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Iridium(III)-vinylidene chemistry: Conversion of an iridacyclopentadiene-chlorido complex and terminal alkynes to iridacyclopentadiene-vinyl complexes

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This paper is dedicated to Professor Robert J. Angelici in recognition of his numerous important contributions to organometallic chemistry.

Abstract

The reactions of $[\kappa^2(C^1, C^4)$ -CR=CRCR=CR](PPh_3)_2Ir(Cl) (9, R = CO_2Me) with propargyl alcohol derivatives (2-propyn-1-ol, 2-methyl-3-butyn-2-ol, 1-ethynylcyclopentanol, and 1-ethynylcyclooctanol), in the presence of water leads to the formation of irid-ium(III)-vinyl complexes bearing the general structure $[\kappa^2(C^1, C^4)$ -CR=CRCR=CR](PPh_3)_2Ir(CO)(\kappa^1-vinyl) where vinyl = -CH=CH_2, - (*E*)-CH=CHMe, -CH=C(CH_2)_4, or -CH=C(CH_2)_7. In these, the CO ligand was derived from the terminal carbon of the starting alkyne and the oxygen atom from water. Under anhydrous conditions, **9** undergoes reaction with 2-propyn-1-ol to give trimethyl 1,3-dihydro-3-oxo-4,5,6-isobenzofurantricarboxylate, the result of a cycloaromatization/transesterification involving the buta-1,3-dien-1,4-diyl ligand in **9** and 2-propyn-1-ol.

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1. Introduction

The transition metal-mediated conversion of terminal alkynes to vinylidene (I) and allenylidene (II) ligands has dramatically expanded the scope of alkyne chemistry in recent years (Scheme 1) [1–4]. Interest in these readily available, strong pi-acceptor ligands stems in part from their potential applications in synthesis, such as anti-Markovnikov addition reactions to alkynes [2]. To this effect, wide-spread research efforts are currently being directed toward the development and understanding of the reactiv-

ity patterns governing these increasingly important ligands [1–4].

Although vinylidene and allenylidene complexes have been observed for many transition metals, most work in this area has focused on the chemistry of the d⁶-metals within the iron triad and the d⁸-metals of the cobalt triad [3,4]. In this investigation, we selected to explore the higher valent d⁶-iridium systems, as the vinylidene and allenylidene ligands are anticipated to be more electrophilic than d⁸ congeners and thereby potentially exhibit enhanced reactivity patterns [5]. As early as 1973, indirect evidence has existed to indicate that unobserved vinylidene intermediates may be generated from terminal alkynes at iridium(III) metal centers. In that year, Clark and Manzer demonstrated that the cationic iridium(III) solvate **1** could undergo reaction with 3-butyn-1-ol to give carbene

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complex 2 (Scheme 2) [6]. The authors proposed this transformation to proceed via an iridium-stabilized carbonium ion, the identity of which in today's parlance would now be described as the vinylidene complex **3**. To our knowledge, the only examples of stable, isolable iridium(III)–vinylidene complexes are those reported by Paneque and Carmona [4b]. In that work, hydridotris(3,5-dimethylpy-razolyl)borate iridium ($Tp^{Me2}Ir$) vinylidene complexes, such as **4**, were generated from dinitrogen complex **5** and bis(trimethylsilyl)acetylene. The remarkable stability observed for these complexes is presumably due to the electron–donor properties of both the Tp^{Me2} ligand itself and the trimethylsilyl (TMS) substituents on the vinylidene ligand.

Allenylidene complexes of iridium(I) are also relatively well-established [7], but – once again – only two examples of isolable iridium(III)–allenylidene complexes, $(P^{i}Pr_{3})_{2}$ - $(H)(Cl)_{2}Ir[=C=C=C(Ph)(R)]$ (6, R = Ph, ^{*t*}Bu), have been reported to date. In these, complexes of general structure 6 were formed via the oxidative addition of HCl to the iridium(I)–allenylidene complexes 7 (Scheme 2) [7b,8]. Notably, allenylidene 7 was prepared from the corresponding propargyl alcohol derivatives and $[(P^{i}Pr_{3})_{2}IrCl(H)_{2}]$ (8) in the presence of light or catalytic amounts of acid. This paper reports the details of our work on the reactions of the unsaturated iridium(III) metallacyclopentadiene complex, $[\kappa^2(C^1, C^4)-CR=CRCR=CR](PPh_3)_2Ir(Cl)$ (9, $R = CO_2Me$) [9], with propargyl alcohols to afford either [2 + 2 + 2]-cycloaromatization products or iridium– carbon monoxide–vinyl complexes, depending upon the reaction conditions.

2. Results and discussion

The reactions of iridacyclopentadiene $[\kappa^2(C^1, C^4)$ -CR= CRCR=CR](PPh_3)_2Ir(Cl) (9, R = CO_2Me) with alkynes depends markedly on the nature of the alkyne substituents (Scheme 3). For example, 9 undergoes reaction with the internal alkyne dimethyl acetylenedicarboxylate to give hexa(carbomethoxy)benzene 10, presumably via an η^2 alkyne intermediate such as 11 [9]. In contrast, the terminal alkynes 3-butyn-1-ol and methyl propiolate undergo reaction with 9 to give metallacycle–carbene complex 12 and α -chlorovinyl complex 13, respectively [10,11]. A reasonable mechanism for the formation of iridacycles 12 and 13 involves the formation of vinylidene intermediates 14 and 15, which are then trapped by nucleophilic attack at the α -carbon of the vinylidene ligand.

An interesting aspect of the vinylidene reactions shown in Scheme 3 is that halide migration to the vinylidene ligand of **15** occurs readily; whereas, for intermediate **14** halide migration is not competitive with intramolecular trapping of the vinylidene ligand by the pendant hydroxyl



Scheme 2.



group. Furthermore, the formation of the iridium(I)– allenylidene complex 6 from propargyl alcohols and 8, and the stability of the iridium(III) allenylidene complexes 6 and 7 with respect to halide migration suggested that iridium(III)–allenylidene complexes generated directly from 9 and propargyl alcohols may lead to allenylidene ligand insertion into the metallacycle ring [12,13]. We therefore set out to investigate the reactivity of 9 toward propargyl alcohols.

The reaction of metallacycle **9** (25 mM) and 2-propyn-1ol (62 mM) in anhydrous methylene chloride- d_2 was monitored periodically by ¹H NMR spectroscopy. After 48 h at room temperature, the quantitative formation of trimethyl 1,3-dihydro-3-oxo-4,5,6-isobenzofurantricarboxylate (16) [14a] was observed by ¹H NMR spectroscopic analysis of the reaction mixture via integration of the product resonances relative to those of an internal standard (*p*-bis(trimethylsilyl)benzene; Scheme 4). From this evidence, it appears that, if vinylidene formation did occur, then it was reversible – with the formation of **16** proceeding via an η^2 -alkyne intermediate [14b]. By analogy to the reaction of **9** with dimethyl acetylenedicarboxylate [9], the initial product of cycloaromatization with 2-propyn-1-ol would be **17**, which then undergoes intramolecular transesterification to **16**.

When the reaction of **9** with 2-propyn-1-ol was performed under similar reaction conditions using wet methylene chloride- d_2 , the unanticipated iridium–vinyl complex $[\kappa^2(C^1, C^4)$ -CR=CRCR=CR](PPh_3)_2Ir(CH=CH_2)(CO) (18, R = CO_2Me) was produced, with no evidence for the formation of **16** (Scheme 4). To investigate this further, a small-scale reaction of **9** (32 mM) and 2-propyn-1-ol



Scheme 4.

(164 mM) in CD₂Cl₂/H₂O (3%) at room temperature was monitored by ¹H NMR spectroscopy. During the course of reaction, an orange to pale-vellow color change was observed and a new series of methyl-hydrogen resonances at δ 3.55, 3.43, 3.38, and 3.21 were observed to grow in intensity with a concomitant decrease in the signals for 9. After 48 h, 9 had quantitatively converted to 18, as determined by integration relative to an internal standard (1,4- $TMS_2C_6H_4$). When the reaction was performed on a larger scale, complex 18 was isolated as a pale pink solid in 33% vield. Table 1 lists the representative spectroscopic properties for 18 and its related vinyl complexes. In the ¹H NMR spectrum of 18 (CD₂Cl₂), the geminal vinyl-hydrogen resonances were observed as doublets at δ 5.84 (br d, J =11.1 Hz) and 4.70 (br d, J = 19.1 Hz). Based on the magnitude of the coupling constants, the signal at δ 4.70 was assigned to the hydrogen *cis* to iridium. The α -vinyl-hydrogen resonance was obscured by resonances in the phenyl region of the spectrum between $\delta 7.27-7.65$. The ¹³C{¹H} NMR spectrum (CD₂Cl₂) of **18** exhibited resonances assigned to the four carbons bound directly to iridium at 175.8 (t, J = 8.4 Hz, IrCO), 162.1 (t, J = 6.87 Hz, IrC-CO₂Me), 152.5 (t, J = 11.83 Hz, IrCCO₂Me), and 136.5 (t, J = 8.73 Hz, IrCH=) ppm, respectively. In addition, the β -carbon of the vinyl ligand was tentatively assigned to a broad singlet at 125.8 ppm. The assignments for the ethenyl carbons were made on the basis of the coupling constants and a comparison of the chemical shifts to those for the ethenyl complex (η^5 -C₅Me₅)(PMe₃)Ir(H)(CH= CH₂), which were observed at 142.5 ($J_{PC} = 17.5$ Hz) and 118.7 ppm ($J_{PC} = 4.8$ Hz) [15].

The structure assigned to 18 is also consistent with the observation that the protonation of 18 in methylene chloride- d_2 with dry HCl gas led to the known chlorido-

Table 1

Spectroscopic characterization of iridium- κ^1 -vinyl complexes

κ^1 -vinyl complex (R = CO ₂ CH ₃)	¹ H NMR ^a , δ	¹³ C{ ¹ H} NMR ^b , ppm
$\begin{array}{c c} R & PPh_3 \\ R & R \\ R & R \\ R & R \\ PPh_3 \\ \hline PPh_3 \\ \hline \\ 28 \end{array}$	(CD ₂ Cl ₂) 3.21 (s, 3H, CO ₂ CH ₃) 3.38 (s, 3H, CO ₂ CH ₃) 3.43 (s, 3H, CO ₂ CH ₃) 3.55 (s, 3H, CO ₂ CH ₃) 4.70 (br d, 1H, $J = 19.1$, =CH ₂) 5.84 (br d, 1H, $J = 11.1$, =CH ₂) 7.51–7.27 (m, 30H, C ₆ H ₅) 7.63 (q, 1H, $J = 6.4$, Ir–CH)	(CD_2C1_2) 175.8 (t, $J = 8.4$, Ir-CO) 162.1 (t, $J = 6.8$, Ir-C(R)=) 154.8 (t, $J = 3.1$, Ir-C(R)=) 136.5 (t, $J = 87$, Ir-CH=) 125.8 (br s, Ir-CH=CH ₂)
$R = R PPh_3 \\ R = R R Me \\ PPh_3 \\ H = Me \\ 31$	1.31 (d, 3H, $J = 6$, =CHCH ₃) 3.28 (s, 3H, CO ₂ CH ₃) 3.37 (s, 3H, CO ₂ CH ₃) 3.46 (s, 3H, CO ₂ CH ₃) 3.57 (s, 3H, CO ₂ CH ₃) 4.66 (dq, 1H, $J = 17.1$, 6, =CHMe) 6.43 (br d, 1H, $J = 17.1$, Ir–CH) 7.31 (m, 18H, C ₆ H ₅) 7.48 (m, 12H, C ₆ H ₅)	175.4 (t, $J = 6.9$, Ir-CO) 161.3 (br s, Ir-C(R)=) 154.3 (t, $J = 11.8$, Ir-C(R)=) 132.7 (br s, Ir-CH=CH ₂) 125.8 (t, $J = 8.4$, Ir-CH=)
$\mathbf{R} \xrightarrow{\mathbf{R}}_{\mathbf{R}} \stackrel{\mathbf{PPh}_{3}}{ _{\mathbf{PPh}_{3}}}$ 33	1.10 (m, 2H, $-CH_2$) 1.26 (m, 4H, $-CH_2$) 2.01 (m, 2H, $-CH_2$) 3.23 (s, 3H, CO ₂ CH ₃) 3.31 (s, 3H, CO ₂ CH ₃) 3.43 (s, 3H, CO ₂ CH ₃) 3.48 (s, 3H, CO ₂ CH ₃) 3.48 (s, 3H, CO ₂ CH ₃) 6.40 (m, 1H, Ir–CH) 7.25–7.80 (m, 30H, C ₆ H ₅)	176.4 (br s, Ir-CO) 159.0 (t, $J = 6.5$)° 157.7 (t, $J = 11.8$)° 152.8 (t, $J = 3.1$)° 151.6° 149.9 (t, $J = 3.5$)°
$R \xrightarrow{R}_{R} R \xrightarrow{R}_{R} I \xrightarrow{r}_{H} CO$ $H \xrightarrow{PPh_{3}} B$ 34	1.10 (m, 2H, $-CH_2$) 1.26 (m, 4H, $-CH_2$) 2.01 (m, 2H, $-CH_2$) 3.23 (s, 3H, CO_2CH_3) 3.31 (s, 3H, CO_2CH_3) 3.43 (s, 3H, CO_2CH_3) 3.48 (s, 3H, CO_2CH_3) 6.40 (m, 1H, Ir- CH) 7.25–7.80 (m, 30H, C_6H_5)	176.7 (t, $J = 8.0$, Ir–CO) 160.2 (t, $J = 7.0$)° 155.8 (t, $J = 12.0$)° 146.2 (t, $J = 2.9$)° 120.7 (t, $J = 9.1$)°

^a ₁H NMR spectra were recorded at 300 MHz in CDC1₃ and are referenced to the residual solvent resonance at δ 7.26 ppm, unless otherwise noted. All couplings are in Hertz.

^{b $\overline{13}$ C{¹H} NMR spectra were recorded at 126 MHz in CDC1₃ and were referenced to the solvent resonance at 77.0 ppm, unless otherwise noted. Couplings are in Hertz.}

 c α -C substituents on the metallacycle were not distinguished from the vinyl-carbons.





carbonyl complex $[\kappa^2(C^1, C^4)$ -CR=CRCR=CR](PPh_3)_2Ir-(CO)(Cl) (19, R = CO_2Me) [9] and free ethylene, as indicated by a resonance at δ 5.4 in the proton spectrum of the sample.

An isotope labeling experiment was employed to determine the source of the carbon monoxide oxygen in 18. This was of particular interest as we had previously observed an oxygen atom transfer from a methoxycarbonyl metallacycle substituent to a vinylidene ligand in the reactions of cationic iridacyclopentadiene complexes, such as that observed in the conversion of cationic iridacycle 20 to 21 (Scheme 5) [16]. When 9 (20 mM) and 2-propyn-1-ol (200 mM) were mixed in a two-phase solution of CD₂Cl₂ and ${}^{18}\text{OH}_2$ (3% v/v), the ${}^{18}\text{O-enriched}$ complex, $[\kappa^2(C^1, C^4)$ -CR=CRCR=CR](PPh₃)₂Ir(CH=CH₂)(CO^{*}) (18-O, $O^* = {}^{18}O$, $R = CO_2Me$) was cleanly formed. The position of the ¹⁸O-label was identified by the isotopic shift of the terminal carbonyl-carbon resonance in the ${}^{13}C{}^{1}H$ NMR spectrum (CD₂Cl₂, 126 MHz) of a ~1:1 mixture of 18-O:18 (Fig. 1). The carbonyl-carbon resonances for 18-O were observed 3.8 Hz upfield of the triplet corresponding to the unlabeled complex at 175.8 ppm. The magnitude of this isotopic shift in the ¹³C NMR spectrum upon substitution of oxygen-18 for oxygen-16 is consistent with literature precedent [17]. No additional isotopic shifts were observed in the ${}^{13}C{}^{1}H$ NMR spectrum (CD₂Cl₂) for the remaining carbon resonances of the 18/18-O sample. A comparison of the high-resolution mass spectra for 18 and 18-O indicated >96% ¹⁸O-incorporation in 18-O. In the IR spectrum (KBr), carbonyl stretches were observed at 2028 and 1985 cm^{-1} for **18** and **18**-O, respectively; thereby confirming the ¹³C NMR chemical shift isotope analysis.

The scope of this new propargyl alcohol reaction was briefly explored by examining the reactions of **9** with 3-butyn-2-ol, 2-methyl-3-butyn-2-ol, 1-ethynylcyclopentanol,



Fig. 1. Lower trace: carbonyl ligand carbon resonance in the ${}^{13}C{}^{1}H$ NMR spectrum of **18**-O. The lines indicated by the stars are the triplet observed for the carbon resonance of the C(${}^{18}O$) ligand. Upper trace: the related spectrum for a ~1:1 mixture of **18:18**-O. The lines indicated by the black dots are the triplet observed for the carbon resonance of the nonenriched C(${}^{16}O$) ligand of **18**. The lines indicated by the stars are the triplet observed for the carbon resonance of the C(${}^{18}O$) ligand in **18**-O.

and 1-ethynylcyclooctanol (Scheme 6, Table 1). The reaction of **9** (0.04 M) with (\pm)-3-butyn-2-ol (0.4 M) in a two-phase CD₂Cl₂/H₂O solvent system followed a similar course to that observed for 2-propyn-1-ol. After 21 h at room temperature, ¹H NMR spectroscopy revealed nearly quantitative conversion to [$\kappa^2(C^1, C^4)$ -CR=CRCR=CR]-(PPh₃)₂Ir[(*E*)-CH=CHMe](CO) (**22**, R = CO₂Me) relative to *p*-bis(trimethylsilyl)benzene as an internal standard. Vinyl complex **22** was isolated as an off-white solid in 95% yield from a preparative-scale reaction of **9** (250 mg, 0.03 M) and 3-butyn-2-ol (0.34 M) using a two-phase chloroform/water mixture (4% v/v). In the ¹H NMR spectrum of **22**, four new carbomethoxy-protons at δ 3.28, 3.37, 3.46,





and 3.57 were observed as singlets in addition to the allylicprotons of the vinyl ligand and the vinyl-hydrogen resonances at δ 1.66 (d, 3H, J = 5.7 Hz), 4.66 (dq, 1H, J =17.1, 5.7 Hz), and 6.43 (br d, 1H, J = 17.1 Hz), respectively. The *trans*-alkene stereochemistry is consistent with the 17-Hz coupling constant observed for the vicinalhydrogen atoms of the vinyl group. The resonance at δ 4.66 was assigned to the proton on the β -carbon of the ethenvl ligand based on its 5.7-Hz coupling constant to the methyl protons. In the ${}^{13}C{}^{1}H$ NMR spectrum (CD₂Cl₂), the Ir-CO carbon resonance was observed at 175.4 ppm as a triplet (J = 6.9 Hz). The two inequivalent α -carbon substituents on the metallacycle were observed as a broad singlet at 161.3 and as a triplet (J = 11.8 Hz)at 154.3 ppm. The vinvl-carbons of the ethenvl ligand were observed in the proton-decoupled carbon NMR spectrum at 132.7 (br s) and 125.8 ppm (t, J = 8.4 Hz).

Unexpectedly, when a similar reaction was run with 9 (0.04 M) and 2-methyl-3-butyn-2-ol (0.42 M), the quantitative formation of the iridium carbon monoxide complex 19 was observed after 48 h at room temperature, suggesting 2methylpropene loss from an initially-formed vinyl complex. This speculation was supported by an NMR tube-scale reaction in which 2-methyl-3-butyn-2-ol (0.22 M) was added to a two-phase solution of metallacycle 9 (0.01 M) in 2% aqueous CDCl₃ (0.50 mL). The formation of a new vinyl complex $[\kappa^2(C^1, C^4)-CR=CRCR=CR](PPh_3)_2$ $Ir(CO)[CH=C(CH_3)_2]$ (23, $R = CO_2Me$) was observed in 38% yield by ¹H NMR spectroscopy. In addition to the formation of 23, complex 19 was formed in 52% yield along with 2-methylpropene. The vinyl hydrogen resonance for 23 was observed at δ 6.28. The hydrogens for 2-methylpropene were observed at δ 4.57 and 1.60, respectively. Attempts to isolate complex 23 were unsuccessful due to conversion of the κ^1 -vinyl complex to **19** and isobutylene upon attempted purification.

The reaction of 9 (0.01 M) and 1-ethynylcyclopentanol (0.06 M) in a two-phase CDCl₃/H₂O solution at room temperature was also monitored by ¹H NMR spectroscopy. After 96 hours, the solution was found to contain a 38% yield of a new complex identified as $[\kappa^2(C^1, C^4)-CR]$ $CRCR=CR(PPh_3)_2Ir[CH=C(CH_2)_4](CO)$ (24, $R = CO_2Me$), as well as a 52% yield of both 24 and methylenecyclopentane. The methylene-protons of the ethenyl ligand in 24 were observed as multiplets from δ 1.10–2.01 and the vinyl-hydrogen was observed at 6.40 as a multiplet. The methylenecyclopentane assignment was confirmed by GC–MS analysis of the sample and comparison of the ¹H and ¹³C NMR spectral data with those of an authentic sample. As we were unable to separate 24 from 19, characterization of 24 by ¹H and ¹³C NMR spectroscopy was conducted by analysis of the crude reaction mixture.

A similar small-scale reaction of 9 with 1-ethynylcyclooctanol in CDCl₃/H₂O led to the formation of $[\kappa^2(C^1, C^4)$ -CR=CRCR=CR](PPh_3)_2Ir[CH=C(CH_2)_7](CO) (25, $R = CO_2Me$) in 98% yield, as determined by integration of the resonances for 25 relative to those of an internal standard. The reaction between metallacycle 9 (100 mg, 0.10 mmol, 12.5 mM) and 1-ethynylcyclooctanol (150 mg, 0.97 mmol, 120 mM) in a CDCl₃/H₂O (3%) solution was carried out on a preparative-scale, and the vinyl complex 25 was isolated as analytically pure crystals by slow evaporation of an ether solution. The spectroscopic properties of 25 are displayed in Table 1. The ¹H NMR spectrum of **25** in CDCl₃ exhibits resonances at δ 6.40 (s, 1H) and 7.25-7.80 (m, 30H), which were assigned to the vinylhydrogen and the methylene-hydrogens of the vinyl ligand, respectively. Four resonances between δ 3.48–3.23 were observed for the four unique carbomethoxy-protons. The iridium carbonyl-carbon was observed in the ${}^{13}C{}^{1}H{}$ NMR spectrum (CDCl₃) at 176.7 ppm as a triplet (J = 8.0 Hz). The two vinyl ligand carbons were in the



same range as the α -carbons of the metallacycle at 160.2–120.7 ppm and could not be unambiguously assigned on the basis of either chemical shift or coupling constants.

One reasonable mechanism for the formation of the vinyl complexes 18 and 22-35 from 9 and propargyl alcohols involves the formation of unobserved vinylidene intermediates, such as complex 26, which undergo rapid dehydration to the corresponding allenylidene 27 (Scheme 7). Nucleophilic attack by water at the α -carbon of the allenvlidene, followed by loss of HCl, would then generate the allenol complex 28. Subsequent tautomerization of 28 to the α , β -unsaturated acyl complex 29, followed by decarbonylation, would then afford the vinyl-carbon monoxide product 22 [18]. An organic analogue of the 28 to α,β -unsaturated acyl **29** tautomerization is found in the conversion of allenol ethers (30) to α , β -unsaturated silvl ketones (31; Scheme 8) [19]. The high selectivity for the E-isomer of 22 mirrors the selectivity observed in the formation of 31.

A number of simple variations of the Scheme 6 mechanism may also be valid, particularly with respect to the loss of chloride from iridium, which could potentially occur at a number of different intermediate stages. It should be noted that there is a growing body of precedent for preferential nucleophilic attack at the γ -carbon of allenylidene ligands, rather than at the α -carbon [1–4,7,8]. However, in the case of **27**, attack by water at the γ -carbon of the allenylidene ligand would simply lead back to vinylidene **26**.

A much different mechanistic possibility for the formation of iridium vinyl complexes from propargylic alcohols involves trapping of vinylidene intermediate 26 by water to give acyl complex 32 (Scheme 9) [20]. Decarbonylation





of **32** would then form hydroxyethyl complex **33**, followed by dehydration to afford complex **22**. Bergman has prepared iridium(III) hydroxyethyl complexes, $Cp^*Ir(Ph)(P-Me_3)CH_2CH_2OH$, from the reaction of iridium hydroxide precursors and ethene, but – as of yet – there is no evidence that these undergo dehydration to iridium vinyl complexes; rather, they are converted to formyl methyl complexes (IrCH₂CHO) [21].

3. Conclusions

The reactions of neutral iridium(III) metallacyclopentadiene-halido complexes with terminal alkynes follow a number of pathways depending on the reaction conditions and the nature of the alkyne substituents. The primary reaction pathway in the case of the propargyl alcohol substrates depends on whether the reaction is carried out under aqueous or anhydrous conditions. Both systems presumably involve the initial formation of an η^2 -alkyne complex. Under anhydrous conditions, this intermediate inserts into the metallacycle ring to give the [2 + 2 + 2]-cycloaromatization product **16**. Under aqueous conditions the η^2 -alkyne intermediate sequentially rearranges first to a vinylidene and then to an allenylidene intermediate, which is trapped by water to ultimately afford iridium(III)–vinyl products. Studies are planned to further evaluate the scope of these new routes to metal–vinyl complexes and to more thoroughly establish the reactivity profile for the iridium–vinyl complexes, with particular emphasis on the conversion of these species into metallacyclopentadiene–alkylidene complexes.

4. Experimental

All reactions and reaction workups were performed in air unless otherwise noted. Organic solvents were obtained commercially and used without further purification unless otherwise indicated. IR spectra were recorded on a Mattson 2020 FTIR spectrometer. ¹H and ³¹P NMR spectra were obtained on a GE QE 300 (¹H 300 MHz, ³¹P 122 MHz) spectrometer. 1,4-(TMS)₂C₆H₄ was used as the internal standard in the integration of all small-scale reactions monitored by ¹H NMR spectroscopy. ¹³C NMR spectra were obtained on a GE QE 300 (75.5 MHz) or a Varian UNITY 500 (126 MHz) spectrometer. Chemical shifts for protons are reported in parts per million from tetramethylsilane and are referenced to residual protium in the NMR solvent. Chemical shifts for carbon are reported in parts per million from tetramethylsilane and are referenced to the carbon resonances of the solvent. ³¹P NMR chemical shifts are referenced to 85% H₃PO₄ ($\delta = 0$ ppm). FAB mass spectra were obtained at the University of California, Riverside Mass Spectroscopy Facility. Elemental analyses were performed by either Desert Analytics or Galbraith Laboratories, Inc. Methyl propiolate, ethyl propiolate, dimethyl acetylene dicarboxylate, propiolic acid, deuterated water, deuterated chloroform (the water concentration in the commercial chloroform-d was ca. 56 mM), and silver tetrafluoroborate were obtained from Aldrich Chemical Company. Sodium bromide and potassium iodide were obtained from Fisher Scientific. ¹⁸Olabeled water (97 atom% ¹⁸O) was purchased from MSD Isotopes.

4.1. Trimethyl 1,3-dihydro-3-oxo-4,5,6-isobenzofurantricarboxylate (16)

A 50-mL round-bottom flask equipped with a magnetic stir bar was charged with **9** (0.50 g, 0.48 mmol, 19.3 mM), dry degassed chloroform (25 mL), and 2-propyn-1-ol (1.21 mmol) under an atmosphere of N₂. The solution was then heated at 50 °C for 44 h. The volatiles were removed in vacuo, and the residue was dried under vacuum to give a viscous brown oil which was taken up in chloroform, filtered through a plug of silica gel, and chromatographed on silica gel (5:1 CHCl₃/ethyl acetate) to afford **16** as a solid in 57% yield: m.p. 151.8 °C; IR (KBr) 2962 (s), 1768 (br s), 1739 (br s), 1613 (s), 1435 (s) cm⁻¹; ¹H

NMR (CDCl₃, 300 MHz) δ 8.00 (s, 1 H), 5.37 (s, 2H), 4.00 (s, 3H), 3.94 (s, 3H), 3.91 (s, 3H); ¹³C{¹H} NMR (CDCl₃, 125.7 MHz) δ 166.9, 166.0, 165.5, 164.8, 148.4, 136.0, 133.1, 132.3, 125.8, 124.8, 68.1, 53.4, 53.4, 53.3. HRMS (EI, 50 eV), *m/z* calc. for C₁₄H₁₂O₈: 308.0532, obsd: 308.0528.

4.2. $[\kappa^2(C^l, C^4) - CR = CRCR = CR](PPh_3)_2 Ir(CO) - (CH = CH_2)$ (18, $R = CO_2 Me$)

A 25-mL round-bottom flask equipped with a magnetic stir bar was charged with 9 (0.30 g, 0.29 mmol, 19.3 mM), chloroform (15 mL), and 2-propyn-1-ol (2.9 mmol, 0.19 M) under an atmosphere of N₂. The solution was stirred at 23 °C for 24 h. The volatiles were evaporated; the residue was taken up in chloroform (20 mL) and filtered to give 18 as a pale pink powder. Recrystallization from methylene chloride/diethyl ether afforded 18 in 33% yield: m.p. 195-197 °C (sealed cap); IR (KBr) 2027 (vs), 1725 (br s), 1692 (s), 1680 (s), 1485 (s), 1435 (s), 1328 (s), 1219 (vs) cm⁻¹; ¹H NMR (CD₂Cl₂, 300 MHz) δ 7.63 (m, 1H), 7.51–7.27 (m, 30 H), 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), 3.21 (s, 3H); ${}^{13}C{}^{1}H{}$ NMR (CD₂Cl₂, 125.7 MHz) δ 176.5 (s), 173.5 (s), 175.8 (t, J = 8.4), 167.5 (s), 167.07 (s), 162.1 (t, J = 6.8), 154.8 (t, J = 3.1), 152.5 (t, J = 11.8), 150.9 (s), 136.5 (t, J = 8.7), 135.4 (t, J = 5.0), 130.4 (t, J = 28.9, 130.5 (s), 127.6 (t, J = 5.4), 125.8 (br s), 51.2, 51.0, 50.9, 50.3; ${}^{31}P{}^{1}H{}NMR$ (CD₂Cl₂, 121.5 MHz) δ -6.60. HRMS(FAB), m/e calc. for $C_{51}H_{45}O_9P_2IrH^+$ -(MH⁺): 1055.2223, obsd: 1055.2252.

4.3. $[\kappa^2(C^1, C^4)-CR=CRCR=CR](PPh_3)_2Ir(CO)[(E)-CH=CHCH_3]$ (22, $R = CO_2Me$)

A 25-mL round-bottom flask equipped with a magnetic stir bar was charged with 9 (250 mg, 0.24 mmol, 34.4 mM), aqueous chloroform (7 mL, 4% v/v), and 2-methyl-3butyn-2-ol, (190 µL, 2.4 mmol). The solution was stirred at 23 °C for 15 h in the air. The volatiles were evaporated, and the residue was recrystallized from benzene/hexanes to give 22 as an off-white powder in 95% yield (244 mg): m.p. 183-185 °C (sealed cap); IR(KBr) 2028 (s), 1720 (s), 1699 (s), 1988 (s), 1482 (s), 1433 (s), 1325 (s), 1209 (vs), 1091 (s), 1067 (s), 1019 (vs), 748 (s), 696 (vs), 523 (s), cm^{-1} ; ¹H NMR (CDCl₃, 300 MHz) & 7.48 (m, 12 H), 7.31 (m, 18 H), 6.43 (br d, 1H, J = 17.1 Hz), 1.66 (dq, 1H, J = 17.1, 5.7 Hz), 3.57 (s, 3H), 3.46 (s, 3H), 3.37 (s, 3H), 3.28 (s, 3H), 1.33 (d, 3H, J = 5.7 Hz); ¹³C{¹H} NMR (CDCl₃, 125.7 MHz) δ 176.47 (s), 175.41 (br s), 173.28 (s), 167.38 (s), 167.17 (s), 161.31 (s), 154.33 (t, J = 11.8 Hz), 153.77 (s), 150.73 (s), 134.99 (s), 132.67 (s), 130.09 (t, J =28.2 Hz), 139.97 (s), 127.22 (br s), 125.24 (t, J = 8.4 Hz), 50.88 (s), 50.67 (s), 50.46 (s), 50.14 (s), 24.68 (s). ³¹P{¹H}NMR (CDCl₃, 121.5 MHz) δ – 6.33 (s). HRMS (FAB), m/z calc. for C₅₂H₄₇O₉P₂Ir: 1070.2325, obsd: 1070.2387.

4.4. $[\kappa^2(C^1, C^4) - CR = CRCR = CR](PPh_3)_2 Ir[CH = C(CH_2)_4](CO)$ (24, $R = CO_2Me$)

A 50-mL round-bottom flask equipped with a magnetic stir bar was charged with 9 (150 mg, 7 mM), chloroform (20 mL), water (0.30 mL) and 1-ethynylcyclopentanol (0.17 mL, 72 mM). The mixture was stirred at 23 °C for 5 d. The volatiles were removed under vacuum, and the residue was recrystallized from methylene chloride/ethanol to give 40 mg of a cream colored solid. ¹H NMR spectroscopy indicated a mixture of 19 and 24. For 24: ¹H NMR (CDCl₃, 300 MHz) & 7.25–7.80 (m, 30H), 6.40 (br s, 1H), 3.48 (s, 3H), 3.43 (s, 3H), 3.31 (s, 3H), 3.23 (s, 3H), 2.02 (m, 2H), 1.10 (m, 2H), 1.26 (m, 4H); ${}^{13}C{}^{1}H$ NMR (CDCl₃, 125.7 MHz) δ 176.4 (br s), 175.4, 173.0, 167.8, 166.7, 159.0 (t, J = 6.5 Hz), 157.7 (t, J = 11.8 Hz), 152.8 (t, J = 3.1 Hz), 151.6, 149.9 (t, J = 3.5 Hz), 135.0 (t, J = 5.3 Hz), 130.3 (t, J = 28.7 Hz), 130.0 (br s), 127.2 (t, J = 5.9 Hz), 114.4 (t. J = 9.9 Hz), 50.8, 50.6, 50.3, 50.2, 39.6, 33.2, 27.1, 26.7.

4.5. $[\kappa^2(C^1, C^4) - CR = CRCR = CR](PPh_3)_2 Ir(CH = C(CH_2)_7)(CO)$ (25, $R = CO_2Me$)

A 50-mL round-bottom flask was charged with 9 (100 mg, 0.97 mmol, 0.12 M), chloroform (8 mL), distilled water (0.20 mL), and 1-ethynylcyclooctanol (147 mg, 0.97 mmol). After 4 d at rt, the mixture was filtered, and the mother liquor was evaporated to give a brown solid. Recrystallization from diethyl ether afforded 25 as clear amber slates (9.7 mg, 8.75%): IR(KBr) 3068 (w), 2924 (w), 2020 (s), 1718 (vs), 1436 (s), 1206 (vs), 1323 (w), 1089 (m), 1089 (m), 1014 (m), 753 (m), 701 (vs) cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) & 7.52 (m, 30H), 6.75 (t, 1H, J = 4.7 Hz), 3.45 (s, 3H), 3.39 (s, 3H), 3.27 (s, 3H), 3.23 (s, 3H), 1.208 (m, 14H); ${}^{13}C{}^{1}H{}$ NMR (CDCl₃, 125.7 MHz) δ 176.7 (t, J = 8.0 Hz), 175.1, 172.8, 167.4, 166.9, 160.2 (t, J = 7.0 Hz), 155.8 (t, J = 12.0 Hz), 153.5, 151.3, 146.2 (t, J = 2.9 Hz), 135.1 (t, J = 4.8 Hz), 130.3 (t, J = 28.6 Hz), 120.7 (t, J = 9.1 Hz), 50.7, 50.7, 50.3, 50.1, 41.0, 36.3, 28.9, 28.1, 27.5, 26.1, 26.0. HRMS(FAB) m/e calc. for $C_{58}H_{57}O_9P_2Ir$: 1152 (M⁺), obsd. 1152 – which matched the calc. isotopic distribution pattern.

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