Prop-2-ynyl Alcohol as a Precursor to the η^1-Ethenyl Ligand

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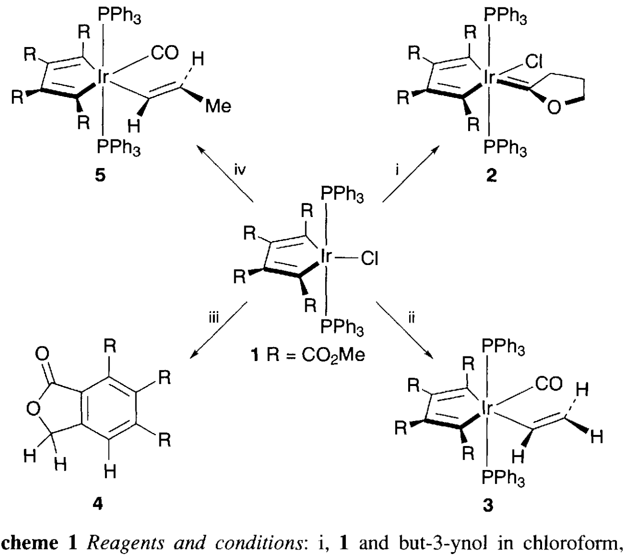
In the presence of water the unsaturated iridium(III) metallacyclopentadiene halide complex Ir(CR=CRCR=CR)(PPh$_3$)$_2$Cl (**1**, R = CO$_2$Me) undergoes reaction with prop-2-ynyl alcohol, or methyl prop-2-ynyl ether at room temperature to give the η^1-ethenyl complex Ir(CR=CRCR=CR)(PPh$_3$)$_2$(CO)(η^1-CH=CH$_2$) (**3**, R = CO$_2$Me) in quantitative yield.

The metal-mediated isomerization of terminal alkynes to vinylidene ligands opens up new reactivity manifolds not accessible with most internal alkynes.[1] As part of our research program on the chemistry of highly reactive iridium(III) vinylidene complexes[2] we were interested in examining the reactivity of prop-2-ynyl alcohol with the unsaturated iridiacyclopentadiene complex Ir(CR=CRCR=CR)(PPh$_3$)$_2$Cl (**1**, R = CO$_2$Me).[3] Selegue,[4] Dixneuf,[5] and others[6] have reported the use of prop-2-ynyl alcohol derivatives as precursors to metal-allenylidene intermediates and complexes. Thus, Cp Ru(PMe$_3$)$_2$Cl (Cp = η^5-C$_5$H$_5$) reacts with Ph$_2$C(OH) (C≡CH) and NH$_4$PF$_6$ to produce the diphenylallenylidene complex Cp Ru(PMe$_3$)$_2$(η^1-C=C=CPh$_2$), by dehydration of a vinylidene intermediate.[4]

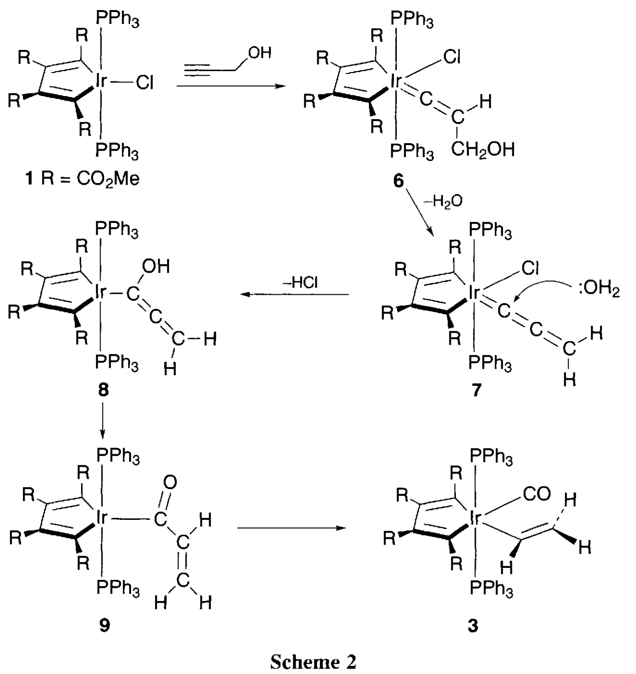
The iridiacyclopentadiene complex Ir(CR=CRCR=CR)(PPh$_3$)$_2$Cl (**1**, R = CO$_2$Me) was previously reported to react with dimethyl acetylenedicarboxylate in benzene at 80 °C to give hexa(carbomethoxy)benzene.[3] In contrast, **1** reacts with the terminal alkyne, but-3-ynol, at room temperature to generate a vinylidene intermediate which rearranges to metallacycle-carbene **2** (Scheme 1).[7] We have now discovered that prop-2-ynyl alcohol and methyl prop-2-ynyl ether undergo reaction with **1** in the presence of water to quantitatively generate the η^1-ethenyl complex **3**. Furthermore, in the absence of water, **1** and prop-2-ynyl alcohol give the alkyne cycloaddition product 5,6,7-tri(carbomethoxy)phthalide **4** under remarkably mild conditions.

When the reaction between iridiacycle **1** (9.6×10^{-3} mmol) and prop-2-ynyl alcohol (0.024 mmol), in a two phase water–[^{2}H$_2$]methylene chloride solution, is monitored by ^{1}H NMR spectroscopy the resonances for **1** are gradually and quantitatively replaced by a new set of resonances , which arise from formation of the iridium ethenyl complex Ir(CR=CRCR=CR)(PPh$_3$)$_2$(CO)(η^1-CH=CH$_2$) (**3**, R = CO$_2$Me).† In the ^{1}H NMR spectrum (CD$_2$Cl$_2$) of **3**, four singlets (3 H each) are observed at δ 3.55, 3.43, 3.38 and 3.21, which are assigned to the hydrogens of four unique carbomethoxy groups. Broad doublets at δ 4.70 (J_{HH} 19.1 Hz) and 5.84 (J_{HH} 11.1 Hz) are assigned to the hydrogens on the β-carbon of the ethenyl ligand. The coupling constants indicate that the upfield signal at δ 4.70 is due to the hydrogen *cis* to iridium. The hydrogen resonance on the α-carbon of the ethenyl ligand is obscured by phenyl hydrogen resonances between δ 7.27 and 7.65. In the ^{13}C{^{1}H} NMR spectrum (CD$_2$Cl$_2$) of **3**, the terminal carbonyl carbon is observed at δ 175.7 (t, J_{CP} 8.4 Hz). A triplet at δ 136.5 (J_{CP} 8.7 Hz) and a broad, unresolved triplet at 125.8 are assigned to C(α) and C(β) of the ethenyl ligand, respectively. For comparison, the iridium(III) vinyl complex [IrH{C(CO$_2$Me)=CH$_2$}(Hpz)(PPh$_3$)$_2$]BF$_4$ (Hpz = pyrazole) exhibits broad resonances in the ^{13}C{^{1}H} NMR spectrum (CDCl$_3$) for C(α) and C(β) at 138 and 118, respectively.[8] In the FAB mass spectrum of **3**, MH$^+$ was observed at 1055 with the expected isotope envelope, and peaks at 1028 (12.21%) and 1000 (25.72%) correspond to loss of the ethenyl and carbon monoxide ligands. The presence of an η^1-ethenyl ligand in **3** is also consistent with the observation that **3** reacts with excess HCl in [^{2}H$_2$]-dichloromethane to give the known metallacycle chloride Ir(CR=CRCR=CR)(PPh$_3$)$_2$(CO)Cl and ethene. Under reaction conditions similar to those employed for the synthesis of **3**, complex **1** and but-3-yn-2-ol quantitatively give the *trans*-propenyl complex **5**.

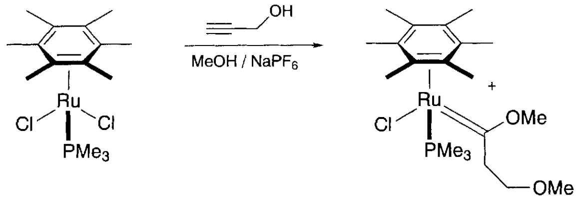
A potential mechanism for the formation of **3** from **1** and prop-2-ynyl alcohol is outlined in Scheme 2. Based on the known chemistry of prop-2-ynyl alcohols with transition metals it is reasonable to envoke the sequential formation of vinylidene **6** and allenylidene **7** intermediates. Attack by water at C(α) of



Scheme 1 *Reagents and conditions*: i, **1** and but-3-ynol in chloroform, 25 °C, 15 h, 88% (ref. 7); ii, **1** and prop-2-ynyl alcohol in methylene chloride saturated with water (two phases), 25 °C, 48 h, 100%; iii, **1** and prop-2-ynyl alcohol in methylene chloride, 25 °C 48 h, 100%; iv, **1** and but-3-yn-2-ol in methylene chloride saturated with water (two phases), 25 °C, 24 h, 100%



Scheme 2



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the allenylidene ligand would give enol **8** from which loss of HCl and enol–keto tautomerization would generate acyl intermediate **9**. Decarbonylation of **9** then gives **3**.

Chloride ligand dissociation from iridium could occur at any step in the sequence. Attack of water at the α-carbon of the allenylidene ligand in **7** is consistent with Dixneuf's observed trapping of a propargyl alcohol-derived allenylidene ligand by methanol.[9] Interestingly, in the Dixneuf system methanol adds twice to the allenylidene ligand to give **10**. An alternative mechanism to that shown in Scheme 2 involves formation of a vinylidene ligand, attack by water, loss of HCl, and decarbonylation to a η^1-hydroxyethyl ligand,[10] which then undergoes an acid-catalysed dehydration.

When the reaction of **1** and prop-2-ynyl alcohol is run at room temperature in [^{2}H$_2$]dichloromethane, under anhydrous conditions, quantitative conversion to 5,6,7-tri(carbomethoxy)phthalide **4** occurs over the course of 48 h.‡

Efforts are underway to ellucidate the mechanism of formation for **3** and **4**, and to determine the scope of these unusual prop-2-ynyl alcohol transformations. We gratefully acknowledge financial support by the National Science Foundation and a generous load of iridium from Johnson Matthey.

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Footnotes

† *Physical and spectroscopic data* for **3**: mp 195–197 °C. IR(KBr)/cm^{-1} 2027 (vs), 1725 (br, s), 1692 (s), 1680 (s), 1485 (m), 1435 (s), 1328 (m) and 1219 (vs). δ_H (CD$_2$Cl$_2$, 300 MHz) 7.63 (q, 1H, J = 6.4), 7.51–7.27 (m, 30H), 5.84 (br, d, 1H, J = 11.1), 4.70 (br, d, 1H, J = 19.1), 3.55 (s, 3H), 3.43 (s, 3H), 3.38 (s, 3H) and 3.21 (s, 3H). ^{31}P{^{1}H}NMR (CD$_2$Cl$_2$, 121.50 MHz) δ −6.60. ^{13}C{^{1}H}NMR (CD$_2$Cl$_2$, 125.7 MHz) δ 176.47 (s), 173.52 (s), 175.66 (t, J = 8.4), 167.52 (s), 167.07 (s), 162.14 (t, J = 6.8), 154.84 (t, J = 3.1), 152.53 (t, J = 11.8), 150.91 (s), 136.49 (t, J = 8.7), 135.43 (t, J = 5.0), 130.39 (t, J = 28.9), 130.48 (s), 127.56 (t, J = 5.4), 125.76 (brs), 51.16 (s), 51.0 (s), 50.91 (s) and 50.32 (s). MS (FAB), *m/z* MH$^+$ = 1055.2252 (calcd for $C_{51}H_{45}O_9P_2Ir + H$: 1055.2223).

‡ *Physical and spectroscopic data* for **4**: mp 151.8 °C. IR(KBr)/cm^{-1} 2962 (s), 1768 (br,s), 1739 (br,s), 1613 (s) and 1453 (br,s). ^{1}H NMR (CDCl$_3$, 300 MHz) δ 8.00 (s, 1-H), 5.37 (s, 2-H), 4.00 (s, 3-H), 3.94 (s, 3-H) and 3.91 (s, 3-H). ^{13}C{^{1}H}NMR (CDCl$_3$, 125.7 MHz) δ 166.93, 165.96, 165.49, 164.77, 148.41, 136.02, 133.08, 132.32, 125.76, 124.84, 68.06, 53.44, 53.36 and 53.32. MS (electron impact, 50 eV), *m/z* 308.0528 (calcd for $C_{14}H_{12}O_8$: 308.0532).

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