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X-ray molecular structures and multinuclear NMR studies of the tetranuclear iridium clusters $[Ir_4(CO)_7(\mu_4\text{-}\eta^3\text{-}PhCC(H)CCPh)(\mu\text{-}PPh_2)_3]$ and $[Ir_4(CO)_7(\mu_3\text{-}\eta^2\text{-}HCCPh)(\eta^1\text{-}CCPh)(\mu\text{-}PPh_2)_3]$

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Abstract

The reaction of $[HIr_4(CO)_{10}(\mu\text{-}PPh_2)]$ with two equiv. of $Ph_2PC{\equiv}CPh$ produced $[HIr_4(CO)_8(Ph_2PC{\equiv}CPh)_2(\mu\text{-}PPh_2)]$ (**1**) in quantitative yield. Mild thermolysis of **1** gave $[Ir_4(CO)_7(\mu_4\text{-}\eta^3\text{-}PhCC(H)CCPh)(\mu\text{-}PPh_2)_3]$ (**2**) and $[Ir_4(CO)_7(\mu_3\text{-}\eta^2\text{-}HCCPh)(\eta^1\text{-}CCPh)(\mu\text{-}PPh_2)_3]$ (**3**) in good yields. These compounds were characterized with analytical and spectroscopic data including ^1H, ^{13}C and ^{31}P NMR (1 and 2D) spectroscopy, and their molecular structures were established by X-ray diffraction studies. The metal frameworks of **2** and **3** are similarly constituted of a spiked metal triangle; in both clusters the seven CO ligands are terminally bound and the three $–PPh_2$ ligands span two consecutive Ir–Ir bonds and an open edge. The difference between the two structures is that compound **2** contains a butadienic chain, $\mu_4\text{-}\eta^3\text{-}PhCC(H)CCPh$, interacting with all four iridium atoms, whereas compound **3** bears two fragments of this ligand, i.e. a phenylacetylene capping a triangular face and a terminally bound phenylacetylide bonded to the fourth atom of the cluster. Although these two fragments are directed in the appropriate fashion to interact further and generate the chain of compound **2**, they do not undergo condensation under thermolytic conditions.

Keywords: Tetrairidium clusters; Acetylide; C–C coupling; X-ray molecular structure

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1. Introduction

Examples of acetylide ligand coupling reactions in the coordination sphere of late transition metal clusters to generate polyene ligands are relatively scarce in the literature [1–6]. In most cases, the acetylide fragments are generated in $R_2PC{\equiv}CR'$ containing dimers or clusters via $P–C_{sp}$ bond cleavage under thermolytic conditions. Coupling of these fragments occurs either under the same conditions or at higher temperatures necessary for the cluster further activation, and results in the formation of several products, frequently of different nuclearities, due to cluster fragmentation and recombination of the reactive fragments. For example, from the

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thermolysis of $[Ru_2(\mu-\eta^1-\eta^2-C_2{}^tBu)(\mu-PPh_2)(CO)_6]$ [4,7] in refluxing toluene the diacetylide complex $[Ru_4(\mu-\eta^1-\eta^2-C_2{}^tBu)(\mu_3-\eta^2-C_2{}^tBu)(\mu-PPh_2)_2(CO)_9]$ was isolated and shown to react further to yield the diyne tetranuclear cluster $[Ru_4(\mu_4-{}^tBuC_4{}^tBu)(\mu-PPh_2)_2(CO)_8]$ resulting from *head-to-head* coupling of the two acetylide ligands. Generally, the outcome of the reaction is sensitive to the substituent on the acetylide, e.g. heating $[Ru_2(\mu-\eta^1-\eta^2-C_2Ph)(\mu-PPh_2)(CO)_6]$ [8] resulted in the formation of the *head-to-head* condensation (acetylide + Ph_2PCPh from P to C bond re-formation), $[Ru_4(CO)_{10}(\mu-PPh_2)(\mu_4-Ph_2PC(Ph)CCC(Ph)]$, and other minor products.

Only two examples have been described in the literature involving the thermolysis of clusters containing two phosphinoalkynes, viz. $[M_3(CO)_{10}(Ph_2PC\equiv CR)(Ph_2PC\equiv CR')]$ (M = Ru [9] R = Ph, R′ = ^{t}Bu and R = R′ = Ph, ^{t}Bu, and M = Os [10], R = R′ = Ph, ^{i}Pr). Whereas the only products obtained from the thermolysis at 125 °C of the osmium clusters were $[Os_3(CO)_7(\mu_3-\eta^2-C\equiv CR)_2(\mu-PPh_2)_2]$ (R = Ph and ^{i}Pr), the nature of the products formed from the analogous ruthenium clusters depended both on the thermolysis temperature and on the substituent on the phosphinoalkyne [9]. For example, when heated at 110 °C, the compound containing two $Ph_2PC\equiv C{}^tBu$ ligands yielded a mixture of tetranuclear products similar to that formed from the thermolysis of $[Ru_2(\mu-\eta^1-\eta^2-C_2{}^tBu)(\mu-PPh_2)(CO)_6]$, but at lower temperature (67 °C) the cluster nuclearity stayed intact and the P–C bond activation product, $[Ru_3(CO)_7(\mu_3-\eta^2-C\equiv C{}^tBu)_2(\mu-PPh_2)_2]$, was isolated instead. Furthermore, from the reaction of the cluster containing two different phosphinoalkyne ligands, both $[Ru_3(CO)_7(\mu_3-\eta^2-C\equiv C{}^tBu)(\mu_3-\eta^2-C\equiv CPh)(\mu-PPh_2)_2]$ and the product from acetylide *head-to-head* condensation, $[Ru_3(CO)_7(\mu_3-\eta^2-PhCCC\equiv C{}^tBu)(\mu-PPh_2)_2]$, were isolated.

Other sources of acetylide fragments for condensation in the coordination sphere of late transition metal clusters include: (i) the $P(C\equiv C{}^tBu)_3$ ligand in $[Ru_3(CO)_{11}\{P(C\equiv C{}^tBu)_3\}]$, whose mild thermolysis led to the formation of $[Ru_3(\mu_3-\eta^2-C\equiv C{}^tBu)_2\{\mu-P(C\equiv C{}^tBu_2)_2\}(CO)_9]$ and then to the diyne tetranuclear compound $[Ru_4(\mu_4-\eta^4-{}^tBuC_4{}^tBu)(CO)_{10}]$ [11]; (ii) $RC\equiv CSEt$ (R = Me, Ph) that was heated in the presence of $[Ru_3(CO)_{12}]$, leading to several products of various nuclearities containing C_4 ligands, e.g. $[Ru_5(\mu_5-\eta^4-CPhCCPhC)(\mu-SEt)_2(CO)_{13}]$ and $[Ru_6(\mu_6-\eta^4-MeC_4Me)(\mu-SEt)_2(CO)_{10}]$ as the result of *head-to-tail* and *head-to-head* couplings, respectively, of two acetylide units [1] and (iii) mononuclear metal acetylide compounds that were shown to undergo condensation with cluster compounds, e.g. $[M(\eta^5-C_5Me_5)(CO)_3(C\equiv CPh)]$ and $[M(\eta^5-C_5H_5)(CO)_3(C\equiv CPh)]$ (M = Mo or W) with $[Fe_3(CO)_9(\mu_3-E)_2]$ (E = S, Se or Te) under thermolytic conditions to yield high nuclearity heterometallic clusters containing C_4 ligands, including that resulting from the rare *head-to-head* acetylide condensation process [12,13].

Activation of the P–C_{sp} bond of the $Ph_2PC\equiv CPh$ ligand in the iridium cluster $[HIr_4(CO)_9(Ph_2PC\equiv CPh)(\mu-PPh_2)]$ (**A**) is an extremely facile process that occurs in refluxing CH_2Cl_2 for 5 h, in the absence of CO, to give $[HIr_4(CO)_8(\mu_3-\eta^2-HCCPh)(\mu-PPh_2)_2]$ (**B**) in yields above 70% [14]. Considering that the reactions of both clusters with $HC\equiv CPh$ result in selective formation of two isomeric compounds, $[Ir_4(CO)_6(\mu_3-\eta^2-HCCPh)\{\mu_2-\eta^4-(H)CC(Ph)C(H)C(Ph)\}(\mu-PPh_2)_2]$ and $[Ir_4(CO)_6(\mu_3-\eta^2-HCCPh)\{\mu_2-\eta^4-(H)CC(Ph)C(Ph)C(H)\}(\mu-PPh_2)_2]$, containing C_4 ligands, as the result of *head-to-tail* and *tail-to-tail* condensations of two HCCPh molecules, respectively [15], we decided to investigate the behavior of the di-substituted cluster $[HIr_4(CO)_8(Ph_2PC\equiv CPh)_2(\mu-PPh_2)]$ (**1**) under mild thermolytic conditions. As described herein this reaction led to high yield formation of two products: $[Ir_4(CO)_7(\mu_4-\eta^3-PhCC(H)CCPh)(\mu-PPh_2)_3]$ (**2**), which contains a butadienic chain resulting formally from *head-to-head* condensation of two acetylide fragments and incorporation of the cluster hydride, and $[Ir_4(CO)_7(\mu_3-\eta^2-HCCPh)(\eta^1-CCPh)(\mu-PPh_2)_3]$ (**3**), bearing the two fragments of the butadienic ligand directed in the appropriate fashion to generate the chain of compound **2**.

2. Results and discussion

2.1. Preparation and characterization of $[HIr_4(CO)_8(Ph_2PC\equiv CPh)_2(\mu-PPh_2)]$ (1)

The reaction between $[HIr_4(CO)_{10}(\mu-PPh_2)]$ [16] and two equiv. of $Ph_2PC\equiv CPh$ in CH_2Cl_2, at 25 °C, for 1 h (Scheme 1, i), afforded the dark orange di-substituted cluster **1** in 90% yield, in addition to the mono-substituted species $[HIr_4(CO)_9(Ph_2PC\equiv CPh)(\mu-PPh_2)]$ (**A**, 10%). Compound **1** was isolated previously as a by product of the reaction of $[HIr_4(CO)_{10}(\mu-PPh_2)]$ with one equiv. of $Ph_2PC\equiv CPh$ in the same solvent, at 30 °C, for 4 h that gives the mono-substituted product **A** in 70% yield (Scheme 1, ii) [14]. Addition of one equiv. of $Ph_2PC\equiv CPh$ to pure **A** under the same reaction conditions (Scheme 1, iii) also led to cluster **1** albeit in lower yield (50%), together with $[HIr_4(CO)_8(\mu_3-\eta^2-HCCPh)(\mu-PPh_2)_2]$ (**B**), the product from the rearrangement of **A** (Scheme 1, iv), isolated in about 30% yield. Conversion of **A** into **B** has been shown to be hampered by the presence of 1 atm of CO [14]. The selectivity of reaction i, therefore, must be due to the presence of dissolved CO in solution, after the first CO substitution, which inhibits P–C bond activation, but not substitution of a second CO ligand to give cluster **1**.