

Alkyne reactions with trimethylphosphine complexes of iridium: Lessons for the catalysis of vinyl ester formation and alkyne dimerization



Joseph S. Merola*, Folami T. Ladipo¹

Department of Chemistry, Virginia Tech, Blacksburg, VA 24061, USA

ARTICLE INFO

Article history:

Received 28 August 2013

Accepted 19 December 2013

Available online 7 January 2014

Keywords:

Iridium

Trimethylphosphine

Catalysis

Alkyne dimerization

Vinyl esters

ABSTRACT

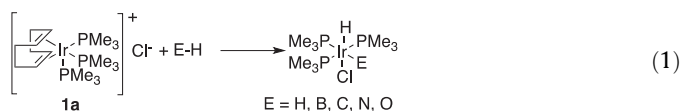
The combination of iridium with trimethylphosphine ligands yields very electron rich iridium compounds that are active for terminal alkyne dimerization chemistry as well as the addition of carboxylic acids to alkynes. The structures, catalytic and stoichiometric chemistry of some iridium tris-trimethylphosphine compounds with benzoate ligands are detailed in this paper. The roles that these compounds may play in the catalytic cycles involved in the dimerization of terminal alkynes and the addition of benzoic acid to terminal alkynes are examined and possible mechanisms for these catalytic reactions are proposed.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Metal phosphine complexes have been widely studied and have played a large role in the development of homogeneous catalysis [1]. For example, the low pressure hydroformylation reaction with $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ has been a significant commercial success [2–5]. The production of L-DOPA uses asymmetric phosphine ligands in combination with rhodium [6–8].

We have found that the combination of iridium with the smallest alkylphosphine, trimethylphosphine, is a powerful one for the study of oxidative addition reactions and have demonstrated that $[\text{Ir}(\text{COD})(\text{PMe}_3)_3]\text{Cl}$, **1a**, is a versatile reactant capable of the oxidative addition a variety of E–H bonds where E = H [9], B [10], C [11,12], N [13], and O [14,15] (Eq. (1)) as well as



inducing the ring-opening oxidative addition of thiophenes, thiazoles and selenophene [11,16].

Alkynes are versatile building blocks for organic syntheses and homogeneous transition metal catalysts have been applied to systems using alkynes in a variety of ways. Addition reactions across alkynes can be catalyzed by quite a variety of metal complex

systems. One example is the head to head dimerization of terminal alkynes in which the C–H bond of one alkyne adds across the triple bond of another [17–23]. Based on our results from the addition of carboxylic acids to iridium we became interested in the addition of carboxylic acids across alkynes to yield vinyl carboxylate esters. This type of addition reaction has been demonstrated by a number of metal complex systems [24–27]. Even when catalytic activity is not great, we have found iridium chemistry to be very useful for shedding light on catalytic systems because of the ability to isolate reaction intermediates that may not be observable in a more reactive system. This paper discusses the lessons learned in an iridium trimethylphosphine system that shed some light on the general catalysis of the reaction between alkynes and carboxylic acids.

2. Experimental

2.1. General procedures

All reactions were carried out under an atmosphere of purified nitrogen. Solvents were purchased from Fisher Scientific. Toluene was distilled from potassium benzophenone; dichloromethane was distilled from P_2O_5 ; ether and pentane were distilled over Na/K alloy. Water was deionized and distilled. Deuterated solvents were purchased from Cambridge Isotope Laboratories and dried over molecular sieves. Hydroiridic acid was purchased from PGN Chemicals and was used as received. The ^1H and ^{31}P NMR spectra were recorded on a Bruker WP200 SY spectrometer operating at 200.132 MHz for protons, 81.015 MHz for phosphorus, 67.925 MHz for carbon, and Bruker WP360 SY spectrometer operating at 360.134 MHz for

* Corresponding author. Tel.: +1 540 231 4510; fax: +1 540 231 3255.

E-mail addresses: jmerola@vt.edu (J.S. Merola), fladipo@uky.edu (F.T. Ladipo).

¹ Present address: Department of Chemistry, University of Kentucky, Lexington, KY 40506, USA.

protons, 145.785 MHz for phosphorus, and 90.556 MHz for carbon. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, Georgia.

GC/MS analysis was performed by the VPI&SU mass spectrometry laboratory on a VG Analytical 7070 E-HF high resolution mass spectrometer using an electron impact ionization (70 eV) mode. $[\text{Ir}(\text{COD})(\text{PMe}_3)_3]\text{Cl}$, **1a**, [28], $\text{Hlr}(\text{O}_2\text{CPh})(\text{PMe}_3)_3\text{Cl}$, **2**, [15], $\text{Hlr}(\text{OPh})(\text{PMe}_3)_3\text{Cl}$, **9**, [15], and $[\text{Ir}(\text{COD})(\text{PMe}_3)_3]\text{O}_2\text{CPh}$, **1b**, [9] were prepared according to previously published methods.

2.2. Syntheses

2.2.1. Synthesis of $\text{Hlr}(\text{O}_2\text{CPh})_2(\text{PMe}_3)_3$ (**10**)

A 100 mL one-necked side-armed flask, equipped with a magnetic stirrer and a septum, was charged with 2.00 g (3.08 mmol) of $[\text{Ir}(\text{COD})(\text{PMe}_3)_3]\text{O}_2\text{CPh}$ and 0.414 g benzoic acid (3.39 mmol, 1.1 eq) under N_2 in a dry box. The flask was then connected to a double manifold (vacuum/nitrogen) Schlenk line and 25.0 mL of mesitylene added by syringe. The reaction mixture was stirred magnetically and heated at $\sim 60^\circ\text{C}$ for 24 h. At completion, the solids were filtered and then re-dissolved in THF (2.00 mL). Diethyl ether was used to precipitate light brown solids. The solids were washed with 10.0 mL of ether and dried under reduced pressure to yield 1.78 g (2.69 mmol) of $\text{Hlr}(\text{O}_2\text{CPh})_2(\text{PMe}_3)_3$, **10**, ($\sim 87\%$ based on amount of $[\text{Ir}(\text{COD})(\text{PMe}_3)_3][\text{O}_2\text{CPh}]$ and identified on the basis of the following data:

Anal. Calc. for $\text{C}_{23}\text{H}_{38}\text{P}_3\text{IrO}_4$: C, 41.56; H, 5.77. Found: C, 41.30; H, 5.64%.

^1H NMR (CDCl_3): δ -23.66 (dt, $J_{\text{P-H}} = 23$ Hz, 14 Hz, 1H, Ir-H), 1.53 (t, $J_{\text{P-H}} = 3.8$ Hz, 18H, trans PMe_3), 1.71 (d, $J_{\text{P-H}} = 10.3$ Hz, cis PMe_3), 7.29–7.40 (m, 6H, phenyl ring), 8.05–8.12 (m, 4H, phenyl ring).

^{31}P NMR (CDCl_3): δ -49.15 (t, $J_{\text{P-P}} = 21$ Hz, 1P, cis PMe_3), -28.89 (d, $J_{\text{P-P}} = 21$ Hz, 2P, trans PMe_3).

^{13}C NMR (d_6 -benzene): δ 16.78 (t, $J_{\text{C-P}} = 18.3$ Hz, 6C, trans PMe_3), 21.48 (d, $J_{\text{C-P}} = 39.6$ Hz, 3C, cis PMe_3), 129.9, 130.2, 130.4, 130.6 (s, 8C, phenyl), 137.2 and 138.3 (s, 2C, phenyl).

2.2.2. Reaction between $\text{Hlr}(\text{O}_2\text{CPh})_2(\text{PMe}_3)_3$ (**10**) and Carbon tetrachloride

A 100 mL one-necked side-armed flask, equipped with a magnetic stirrer and a septum, was charged with 1.50 g (2.26 mmol) of $\text{Hlr}(\text{O}_2\text{CPh})_2(\text{PMe}_3)_3$ under N_2 in a dry box. The flask was then connected to a double manifold (vacuum/nitrogen) Schlenk line and 16.0 mL of carbon tetrachloride added by syringe. The reaction mixture was stirred magnetically at room temperature for 3 days. At completion, the carbon tetrachloride was stripped off under reduced pressure. The solids obtained were dissolved in CH_2Cl_2 (2.00 mL) and pentane was used to recrystallize yellow solids. The CH_2Cl_2 /pentane solution was filtered off and the solids were dried under reduced pressure to yield 0.727 g of a 1:2 mixture of $\text{Ir}(\text{O}_2\text{CPh})_2(\text{PMe}_3)_3\text{Cl}$ (**11a**) and $\text{Ir}(\text{O}_2\text{CPh})(\text{PMe}_3)_3\text{Cl}_2$ (**11b**). The mixture was redissolved in CH_2Cl_2 and diethyl ether used to recrystallize a pure sample of $\text{Ir}(\text{O}_2\text{CPh})(\text{PMe}_3)_3\text{Cl}_2$ (**11b**). The dichloro benzoate complex, (**11b**) was identified on the basis of the following data:

Anal. Calc. for $\text{C}_{16}\text{H}_{32}\text{IrCl}_2\text{O}_2\text{P}_3$: C, 31.38; H, 5.27. Found: C, 31.9; H, 5.66%.

^1H NMR (CDCl_3): δ 1.58 (t, $J_{\text{P-H}} = 3.9$ Hz, 18H, trans PMe_3), 1.63 (d, $J_{\text{P-H}} = 10.6$ Hz, cis PMe_3), 7.26–7.37 (m, 3H, phenyl ring), 8.01–8.05 (m, 2H, phenyl ring).

^{31}P NMR (CDCl_3): δ -52.69 (t, $J_{\text{P-P}} = 19$ Hz, 1P, cis PMe_3), -34.07 (d, $J_{\text{P-P}} = 19$ Hz, 2P, trans PMe_3).

^{13}C NMR (CDCl_3): δ 12.55 (t, $J_{\text{C-P}} = 21.6$ Hz, 6C, trans PMe_3), 15.51 (d, $J_{\text{C-P}} = 42.8$ Hz, 3C, cis PMe_3), 127.4 (s, 2C, phenyl), 129.7 (s, 2C, phenyl).

The chloro dibenzoate complex, (**11a**) was identified on the basis of the following data from the nmr of the mixture:

^1H NMR (CDCl_3): δ 1.57 (t, $J_{\text{P-H}} = 3.9$ Hz, 18H, trans PMe_3), 1.67 (d, $J_{\text{P-H}} = 10.6$ Hz, cis PMe_3), 7.30–7.60 (m, 3H, phenyl ring), 8.01–8.10 (m, 2H, phenyl ring). The phenyl resonances overlap to some degree with those of the dichloro benzoate complex (**11b**).

2.2.3. Reaction between $\text{Hlr}(\text{O}_2\text{CPh})(\text{PMe}_3)_3\text{Cl}$ (**2**) and phenylacetylene at room temperature

A screw-capped NMR tube was charged with 0.100 g (0.173 mmol) of $\text{Hlr}(\text{O}_2\text{CPh})(\text{PMe}_3)_3\text{Cl}$ (**2**) under N_2 in a dry box. The tube was brought out of the dry box and 19.0 μl (~ 0.173 mmol, 1.0 eq) of phenylacetylene was added by syringe followed by 0.500 mL of CD_2Cl_2 . The tube was shaken vigorously and the reaction was monitored at room temperature for 3 weeks by ^1H NMR spectroscopy. After 3 weeks at room temperature, the reaction mixture was poured into a 10.0 mL one-necked, side-armed flask and the CD_2Cl_2 was stripped off under reduced pressure to give a yellow oil. The oil was dissolved in ~ 0.200 mL of CH_2Cl_2 and diethyl ether was used to recrystallize a thick yellow oil. The CH_2Cl_2 /ether solution was filtered into a 10.0 mL one-necked, side-armed flask and stripped to give yellow solids which were dried under reduced pressure to give the “orthometallated-vinyl” complex **6** identified on the basis of the following data and X-ray crystallography:

^1H NMR (d_6 -acetone): δ 1.10 (t, $J_{\text{P-H}} = 3.7$ Hz, 18H, trans PMe_3), 1.66 (d, $J_{\text{P-H}} = 7.7$ Hz, cis PMe_3), 6.67–6.72 (m, 1H, phenyl ring), 6.76–6.82 (m, 1H, phenyl ring), 6.85–6.93 (m, 2H, vinyl protons), 7.02–7.08 (m, 1H, phenyl ring), 7.87–7.92 (m, 1H, phenyl ring).

2.2.4. Reaction between $\text{Hlr}(\text{O}_2\text{CPh})(\text{PMe}_3)_3\text{Cl}$ (**2**) and phenylacetylene at 40°C

A 10.0 mL one-necked side-armed flask, equipped with a magnetic stirrer and a septum, was charged with 0.200 g (0.346 mmol) of $\text{Hlr}(\text{O}_2\text{CPh})(\text{PMe}_3)_3\text{Cl}$ (**2**) and under N_2 in a dry box. The flask was then connected to a double manifold (vacuum/nitrogen) Schlenk line and 3.00 mL of mesitylene was added by syringe followed by 8.0 μl (~ 0.381 mmol, 1.1 eq) of phenylacetylene. The reaction mixture was stirred magnetically and heated at 40°C for 19 h. At completion, a yellow heterogeneous mixture was observed. The mesitylene solution was filtered off the white precipitate and was stripped under reduced pressure to give yellow solids. Diethyl ether was used to extract a yellow solution that was concentrated to give yellow solids. The white precipitate was recrystallized from CH_2Cl_2 /ether solution. Both solids were dried under reduced pressure. The white solids were identified as $\text{Hlr}(\text{O}_2\text{CPh})(\text{PMe}_3)_3\text{Cl}\cdot\text{HO}_2\text{Ph}$ (**11a-benzoic acid**) on the basis of the following data and X-ray crystallography:

^1H NMR (d_6 -acetone): δ -20.54 (dt, $J_{\text{P-H}} = 22$ Hz, 12 Hz, 1H, Ir-H), 1.53 (t, $J_{\text{P-H}} = 3.8$ Hz, 18H, trans PMe_3), 1.72 (d, $J_{\text{P-H}} = 10.3$ Hz, cis PMe_3), 7.29–7.38 (m, 2H, phenyl), 7.47–7.52 (m, 2H, phenyl), 7.58–7.63 (m, 2H, phenyl), 8.01–8.05 (m, 4H, phenyl ring). The yellow solids were the “orthometallated-vinyl” complex (**6**) obtained above.

2.2.5. Reaction between $\text{Hlr}(\text{O}_2\text{CPh})(\text{PMe}_3)_3\text{Cl}$ (**2**), phenylacetylene and benzoic acid at 120°C

A 100 mL screw-capped, heavy glass-walled pressure tube, equipped with a magnetic stirrer and a septum, was charged with 0.200 g (~ 0.346 mmol) of $\text{Hlr}(\text{O}_2\text{CPh})(\text{PMe}_3)_3\text{Cl}$ (**2**) and 0.044 g (0.363 mmol, 1.05 eq) of benzoic acid under N_2 in a dry box. The tube was then connected to a double manifold (vacuum/nitrogen) Schlenk line and 3.00 mL of benzene was added by syringe followed by 40.0 μl (0.363 mmol, 1.05 eq) of phenylacetylene. The reaction mixture was heated at 120°C for 20 h. At completion, a yellow solution was observed. The mesitylene solution was

Download English Version:

<https://daneshyari.com/en/article/1336503>

Download Persian Version:

<https://daneshyari.com/article/1336503>

[Daneshyari.com](https://daneshyari.com)