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An Unprecedented Iridium(III) Catalyst for Stereoselective Dimerisation of Terminal Alkynes

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Abstract: A novel iridium(III) hydride complex, IrHCl(TIMP$_3$) {HTIMP$_3$ = tris[1-(diphenylphosphino)-3-methyl-1*H*-indol-2-yl]methane} was prepared and fully characterized in both the solid state and in solution. Chloride abstraction by silver cations provides a more reactive compound, [IrH(TIMP$_3$)][BF$_4$], which can react with pyridine (py) and phenylacetylene to yield the complexes [IrH(TIMP$_3$)(py)][BF$_4$] and [Ir(PhCH=C−CH=CHPh)(TIMP$_3$)][BF$_4$], respectively. Interestingly, IrH(TIMP$_3$)(py)][BF$_4$] efficiently catalyses the stereoselective dimerisation of model terminal alkynes to the 1,4-disubstituted (*E*)-but-1-en-3-yne only.

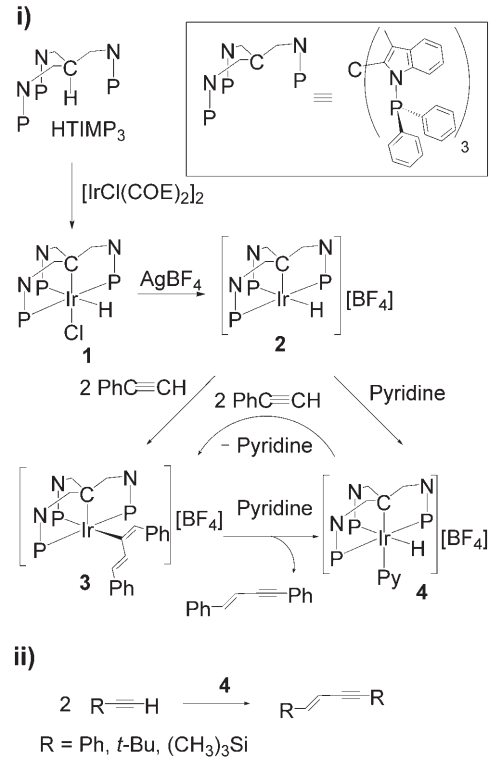
Keywords: alkyne dimerisation; catalyst design; diastereoselectivity; iridium(III) complexes

The transition metal-catalysed dimerisation of terminal alkynes is an efficient method for the synthesis of branched and linear enynes, which are versatile intermediates in organic synthesis.[1,2] This process for the iridium complexes appears to involve an Ir(I)/Ir(III) cycle consisting of i) oxidative addition of the alkyne C−H bond to the Ir(I) complex, which leads to an RC≡C−Ir(III)−H compound, ii) insertion of a second alkyne molecule into the Ir−H or the Ir−C bond, which affords a vinyl-Ir(III) species, and iii) reductive elimination, which regenerates the iridium(I) compound and produces a linear (*E*)-enyne, a (*Z*)-enyne, or a mixture of both in most cases.[2b,3] To our knowledge, there is no example in the literature of a well-defined Ir(III) complex that catalyses alkyne dimerisation.

In this context, here we report the synthesis of the Ir(III) hydride derivative, IrHCl(TIMP$_3$) (**1**), starting from the P-tripodal ligand HTIMP$_3$,[4] and its derivatives [IrH(TIMP$_3$)][BF$_4$] (**2**), [Ir(PhCH=C−CH=CHPh)(TIMP$_3$)][BF$_4$] (**3**) and [IrH(TIMP$_3$)(py)][BF$_4$] (**4**) (Scheme 1, reaction i). We also report preliminary catalytic studies which demonstrate the activity of **4** in the stereoselective dimerisation of model terminal alkynes (Scheme 1, reaction ii).

To assess the binding ability of HTIMP$_3$ to iridium, it was refluxed in deaerated toluene containing [IrCl(COE)$_2$]$_2$ (HTIMP$_3$/Ir molar ratio = 1) for 5 days. A non-symmetrical complex was obtained; whose structure in solution was compatible with **1**, based on ^{1}H and ^{31}P NMR spectroscopy, and fully in agreement with its solid state structure (see below, X-ray analysis). Thus, its ^{31}P{^{1}H} NMR spectrum shows three signals (1:1:1 ratio) at 31.7, 38.1, and 43.5 ppm. Moreover, its ^{1}H NMR spectrum evidences the disappearance of the C_{sp^3}–H methyne hydrogen and shows three non-equivalent methyl groups (1.6, 1.7 and 2.0 ppm), as well as a doublet of triplets at −8.4 ppm [$^2J_{H,P(trans)}$ = 142.5 Hz, $^2J_{H,P(cis)}$ = 15.9 Hz], which can clearly be assigned to the hydride. The X-ray analysis (Figure S1 in Supporting Information) of a single crystal of **1** shows the distorted square pyramidal geometry of the complex, in which the three P atoms, the deprotonated methylene carbon and a chloride ligand are coordinated to thconditionse metal centre. The hydride is not located in the structure refinement but is visible in the ^{1}H NMR spectrum.

Compound **1** was found to be unreactive towards phenylacetylene under a variety of reaction.[5] To



Scheme 1. i) Synthesis of Ir(III) complexes **1**–**4** containing the tripodal $HTIMP_3$ phosphine ligand, and **ii)** the catalysed dimerisation of model terminal alkynes.

obtain a more reactive complex, a methanol solution of **1** was treated with $AgBF_4$ at room temperature for 12 h. Under these conditions the chloride group from **1** was efficiently abstracted and the resulting product was assigned the structure $[IrH(TIMP_3)][BF_4]$ (**2**) on the basis of its ^1H, ^{19}F and ^{31}P NMR data (see Supporting Information). This compound is thermally stable in air and in non-chlorinated solvents, but again leads to complex **1** in the presence of trace amounts of $CHCl_3$ or CH_2Cl_2.

Cationic complex **2** does react with phenylacetylene in methanol and quantitavely gives rise to a new compound, identified as the butadienyl species **3** (Scheme 1, reaction i).[6] The ^{19}F NMR spectrum of **3** shows a singlet at −154.6 ppm, indicating an uncoordinated BF_4^- anion. The presence of three non-equivalent phosphorus atoms in a pseudo T-shaped arrangement can be assumed from its $^{31}P\{^1H\}$ NMR spectrum (three signals at 30.3, 46.2, and 50.4 ppm). Regarding the butadienyl moiety, its main ^1H NMR spectrum features are the three 1:1:1 signals at 5.3, 5.5, and 5.55 ppm. A quaternary carbon is observed at 133.7 ppm (from the $^1H\,^{13}C$ HMBC spectrum), corresponding to the carbon atom directly bonded to the metal. The X-ray analysis of a single crystal of **3** shows that the Ir centre is coordinated to three phosphorus atoms and to a carbon atom from the $TIMP_3$ ligand (Figure 1), the coordination sphere being completed by the butadienyl moiety, with an Ir(1)–C(100) bond distance of 2.052 Å. Interestingly, C(101) and C(102) of the butadienyl residue are weakly bound to the metal [Ir(1)–C(101) = 2.427 Å and Ir(1)–C(102) 2.751 Å]. Thus, these distances are shorter than those reported for the η^2-butadienyl Ir(III) complex of the formula $Ir(PPh_3)_2(L)(PhCH{=}C{-}CH{=}CHPh)^+$ [L = PhC=CH–C(=O)CH_3], where they are 2.509 and 3.092 Å, respectively.[7] Furthermore, the C–C bond distances along the C_4 chain in **3** exhibit an irregular short-long-short pattern [C(109)–C(100), 1.30; C(100)–C(101), 1.46; and C(101)–C(102), 1.36 Å] when compared with the more regular one observed in the above-mentioned compound of reference (1.33, 1.47 and 1.32 Å).

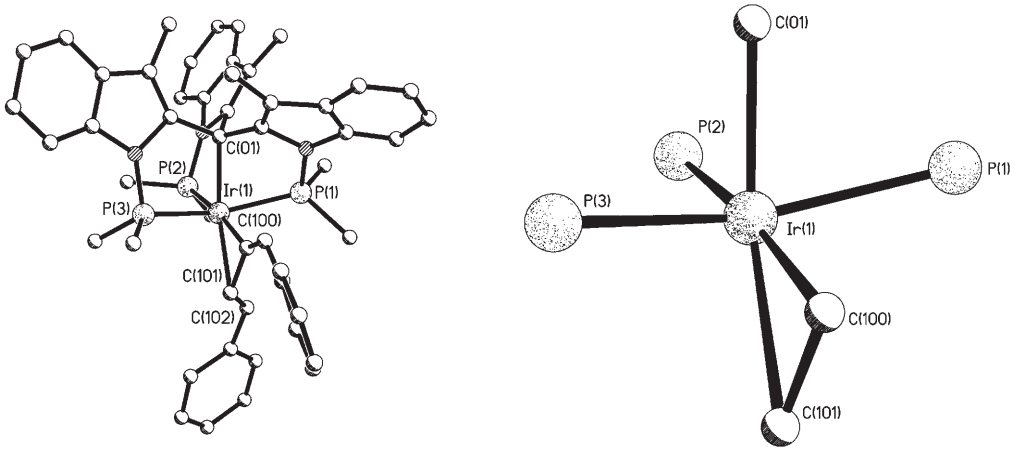


Figure 1. (*Left*) Molecular structure of **3** (only the *ipso* carbon atoms are reported for the PPh_2 moieties) and (*right*) its coordination polyhedron. Selected bond distances [Å] and angles [°] are: Ir(1)–C(100) 2.052(19), Ir(1)–C(101) 2.427, Ir(1)–C(01) 2.134(16), Ir(1)–P(1) 2.397(5), Ir(1)–P(2) 2.374(5), Ir(1)–P(3) 2.305(5), C(100)–Ir(1)–C(01) 106.9(7), C(100)–Ir(1)–P(3) 86.4(5), C(01)–Ir(1)–P(2) 81.8(5) C(01)–Ir(1)–P(1) 77.8(5), P(2)–Ir(1)–P(1) 99.76(17).

Since the β-hydrogen elimination from **3** could give rise to highly unsaturated four-carbon derivatives, which are nowadays compounds of great relevance,[8] the capacity of **3** to undergo β-hydrogen elimination was investigated: i) no decomposition occurs even after 3 days in refluxing $CHCl_3$ or MeOH, but ii) **3** readily reacts with stoichiometric amounts of pyridine in refluxing MeOH, releasing the butadienyl moiety as (*E*)-1,4-diphenylbut-1-en-3-yne and yielding the hexacoordinated complex **4** (Scheme 1, reaction i). In addition, **4** converts to **3** when reacted with phenylacetylene (PhC≡CH/Ir = 2/1 molar ratio).

In view of this, the capacity of **4** to catalyse the dimerisation of model terminal alkynes [PhC≡CH, *t*-BuC≡CH and $(CH_3)_3SiC{\equiv}CH$] was tested. Interestingly, complex **4** (2% mol Ir) cleanly and selectively led to the corresponding (*E*)-but-1-en-3-yne after heating the reaction mixture in sealed tube at 80 °C. The evolution of all these reactions was followed by ^1H NMR (see Figures S2 and S3 in the Supporting Information), which showed shorter reaction times for both $(CH_3)_3SiC{\equiv}CH$ (24 h, 98% yield) and *t*-BuC≡CH (8 h, 95% yield) than in the case of PhC≡CH (35 h, 95%). Moreover, ^{31}P NMR spectra obtained at different reaction times demonstrated that complex **4** is recovered unchanged after dimerisation of the alkyne.

In summary, the rigid tripodal phosphorus-based ligand tris[1-(diphenylphosphino)-3-methyl-1*H*-indol-2-yl]methane ($HTIMP_3$) leads to the non-symmetrical $IrHCl(TIMP_3)$ Ir(III) hydride complex. This complex converts to the more reactive Ir(III) compound $[IrH(TIMP_3)(py)][BF_4]$, which behaves as a catalyst for the diastereoselective dimerisation of terminal alkynes by means of an unprecedented Ir(III)-based mechanism. The participation of Ir(III) complexes throughout the catalytic process and the involvement of a η^3-butadienyl intermediate species are clearly established in the dimerisation of PhC≡CH.

Experimental Section

Synthesis of 1

A toluene solution of $[IrCl(COE)_2]_2$ (565 mg, 1.26 mmol of Ir) and $HTIMP_3$ (1.20 g, 1.26 mmol) was refluxed for 5 d under an argon atmosphere, and finally evaporated yielding a colourless residue, which was recrystallised from $CHCl_3$/Et_2O and identified as **1**; yield: 969 mg, (65%, MW 1183.71). ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded.

Representative Procedure for Catalytic Tests

To a solution of **4** (6 mg; 5 μmol) in CD_3OD (0.7 mL), the alkyne (500 μmol) was added. The reaction was conducted in a sealed tube, and the mixture was heated at 80 °C. The reaction evolution was followed by ^1H NMR, showing the clean and progressive conversion of the alkyne into the (*E*)-enyne.

Supporting Information

Data for **1–4**, X-ray structure of **1**, and time evolution of the catalytic reactions.

Acknowledgements

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[5] Different Ir/PhC≡CH ratios (1:1, 1:2, 1:20), solvents ($CHCl_3$, toluene), reaction times (between 1–3 days) and temperatures (room temperature and reflux) were tested.

[6] The mono-insertion product was not observed even if the reaction was carried out at 240 K and using a **1**/phenylacetylene molar ratio in the 0.5–1 range.

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