cl₂) 24.36 (s, CH₃), 46.75 (m, CH₂), 73.67, 73.91, 75.15 and 75.43 (br, CH of C₅H₄), 79.83 (d, J(C,P) = 53.0 Hz, C of C₅H₄), 118.83 (s, C), 129.00-136.50 (m, Ph), 196.91 (t, J(C,P) = 14.2 Hz, CO), 201.13 (t, J(C,P) = 16.1 Hz, CO).

Synthesis of [Ru(η^3-2-C₃H₄Me)(CO)(CNBz)(dppf)][SbF₆] (5). A solution of complex [Ru(η^3-2-C₃H₄Me)(CO)(dppf)][SbF₆] (2) (0.974 g, 1 mmol) in dichloromethane (30 cm^3) was treated, at room temperature, with benzyl isocyanide (1.22 cm³, 10 mmol) for 2 h. The resulting solution was then evaporated to dryness to afford a yellow solid which was washed with diethyl ether (3 x 50 cm^3) and vacuum-dried. Yield: 0.922 g, 91% (Found: C, 48.31; H, 3.42; N, 1.31. RuFeC₄₄H₄₂F₆P₂NOSb requires C, 48.50; H, 3.77; N, 1.38%). Conductivity (acetone, 20°C) 120.4 Ω⁻¹ cm² mol⁻¹. ν/cm⁻¹ (CO) 1959s, (CN) 2291w (KBr). δ_p (CD₂Cl₂) 39.30 (s); δ_H (CD₂Cl₂) 1.25 (s, 3 H, NCCH₃), 1.66 (s, 2 H, CHH(anti)), 2.28 (s, 3 H, CH₃), 3.58 (s, 2 H, CHH(syn)), 4.38, 4.55, 4.73 and 4.86 (br, 2 H each, C₅H₄), 7.40-7.70 (m, 20 H, Ph); δ_C (CD₂Cl₂) 2.19 (s, NCCH₃), 25.39 (s, CH₃), 55.58 (m, CH₂), 72.73, 72.92, 74.87 and 75.04 (br, CH of C₅H₄), 81.36 (d, J(C,P) = 48.5 Hz, C of C₅H₄), 119.59 (s, C), 124.26 (s, NCCH₃), 128.65-135.95 (m, Ph), 205.02 (t, J(C,P) = 16.2 Hz, CO).
dried. Yield: 0.993 g, 91% (Found: C, 51.47; H, 3.92; N, 1.31. RuFeC₄H₂F₆P₂NOSb requires C, 51.72; H, 3.88; N, 1.28%). Conductivity (acetone, 20°C) 116.1 Ω⁻¹ cm² mol⁻¹. ν/cm⁻¹ (CO) 1982s, (CN) 2202s (KBr). δP (CD₂Cl₂) 37.31 (s); δH (CD₂Cl₂) 4.07, 4.53, 4.61, 4.67 and 4.70 (br, 2 H each, C₅H₄ and NCH₂), 7.00-7.60 (m, 25 H, Ph); δC (CDCl₃) 52.50 (s, OCH₃), 77.84 (s, ≡CH), 81.01 (s, ≡C), 83.15 (s, CPh₂), 126.59, 127.89 and 128.31 (s, CH of Ph), 143.04 (s, C of Ph); MS (EI 70eV) m/z 222 [M⁺], 207 [M⁺ - Me], 191 [M⁺ - OMe], 165 [M⁺ - OMe - C≡CH], 145 [M⁺ - Ph].

**General procedure for the catalytic propargylic substitution reactions.** In a Schlenk tube, [Ru(η³-2-C₃H₄Me)(CO)(dppf)][SbF₆] (2) (0.049 g, 0.05 mmol) and 1,1-diphenyl-2-propyn-1-ol (0.208 g, 1 mmol) were dissolved, under inert atmosphere, in the corresponding alcohol (1 cm³) and the reaction mixture stirred at 75°C for the indicated time. The course of the reaction was monitored by GC. Column chromatography (SiO₂) using a mixture EtOAc/hexane (1/30) as eluent afforded ethers as pale yellow oils.

**1,1-diphenyl-2-propynyl)methylether (6a)**

\[
\text{H} \equiv \text{Ph} \equiv \text{Ph} \\
\text{OMe}
\]

Time = 4 h; Yield: 0.167 g, 75%; ν/cm⁻¹ (C≡C) 2114w, (≡C-H) 3301m (Nujol); δH (CDCl₃) 3.02 (s, 1 H, ≡CH), 3.56 (s, 3 H, OCH₃), 7.41-7.81 (m, 10 H, Ph); δC (CDCl₃) 52.50 (s, OCH₃), 77.84 (s, ≡CH), 81.01 (s, ≡C), 83.15 (s, CPh₂), 126.74, 127.81 and 128.26 (s, CH of Ph), 143.04 (s, C of Ph); MS (EI 70eV) m/z 222 [M⁺], 207 [M⁺ - Me], 191 [M⁺ - OMe], 165 [M⁺ - OMe - C≡CH], 145 [M⁺ - Ph].

**1,1-diphenyl-2-propynyl)ethylether (6b)**

\[
\text{H} \equiv \text{Ph} \equiv \text{Ph} \\
\text{OEt}
\]

Time = 6 h; Yield: 0.170 g, 72%; ν/cm⁻¹ (C≡C) 2109w, (≡C-H) 3286m (Nujol); δH (CDCl₃) 1.29 (t, 3 H, J(H,H) = 7.1 Hz, CH₃), 2.95 (s, 1 H, ≡CH), 3.57 (q, 2 H, J(H,H) = 7.1 Hz, OCH₂), 7.28-7.70 (m, 10 H, Ph); δC (CDCl₃) 15.37 (s, CH₃), 65.76 (s, OCH₂), 77.50 (s, ≡CH), 81.01 (s, ≡C), 83.15 (s, CPh₂), 126.59, 127.89 and 128.31...
(s, CH of Ph), 143.51 (s, C of Ph); MS (EI 70eV) \textit{m}/\textit{z} 236 [M\textsuperscript{+}], 207 [M\textsuperscript{+} - Et], 191 [M\textsuperscript{+} - OEt], 159 [M\textsuperscript{+} - Ph].

\textbf{(1,1-diphenyl-2-propynyl)allylether (6c)}

\begin{center}
\includegraphics[width=0.5\textwidth]{image}
\end{center}

Time = 5 h; Yield: 0.216 g, 87%; \(\nu\text{cm}^{-1}\) (C=C) 1664m, (C≡C) 3111w, (≡C-H) 3307m (Nujol); \(\delta\text{H (CDCl}_3\)) 2.94 (s, 1 H, ≡CH), 4.11 (d, 2 H, \(^3J(H,H) = 4.8\text{ Hz}, \text{OCH}_2\)), 5.23 (d, 1 H, \(^3J(H,H) = 10.3\text{ Hz}, \text{=CH}_2\)), 5.43 (d, 1 H, \(^3J(H,H) = 17.4\text{ Hz}, \text{=CH}_2\)), 6.05 (ddt, 1 H, \(^3J(H,H) = 17.4, 10.3\text{ and } 4.8\text{ Hz}, \text{=CH}\)), 7.28-7.66 (m, 10 H, Ph); \(\delta\text{C (CDCl}_3\)} 65.91 (s, OCH\textsubscript{2}), 77.59 (s, ≡CH), 80.03 (s, ≡C), 83.23 (s, C\textsubscript{Ph2}), 116.12 (s, =CH\textsubscript{2}), 126.56, 127.72 and 128.19 (s, CH of Ph), 134.73 (s, ≡CH), 143.11 (s, C of Ph); MS (EI 70eV) \textit{m}/\textit{z} 248 [M\textsuperscript{+}], 207 [M\textsuperscript{+} - CH\textsubscript{2}CH=CH\textsubscript{2}], 191 [M\textsuperscript{+} - OCH\textsubscript{2}CH=CH\textsubscript{2}], 165 [M\textsuperscript{+} - OCH\textsubscript{2}CH=CH\textsubscript{2} - ≡CH].

\textbf{(E)-(1,1-diphenyl-2-propynyl)-2-butenylether (6d)}

\begin{center}
\includegraphics[width=0.5\textwidth]{image}
\end{center}

Time = 8 h; Yield: 0.210 g, 80%; \(\nu\text{cm}^{-1}\) (C=C) 1660m, (C≡C) 3112w, (≡C-H) 3306m (Nujol); \(\delta\text{H (CDCl}_3\)) 1.75 (d, 3 H, \(^3J(H,H) = 5.8\text{ Hz}, \text{CH}_3\)), 2.91 (s, 1 H, ≡CH), 4.00 (d, 2 H, \(^3J(H,H) = 5.1\text{ Hz}, \text{OCH}_2\)), 5.51 (dt, 1 H, \(^3J(H,H) = 15.1\text{ and } 5.1\text{ Hz}, \text{=CHCH}_2\)), 5.72 (dq, 1 H, \(^3J(H,H) = 15.1\text{ and } 5.8\text{ Hz}, \text{=CHCH}_3\)), 7.28-7.61 (m, 10 H, Ph); \(\delta\text{C (CDCl}_3\)} 18.31 (s, CH\textsubscript{3}), 66.28 (s, OCH\textsubscript{2}), 76.09 (s, ≡CH), 80.43 (s, ≡C), 83.87 (s, C\textsubscript{Ph2}), 127.06, 128.09 and 128.60 (s, CH of Ph), 128.71 and 132.85 (s, ≡CH), 143.67 (s, C of Ph); MS (EI 70eV) \textit{m}/\textit{z} 262 [M\textsuperscript{+}], 207 [M\textsuperscript{+} - CH\textsubscript{2}CH=CHMe], 191 [M\textsuperscript{+} - OCH\textsubscript{2}CH=CHMe], 165 [M\textsuperscript{+} - OCH\textsubscript{2}CH=CHMe - ≡CH].

\textbf{(1,1-diphenyl-2-propynyl)-3-methyl-2-butenylether (6e)}

\begin{center}
\includegraphics[width=0.5\textwidth]{image}
\end{center}
(1,1-diphenyl-2-propynyl)-2-cyclohexenylether (6f)

\[
\begin{align*}
\text{Time} &= 24 \text{ h;} \quad \text{Yield: 0.161 g, 56\%;} \\
\nu/cm^{-1} &= (\text{C}=\text{C}) 1648m, (\text{C}≡\text{C}) 2129w, (\text{≡C}-\text{H}) 3284m (\text{Nujol}); \\
\delta_t \text{(CDCl}_3) &= 1.54-2.06 (\text{m, 6 H, CH}_2), 2.93 (\text{s, 1 H, }\equiv\text{CH}), 4.04 (\text{br, 1 H, OCH}), 5.83 (\text{m, 2 H, =CH}), 7.29-7.65 (\text{m, 10 H, Ph}); \\
\delta_c \text{(CDCl}_3) &= 19.59, 25.19 \text{ and } 30.21 (\text{s, CH}_2), 69.47 (\text{s, OCH}), 70.57 (\text{s, =CH}), 79.57 (\text{s, =C}), 84.52 (\text{s, CPh}_2), 127.10, 127.59 \text{ and } 127.92 (\text{s, CH of Ph}), 129.43 \text{ and } 130.13 (\text{s, =CH}), 144.00 (\text{s, C of Ph}); \\
\text{MS (EI 70eV)} m/z &= 288 [\text{M}^+], 207 [\text{M}^+ - \text{C}_6\text{H}_9], 191 [\text{M}^+ - \text{OC}_6\text{H}_9], 165 [\text{M}^+ - \text{OCH}_2\text{CH}≡\text{CMe}_2 - \equiv\text{CH}].
\end{align*}
\]

(1,1-diphenyl-2-propynyl)-3-methyl-3-butenylether (6g)

\[
\begin{align*}
\text{Time} &= 24 \text{ h;} \quad \text{Yield: 0.246 g, 89\%;} \\
\nu/cm^{-1} &= (\text{C}=\text{C}) 1649m, (\text{C}≡\text{C}) 2110w, (\text{≡C}-\text{H}) 3286m (\text{Nujol}); \\
\delta_t \text{(CDCl}_3) &= 1.80 (\text{s, 3 H, CH}_3), 2.46 (\text{t, 2 H, }\equiv\text{J(H,H)} = 6.8 \text{ Hz, CH}_2), 2.93 (\text{s, 1 H, }\equiv\text{CH}), 3.67 (\text{t, 2 H, }\equiv\text{J(H,H)} = 6.8 \text{ Hz, OCH}_2), 4.85 (\text{br, 2 H, =CH}_2), 7.28-7.70 (\text{m, 10 H, Ph}); \\
\delta_c \text{(CDCl}_3) &= 23.21 (\text{s, CH}_3), 38.52 (\text{s, CH}_2), 63.58 (\text{s, OCH}_2), 77.90 (\text{s, =CH}), 80.31 (\text{s, =C}), 83.91 (\text{s, CPh}_2), 112.09 (\text{s, =CH}_2), 127.07, 128.11 \text{ and } 128.62 (\text{s, CH of Ph}), 143.49 (\text{s, =C}), 143.87 (\text{s, C of Ph}); \\
\text{MS (EI 70eV)} m/z &= 276 [\text{M}^+], 261 [\text{M}^+ - \text{Me}], 207 [\text{M}^+ - \text{CH}_2\text{CH}_2\text{CMe}≡\text{CH}_2], 191 [\text{M}^+ - \text{OCH}_2\text{CH}_2\text{CMe}≡\text{CH}_2], 165 [\text{M}^+ - \text{OCH}_2\text{CH}_2\text{CMe}≡\text{CH}_2 - =\text{CH}].
\end{align*}
\]
(1,1-diphenyl-2-propynyl)-2-butynylether (6h)

$$\begin{align*}
H & \equiv \text{Ph} \\
\equiv & \text{O} \\
\equiv & \text{Ph}
\end{align*}$$

Time = 11 h; Yield: 0.211 g, 81%; $\nu/cm^{-1}$ (C≡C) 2111w and 2241w, (≡C-H) 3280m (Nujol); $\delta_H$ (CDCl$_3$) 1.87 (t, 3 H, 5 $J$(H,H) = 2.3 Hz, CH$_3$), 2.94 (s, 1 H, ≡CH), 4.17 (q, 2 H, 5 $J$(H,H) = 2.3 Hz, OCH$_2$), 7.25-7.61 (m, 10 H, Ph); $\delta_C$ (CDCl$_3$) 4.25 (s, CH$_3$), 54.36 (s, OCH$_2$), 75.77, 77.11 and 82.51 (s, ≡C), 78.63 (s, ≡CH), 83.04 (s, CPh$_2$), 127.15, 128.33 and 128.67 (s, CH of Ph), 142.86 (s, C of Ph); MS (EI 70eV) $m/z$ 260 [M$^+$], 245 [M$^+$ - Me], 183 [M$^+$ - Ph], 165 [M$^+$ - OCH$_2$C≡CMe - C≡CH].

(1,1-diphenyl-2-propynyl)-3-hexynylether (6i)

$$\begin{align*}
\equiv & \text{Ph} \\
\equiv & \text{O} \\
\equiv & \text{Et}
\end{align*}$$

Time = 10 h; Yield: 0.259 g, 90%; $\nu/cm^{-1}$ (C≡C) 2135w and 2250w, (≡C-H) 3282m (Nujol); $\delta_H$ (CDCl$_3$) 1.15 (t, 3 H, 3 $J$(H,H) = 7.4 Hz, CH$_3$), 2.18 and 2.57 (m, 2 H each, CH$_2$), 2.92 (s, 1 H, ≡CH), 3.63 (t, 2 H, 3 $J$(H,H) = 7.3 Hz, OCH$_2$), 7.28-7.62 (m, 10 H, Ph); $\delta_C$ (CDCl$_3$) 12.68 and 20.66 (s, CH$_2$), 14.66 (s, CH$_3$), 64.13 (s, OCH$_2$), 76.50, 80.43 and 83.64 (s, ≡C), 78.05 (s, ≡CH), 83.13 (s, CPh$_2$), 127.04, 128.17 and 128.62 (s, CH of Ph), 143.56 (s, C of Ph); MS (EI 70eV) $m/z$ 288 [M$^+$], 273 [M$^+$ - Me], 191 [M$^+$ - OCH$_2$CH$_2$C≡CEt], 165 [M$^+$ - OCH$_2$CH$_2$C≡CEt - C≡CH].

Procedure for the isomerization of 1,1-diphenyl-2-propyn-1-ol into 3,3-diphenyl-2-propen-1-al (7).

In a Schlenk tube, [Ru(η$_3$-2-C$_3$H$_4$Me)(CO)(dppf)]$\text{[SbF}_6$] (2) (0.049 g, 0.05 mmol) and 1,1-diphenyl-2-propyn-1-ol (0.208 g, 1 mmol) were dissolved, under inert atmosphere, in undistilled THF (1 cm$^3$) and the reaction mixture stirred at 75ºC for 1.5 h. The course of the reaction was monitored by GC. Column chromatography (SiO$_2$) using a mixture EtOAc/hexane (1/5) as eluent afforded 7 as pale yellow oil.$^5$ Yield: 0.198 g, 95%; $\nu/cm^{-1}$ (C=C) 1650m, (C=O) 1663s (Nujol); $\delta_H$ (CDCl$_3$) 6.63 (d, 1 H, 3 $J$(H,H) = 7.9 Hz, =CH), 7.28-7.66 (m, 10 H, Ph), 9.56 (d, 1 H, 3 $J$(H,H) = 7.9 Hz, CHO); $\delta_C$ (CDCl$_3$) 125.92, 127.24, 128.26, 128.31, 129.43, 130.47
and 130.72 (s, =CH and CH of Ph), 136.63 and 139.67 (s, C of Ph), 162.26 (s, =C), 193.54 (s, CHO); MS (EI 70eV) m/z 207 [M¹], 178 [M¹ - CHO], 165 [M¹ - CHCHO], 102 [M¹ - CHO - Ph], 89 [M¹ - CHCHO - Ph].

Crystal data for [Ru(η³-2-C₃H₄Me)(CO)(CNBz)(dppf)][SbF₆] (5):
RuFeC₄₇H₄₂F₆P₂NOSb, \( M = 1091.43 \), yellow prism (0.297 x 0.132 x 0.132 mm), monoclinic, \( P₂_1/c \), \( a = 10.884(11) \) Å, \( b = 30.69(6) \) Å, \( c = 13.706(4) \) Å, \( \alpha = 90^\circ \), \( \beta = 104.55(3)^\circ \), \( \gamma = 90^\circ \), \( V = 4431(10) \) Å³, \( Z = 4 \), \( D_{calc} = 1.636 \) g cm⁻³, \( \mu(\text{Mo-K} \alpha) = 1.399 \) mm⁻¹, Enraf Nonius CAD4 diffractometer, Mo-K\( \alpha \) radiation (\( \lambda = 0.71073 \) Å). 9152 reflections collected, 8687 unique (\( R_{int} = 0.0610 \)). \( R_1 = 0.0617; wR_2 = 0.1326 \) both for \( I > 2\sigma(I) \). CCDC 245208.

**Fig.S1** Molecular structure of [Ru(η³-2-C₃H₄Me)(CO)(CNBz)(dppf)][SbF₆] (5). SbF₆⁻ anion, hydrogen atoms and phenyl groups of the dppf ligand have been omitted. Selected bond distances (Å) and angles (°): Ru-C(1) 2.255(9); Ru-C(2) 2.229(9); Ru-C(3) 2.282(9); Ru-C(5) 2.022(9); Ru-C(47) 1.891(10); Ru-P(1) 2.381(3); Ru-P(2) 2.362(3); C(1)-C(2) 1.402(13); C(2)-C(3) 1.378(13); C(47)-O(1) 1.114(10); C(5)-N(1) 1.156(10); Ru-C(47)-O(1) 176.0(8); C(47)-Ru-C(5) 173.4(3); Ru-C(5)-N(1) 175.4(8); C(1)-C(2)-C(3) = 121.6(9).


