An unusual trimerization reaction of an alkyne on iridium

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(Received November 3, 1992; in revised form August 2, 1993)

Abstract

Reactions between *mer*-$(Me_3P)_3Ir(H)(H)(Cl)$ and 2-ethynylpyridine in water or *mer*-$(Me_3P)_3Ir(H)(Ph)(Cl)$ and 2-ethynylpyridine and $Tl[PF_6]$ in CH_2Cl_2 both lead to the formation of an unusual 3.3.0-azairidabicyclooctatriene, **3**. Complex **3** was characterized by single crystal X-ray diffraction and was found to crystallize in the triclinic space group $P\bar{1}$ with $a = 12.060(3)$ Å, $b = 12.512(3)$ Å, $c = 14.833(3)$ Å, $\alpha = 87.25(2)°$, $\beta = 73.21(2)°$, $\gamma = 69.93(2)°$ and $V = 2009.4(9)$ Å^3 for $Z = 2$. Complex **3** appears to form *via* a
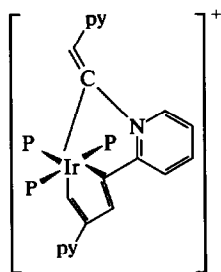
3, P = PMe; py = pyridyl

sequence of reactions involving (i) coupling of two equivalents of 2-ethynylpyridine at iridium (I) to yield a metallacylopentadiene complex; (ii) addition of a third equivalent of 2-ethynylpyridine; (iii) rearrangement of the third equivalent of 2-ethynylpyridine to a vinylidene; and (iv) nucleophilic attack of a pendant pyridine on the α carbon of the vinylidene.

Key words: Iridium; Alkyne; Metallacycle

1. Introduction

In 1990, while investigating the chemistry of iridium metallacycles, O'Connor and co-workers discovered the serendipitous preparation of metallabicyclooctatriene complexes with iridium at the bridgehead [1]. Lately, we have been investigating the chemistry of iridium hydride complexes formed by the oxidative addition of H–H, B–H, C–H, N–H and O–H [2–7] bonds. In developing the chemistry of two of these systems, we uncovered reactions leading to the formation of a similar metallabicyclic complex through the trimeriza-tion of 2-ethynylpyridine. This report discusses the synthesis and molecular structure of that unusual met-allacyclic complex.

2. Experimental details

2.1. General comments

Even though most of the iridium complexes used in this study are relatively air stable, all reactions were carried out under an atmosphere of purified nitrogen using standard Schlenk line techniques. *mer*-$(Me_3P)_3$-$Ir(H)(H)(Cl)$ [3] and *mer*-$(Me_3P)_3Ir(H)(Ph)(Cl)$ [5] were prepared as described previously. 2-Ethynylpyridine and 2-ethenylpyridine (2-vinylpyridine) were purchased from Aldrich Chemicals and used as received. Elemen-

tal analyses were obtained from Atlantic Microlab, Norcross, GA. ^{1}H and ^{13}C NMR spectra were obtained on either a Bruker WP-270 or WP-200 NMR spectrometer while ^{31}P NMR spectra were obtained on the Bruker WP-200 spectrometer.

2.2. Reaction between mer-(Me₃P)₃Ir(H)(H)(Cl) and 2-ethynylpyridine

A 25 ml one-necked side-armed flask equipped with a magnetic stir bar and a septum was charged with 0.200 g (0.437 mmol) of mer-(Me₃P)₃Ir(H)(H)(Cl) under nitrogen in a dry box. The flask was then connected to a double manifold (vacuum/nitrogen) Schlenk line and 14.0 ml of water was added by syringe. Next, 143 μl (1.35 mmol) of 2-ethynylpyridine were added by syringe. In the first few minutes of the reaction, the solution's color went from light yellow to orange to red to purple. The reaction mixture was stirred at room temperature. After 3 days, 0.080 g (0.437 mmol) of K[PF₆] was added to the dark purple solution and purple solids precipitated immediately. The purple solids were collected by filtration, washed with more water and dried under vacuum. The solids were redissolved in 0.5 ml of methylene chloride, and 5.00 ml of toluene was added to precipitate the product. The purple solids were filtered and dried in vacuo to give 0.260 g of 3 (0.297 mmol, 68.0% yield). Analysis calcd C₃₀H₄₂F₆IrN₃P₄: C 41.19, H 4.85. Found: C 41.82, H 4.94. ^{1}H NMR (CD₂Cl₂): δ 1.20 (vt, sep = 3.6 Hz, 18H, trans PMe₃), 1.83 (d, J(P–H) = 7.4 Hz, 9H, cis PMe₃), 6.5 (br s, 1H, vinyl), 8.8 (m, 1H, metallacycle), 9.4 (m, 1H, metallacycle), 6.85 (m, 1H, aromatic), 7.15 (m, 6H, aromatic), 7.67, 7.80, 8.18, 8.5 and 8.27 ppm (m, 5H, aromatic).

^{13}C NMR (CDCl₃): δ 18.3 ppm (d, J(P–C) = 114.28 Hz, cis PMe₃), 15.3 ppm (vt, sep = 78.74 Hz, trans PMe₃) A number of resonances were observed in the aromatic and vinyl region of the spectrum: 199, 155, 149, 147, 140, 139, 137, 136, 128, 127, 123, 121, 120, 119.6, and 119.0 ppm. No specific assignments were made. ^{31}P NMR (CD₂Cl₂) δ 43.1 ppm (d, J(P–C) = 60.9 Hz, cis PMe₃), 60.5 ppm (tJ(P–C) = 61.2 Hz, trans PMe₃).

2.3. NMR monitoring of reaction between mer-(Me₃P)₃Ir(H)(H)(Cl) and 2-ethynylpyridine

A screw-capped NMR tube equipped with a septum was charged with 0.040g (0.073 mmol) of mer-(Me₃P)₃Ir(H)(H)(Cl) under nitrogen in a dry box. 1.0 ml of D₂O and 32.0 μl (0.30 mmol) of 2-ethynylpyridine were added by syringe. The tube was shaken vigorously and the color of the solution changed quickly from light yellow to orange to red to violet. The reaction was monitored at room temperature over a 1 week

period. ^{1}H NMR spectroscopy indicated that both ethenylpyridine and complex 3 were formed: ^{1}H NMR(D₂O). In addition to the above listed resonances for 3, the following resonances attributable to 2-ethenylpyridine were found: δ 5.82 (dd, $J_{(H-H)cis}$ = 10.7 Hz, $J_{(H-H)gem}$ = 1.6 Hz, 1H), 6.85 (dd, $J_{(H-H)trans}$ = 17.4 Hz, $J_{(H-H)gem}$ = 1.6 Hz, 1H) for 2-ethenylpyridine with an ABX pattern. This was identical to the NMR spectrum obtained for an authentic sample of 2-ethenyl-pyridine.

2.4. Reaction between mer-(Me₃P)₃Ir(H)(Ph)(Cl) and 2-ethynylpyridine

A 25 ml flask equipped with a stir bar and septum was charged with mer-(Me₃P)₃Ir(H)(Ph)(Cl) (0.10 g, 0.187 mmol) under nitrogen in a dry box. The flask was connected to a double manifold Schlenk line. Dry methylene chloride (10 ml) and 2-ethynylpyridine (0.576 g, 5.59 mmol) were added by syringe. Thallium hexafluorophosphate (0.066 g, 0.187 mmol) was added as a solid against a counter-stream of nitrogen and the mixture was stirred for 24 h. The dark purple solution was then filtered to remove the thallium chloride. The product was forced out of solution using toluene (10 ml) and pentane (15 ml). This procedure was repeated twice to yield 0.133 g (0.152 mmol, 81.0% yield) of metallabicycle 3.

2.5. Other alkynes

A number of other alkynes which could potentially follow the same reaction path as 2-ethynylpyridine were investigated. None gave a stable, isolable product but there was some information to suggest that reactions might have been similar to the 2-ethynylpyridine. With mer-(Me₃P)₃Ir(H)(Ph)(Cl) and Tl[PF₆], 3-methyl-3-hydroxy-1-butyne yielded a green solution, 3-butyne-2-one yielded a deep-blue colored solution. However, both solutions decomposed to intractable tars. Reaction between mer-(Me₃P)₃Ir(H)(Ph)(Cl) and methyl propiolate and Tl[PF₆] yielded a yellow complex which had resonances in the 8–11 ppm region indicating that the bicyclic complex may have been formed. However, attempts to isolate this complex in a pure form were unsuccessful.

2.6. X-Ray diffraction study of 3

A single crystal of 3 suitable for X-ray diffraction was grown by diffusion of toluene into an acetone solution of 3. A crystal of approximate dimension 0.2 × 0.2 × 0.2 mm³ was chosen for this study and mounted on the end of a glass fiber with epoxy resin. Using random search techniques, 30 reflections were found, centered, and used to calculate unit cell parameters and an orientation matrix. These parameters and the

details of data collection and structure solution and refinement can be found in Table 1 [2]. The resulting molecular structure of **3** is depicted in Fig. 1, a listing of atomic coordinates and equivalent isotropic displacement coefficients is given in Table 2 and important bond lengths and angles can be found in Tables 3 and 4. Lists of structure factors and thermal parameters are available from the authors.

3. Results and discussion

We have found that [Ir(COD)(PMe$_3$)$_3$]Cl [8] acts as a source of highly reactive "Ir(PMe$_3$)$_3$Cl" upon moderate heating and will undergo oxidative addition reactions with a variety of "E–H" bonds (E = H, B, C, N, O) [3–7] (eqn. (1)). We have already published several reports on reactions of those resulting hydrido iridium

(1)
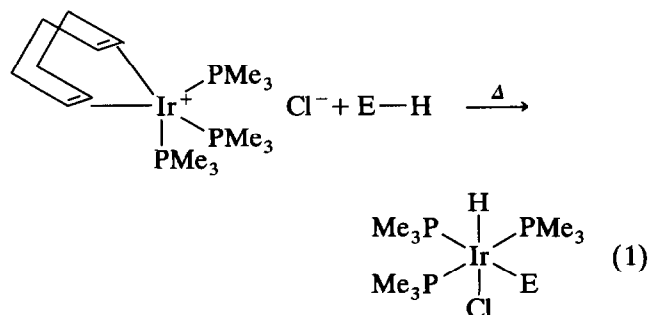
complexes with alkynes. For the most part, those reactions proceed *via* insertion of the alkyne into the Ir–H bond. For example, reaction between *mer*-(Me$_3$P)$_3$Ir(H)(Ph)(Cl), **1**, t-butylacetylene and Tl[PF$_6$] results in the formation of the unusual dienyl product

shown in eqn. (5). Reaction between *mer*-(Me$_3$P)$_3$Ir-(H)(H)(Cl) and ^{t}-butylacetylene in water leads to the production of the vinyl iridium hydride complex shown in eqn. (3) [4]. However, 2-ethynylpyridine reacts in

(2)
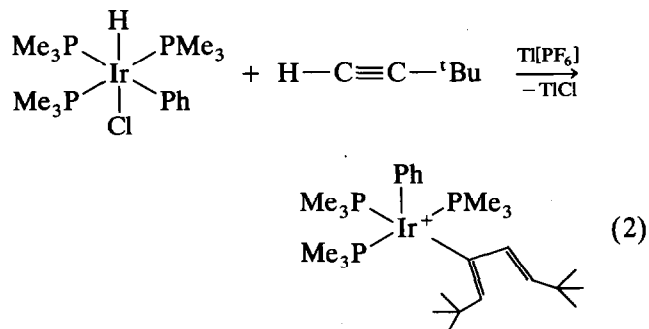
a very unusual manner for these two systems. Reaction between *mer*-(Me$_3$P)$_3$Ir(H)(Ph)(Cl), **1**, and excess 2-ethynylpyridine and Tl[PF$_6$] in methylenechloride

(3)
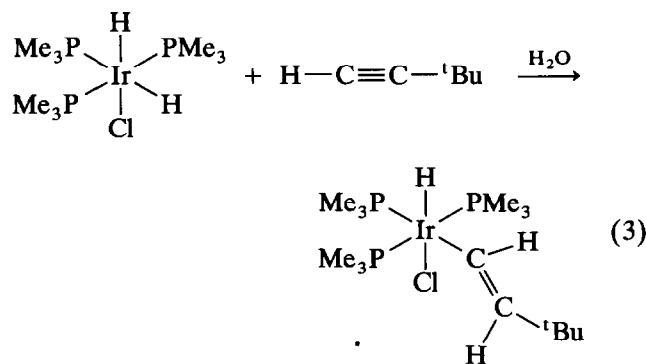
(eqn. (4)) or reaction between *mer*-(Me$_3$P)$_3$Ir(H)-

Fig. 1. Molecular structure of complex **3** showing atom labeling scheme. Methyl groups on phosphorus omitted for clarity.

Fig. 2. Schematic of bicyclic core of complex 3 indicating bond lengths around the ring system.
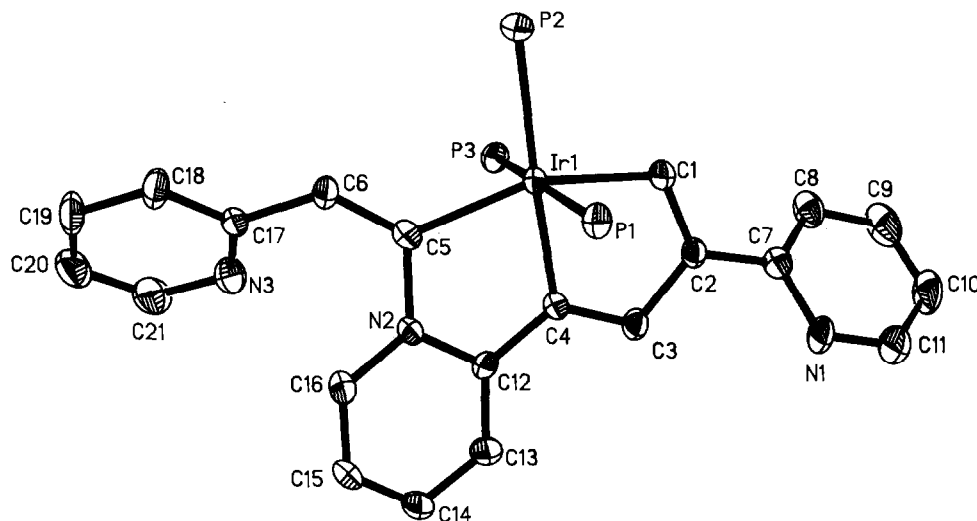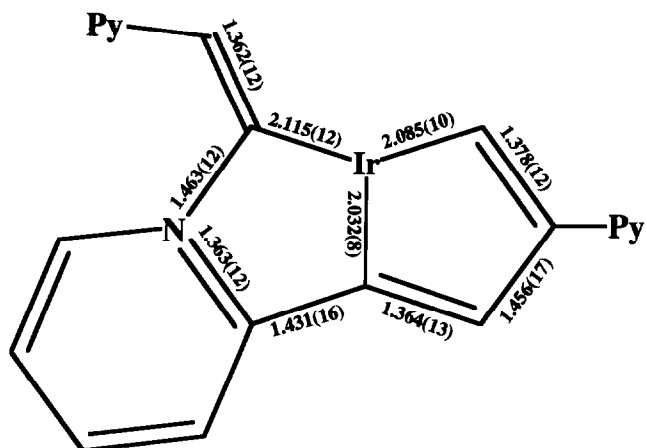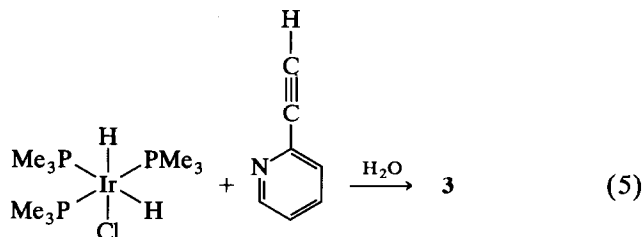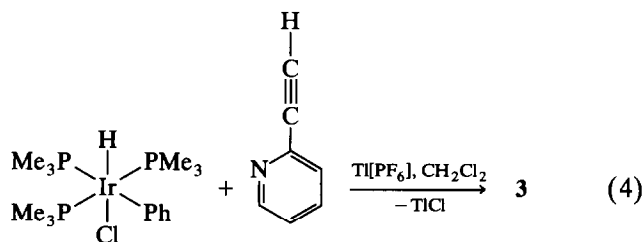
crystal structure determination show that complex 3 is an unusual bicyclic complex which could be described as an 3.3.0-azairidabicyclooctatriene with an exocyclic double bond and is formed by the "trimerization" of three equivalents of the 2-ethynylpyridine on the irid-

(H)(Cl), 2, in water (eqn. (5)) both yield the same intensely purple cation, 3.

$$(4)$$

$$(5)$$

From the reaction shown in eqn. (4), pure 3 was isolated as its PF_6 salt following filtration to remove TlCl and addition of diethyl ether. From the reaction shown in eqn. (5), the PF_6 salt of 3 could also be isolated by addition of $K[PF_6]$ to the resulting aqueous solution. The NMR spectral data (see Experimental section) for the complexes derived from both sets of reactions showed that they were indeed identical compounds, but the complicated nature of the resonances in the aromatic region precluded absolute identification. Therefore, a single crystal X-ray diffraction study was undertaken.

Single crystals of 3 suitable for X-ray diffraction were grown by slow diffusion of toluene into an acetone solution of 3. Although the crystals grown were relatively small, they diffracted well and a suitable data set could be obtained. The resulting molecular structure for 3 is shown in Fig. 1. The results of the single

TABLE 1. Structure determination summary and crystal data for 3

Empirical formula	$C_{33}H_{48}F_6IrN_3OP_4$
Color; habit	Purple irregular prism
Crystal size (mm³)	0.2×0.2×0.2
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 12.060(3)$ Å
	$b = 12.512(3)$ Å
	$c = 14.833(3)$ Å
	$\alpha = 87.25(2)°$
	$\beta = 73.21(2)°$
	$\gamma = 69.93(2)°$
Volume	2009.4(9) Å³
Z	2
Formula weight	932.8
Density (calc.)	1.542 mg m⁻³
Absorption coefficient	3.521 mm⁻¹
F(000)	932
Diffractometer used	Siemens R3m/V
Radiation	Mo K_α ($\lambda = 0.71073$ Å)
Temperature (K)	298
Monochromator	Highly oriented graphite crystal
2θ range	3.5 to 45.0°
Scan type	Wyckoff
Scan speed	Variable; 3.00 to 14.65° min⁻¹ in ω
Scan range (ω)	0.60°
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard reflections	2 measured every 300 reflections
Index ranges	$0 < h < 12$, $-12 < k < 13$, $-15 < l < 15$
Reflections collected	5554
Independent reflections	5251 ($R_{int} = 2.38\%$)
Observed reflections	4376 ($F > 3.0\sigma(F)$)
Absorption correction	Semi-empirical
Min/Max transmission	0.7940/1.0000
Software used	Siemens SHELXTL PLUS (VMS)
Solution	Direct methods
Refinement method	Full matrix least squares
Quantity minimized	$\Sigma w(F_o - F_c)^2$
Extinction correction	$\chi = -0.00016(5)$, where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$
Hydrogen atoms	Riding model, fixed isotropic U
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.008F^2$
Number of parameters refined	434
Final R indices (obs. data)	$R = 4.69\%$, $wR = 5.12\%$
Goodness-of-fit	1.16
Largest and mean Δ/σ	3.309, 0.024
Data-to-parameter ratio	10.1 : 1
Largest difference peak	1.11 e Å⁻³
Largest difference hole	−1.31 e Å⁻³

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å} \times 10^3$) for **3**

	x	y	z	U [a]
Ir(1)	2092(1)	1455(1)	2895(1)	38(1)
P(1)	2002(2)	1625(3)	4475(2)	53(1)
C(1A)	3362(12)	1439(17)	4773(10)	137(11)
C(1B)	1032(20)	2908(15)	5081(10)	198(15)
C(1C)	1381(16)	679(16)	5243(9)	145(13)
P(2)	3211(3)	−519(2)	2776(2)	59(1)
C(2A)	4168(16)	−1212(13)	1628(12)	141(11)
C(2B)	2350(13)	−1426(11)	3223(14)	142(11)
C(2C)	4474(13)	−1047(11)	3289(13)	125(9)
P(3)	1895(3)	1450(2)	1371(2)	53(1)
C(3A)	1149(13)	499(13)	1143(9)	100(8)
C(3B)	889(14)	2775(12)	1079(9)	119(9)
C(3C)	3239(10)	1184(12)	377(8)	82(6)
C(1)	312(8)	1392(8)	3360(7)	51(4)
C(2)	−615(8)	2442(8)	3551(7)	50(4)
C(3)	−193(8)	3413(9)	3372(7)	52(4)
C(4)	1054(9)	3138(8)	3035(6)	46(4)
C(5)	3503(9)	2164(8)	2398(7)	51(5)
C(6)	4692(8)	1660(9)	1863(7)	52(4)
C(7)	−1931(9)	2605(9)	3913(8)	54(5)
C(8)	−2474(10)	1970(11)	3570(9)	73(6)
C(9)	−3728(13)	2198(14)	3942(12)	102(9)
C(10)	−4405(12)	3029(14)	4629(12)	102(8)
C(11)	−3786(12)	3618(12)	4916(11)	95(7)
C(12)	1728(9)	3909(8)	2824(6)	48(4)
C(13)	1203(10)	5100(9)	2888(9)	72(6)
C(14)	1941(11)	5747(10)	2780(10)	90(7)
C(15)	3175(12)	5209(10)	2656(10)	89(7)
C(16)	3698(10)	4060(10)	2538(7)	63(5)
C(17)	5567(9)	2124(9)	1203(7)	52(5)
C(18)	6813(9)	1648(10)	1076(8)	69(5)
C(19)	7615(12)	2050(14)	410(10)	90(7)
C(20)	7132(16)	2923(14)	−107(11)	99(9)
C(21)	5887(15)	3359(12)	34(9)	94(8)
N(1)	−2607(8)	3455(8)	4576(7)	73(5)
N(2)	2980(7)	3403(6)	2569(6)	50(4)
N(3)	5095(9)	2990(9)	685(7)	76(5)
P(4)	1233(4)	1767(3)	−1953(2)	83(2)
F(1)	387(12)	2829(10)	−1303(8)	191(8)
F(2)	867(11)	1016(11)	−1141(7)	168(8)
F(3)	2100(11)	732(10)	−2626(8)	182(7)
F(4)	1559(12)	2525(11)	2774(7)	174(8)
F(5)	165(10)	1757(12)	−2331(8)	184(8)
F(6)	2293(9)	1750(11)	1574(7)	165(7)
C(1S)	7297(24)	5017(27)	2384(21)	403(38)
C(2S)	6660(18)	5495(16)	1792(19)	150(13)
C(3S)	7409(24)	5624(20)	837(20)	253(27)
O(1S)	5612(14)	5891(15)	2007(15)	223(13)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Bond lengths (Å) for complex **3**

Ir(1)–P(1)	2.332 (3)	C(5)–N(2)	1.463 (12)
Ir(1)–P(2)	2.360 (3)	C(6)–C(17)	1.477 (15)
Ir(1)–P(3)	2.341 (3)	C(7)–C(8)	1.381 (21)
Ir(1)–C(1)	2.085 (10)	C(7)–N(1)	1.343 (13)
Ir(1)–C(4)	2.032 (8)	C(8)–C(9)	1.382 (18)
Ir(1)–C(5)	2.115 (12)	C(9)–C(10)	1.351 (22)
P(1)–C(1A)	1.757 (17)	C(10)–C(11)	1.369 (27)
P(1)–C(1B)	1.731 (15)	C(11)–N(1)	1.309 (17)
P(1)–C(1C)	1.801 (20)	C(12)–C(13)	1.401 (13)
P(2)–C(2A)	1.818 (15)	C(12)–N(2)	1.363 (12)
P(2)–C(2B)	1.773 (17)	C(13)–C(14)	1.368 (20)
P(2)–C(2C)	1.806 (18)	C(14)–C(15)	1.366 (18)
P(3)–C(3A)	1.813 (19)	C(15)–C(16)	1.354 (16)
P(3)–C(3B)	1.806 (14)	C(16)–N(2)	1.375 (17)
P(3)–C(3C)	1.791 (10)	C(17)–C(18)	1.371 (14)
C(1)–C(2)	1.378 (12)	C(17)–N(3)	1.355 (14)
C(2)–C(3)	1.456 (17)	C(18)–C(19)	1.378 (19)
C(2)–C(7)	1.465 (14)	C(19)–C(20)	1.364 (22)
C(3)–C(4)	1.364 (13)	C(20)–C(21)	1.365 (25)
C(4)–C(12)	1.431 (16)	C(21)–N(3)	1.336 (19)
C(5)–C(6)	1.362 (12)		

TABLE 4. Bond angles (°) for complex **3**

P(1)–Ir(1)–P(2)	92.6(1)	C(3)–C(2)–C(7)	121.0(8)
P(1)–Ir(1)–P(3)	172.0(1)	C(2)–C(3)–C(4)	114.8(8)
P(2)–Ir(1)–P(3)	93.2(1)	Ir(1)–C(4)–C(3)	117.0(8)
P(1)–Ir(1)–C(1)	87.6(3)	Ir(1)–C(4)–C(12)	115.7(6)
P(2)–Ir(1)–C(1)	98.7(3)	C(3)–C(4)–C(12)	127.1(8)
P(3)–Ir(1)–C(1)	86.2(3)	Ir(1)–C(5)–C(6)	129.3(8)
P(1)–Ir(1)–C(4)	86.5(3)	Ir(1)–C(5)–N(2)	109.7(6)
P(2)–Ir(1)–C(4)	177.2(3)	C(6)–C(5)–N(2)	120.2(10)
P(3)–Ir(1)–C(4)	87.3(3)	C(5)–C(6)–C(17)	131.9(9)
C(1)–Ir(1)–C(4)	78.6(4)	C(2)–C(7)–C(8)	122.8(9)
P(1)–Ir(1)–C(5)	94.3(3)	C(2)–C(7)–N(1)	116.0(11)
P(2)–Ir(1)–C(5)	102.6(2)	C(8)–C(7)–N(1)	121.1(10)
P(3)–Ir(1)–C(5)	89.7(3)	C(7)–C(8)–C(9)	118.8(12)
C(1)–Ir(1)–C(5)	158.5(4)	C(8)–C(9)–C(10)	120.3(18)
C(4)–Ir(1)–C(5)	80.1(4)	C(9)–C(10)–C(11)	116.6(13)
Ir(1)–P(1)–C(1A)	119.4(5)	C(10)–C(11)–N(1)	125.8(13)
Ir(1)–P(1)–C(1B)	116.5(6)	C(4)–C(12)–C(13)	125.4(9)
C(1A)–P(1)–C(1B)	101.3(10)	C(4)–C(12)–N(2)	115.0(8)
Ir(1)–P(1)–C(1C)	115.7(6)	C(13)–C(12)–N(2)	119.6(10)
C(1A)–P(1)–C(1C)	101.9(9)	C(12)–C(13)–C(14)	119.8(10)
C(1B)–P(1)–C(1C)	98.9(8)	C(13)–C(14)–C(15)	118.7(11)
Ir(1)–P(2)–C(2A)	119.4(5)	C(14)–C(15)–C(16)	121.6(14)
Ir(1)–P(2)–C(2B)	116.7(4)	C(15)–C(16)–N(2)	120.1(11)
C(2A)–P(2)–C(2B)	102.3(8)	C(6)–C(17)–C(18)	121.1(9)
Ir(1)–P(2)–C(2C)	119.4(5)	C(6)–C(17)–N(3)	117.2(9)
C(2A)–P(2)–C(2C)	92.7(8)	C(18)–C(17)–N(3)	121.6(10)
C(2B)–P(2)–C(2C)	102.4(8)	C(17)–C(18)–C(19)	120.0(11)
Ir(1)–P(3)–C(3A)	115.4(4)	C(18)–C(19)–C(20)	118.1(13)
Ir(1)–P(3)–C(3B)	114.7(5)	C(19)–C(20)–C(21)	119.9(15)
C(3A)–P(3)–C(3B)	99.2(8)	C(20)–C(21)–N(3)	122.8(13)
Ir(1)–P(3)–C(30)	119.3(5)	C(7)–N(1)–C(11)	117.4(13)
C(3A)–P(3)–C(30)	104.4(6)	C(5)–N(2)–C(12)	118.3(9)
C(3B)–P(3)–C(30)	101.0(6)	C(5)–N(2)–C(16)	122.4(8)
Ir(1)–C(1)–C(2)	114.7(8)	C(12)–N(2)–C(16)	119.2(8)
C(1)–C(2)–C(3)	114.8(9)	C(17)–N(3)–C(21)	117.7(11)
C(1)–C(2)–C(7)	124.2(10)		

ium center. The coordination about the iridium can best be described as highly distorted octahedral. The Ir(1)–P(1) and Ir(1)–P(3) bond distances are equal within experimental error (2.332(3) Å and 2.341(3) Å) with the Ir(1)–P(2) bond distance being slightly longer (2.360(3) Å). The Ir(1)–C(1) and Ir(1)–C(5) distances are approximately equal (2.085(10) Å and 2.115(12) Å)

with the Ir(1)–C(4) distance being significantly shorter (2.032(8) Å). The bond angles involving P and Ir are fairly regular octahedral angles: P(1)–Ir(1)–P(2), 92.6(1)°; P(3)–Ir(1)–P(2), 93.2(1)°; and P(1)–Ir(1)–P(3), 172.0(1)°. The angles involving the metallacycle and the iridium, however, are very distorted with C(1)–Ir(1)–C(4) of 78.6(4)°, C(4)–Ir(1)–C(5) of 80.1(4)° and C(1)–Ir(1)–C(5) of 158.5(4)°. Figure 2 is a diagram of the metallacyclic portion of the structure showing the bond lengths around the metallacycle and, although the bond lengths show some alternation around the rings, taking into account the large esd's for the bond distances, the C–C distances show a high degree of delocalization around the ring system. Overall, complex 3 is very similar to the bicyclic system reported by O'Connor and co-workers [1] with the main differences being the presence of nitrogen in one of the rings in 3 and the presence of the exocyclic double bond.

With the structure of 3 in hand, we can now make some sense of the NMR spectra obtained for 3. In the ¹H NMR spectrum of 3, the PMe₃ methyl protons give rise to two sets of resonances: a virtual triplet at δ 1.2 ppm and a doublet at δ 1.83 ppm, indicative of the meridional arrangement of the phosphines. Two down-field resonances at δ 8.8 and 9.4 ppm can be attributed

to protons on C(1) and C(3) of the metallacycle and are multiplets due to P–H coupling. The pyridyl ring protons give rise to a complicated series of multiplets from δ 6.8 to 8.5 ppm and the proton on C(6) resonates at δ 6.5 ppm. Complete assignments in the ¹³C NMR spectrum were not made, but the spectrum is consistent with the structure found by X-ray crystallography. The ³¹P NMR spectrum consists of a doublet at δ 43.1 ppm and a triplet at δ 60.5 ppm, again consistent with a meridional arrangement of phosphine ligands.

The mechanism of formation of 3 in the two reactions discussed above is an intriguing matter for speculation and we have some information which sheds light on the reaction paths. In the case of the reaction involving mer-(Me₃P)₃Ir(H)(H)(Cl), monitoring of the reaction mixture in D₂O via ¹H NMR showed that, while 3 was being produced, an equivalent of 2-ethenylpyridine was also being formed. This suggested that the reaction between 2 and 2-ethynylpyridine initially followed the same course followed by other acetylenes (eqn. (2)). However, following initial insertion, 2-ethenylpyridine is then released via reductive elimination. This leaves in solution some form of "Ir(PMe₃)₃⁺" as the iridium species. There are a number of reactions that this species can undergo, but to
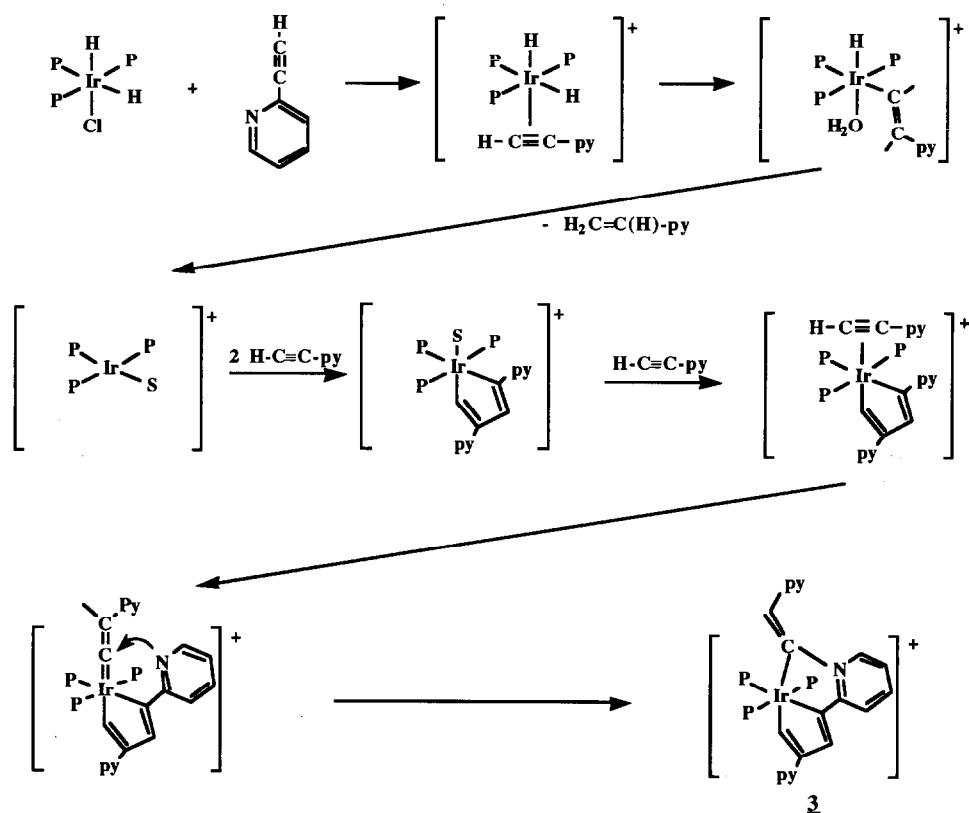

Fig. 3. Proposed scheme for the formation of complex 3. P = PMe₃; S = solvent.

lead to the final product it is not unreasonable to speculate that an oxidative coupling of two alkynes will occur to form an iridacyclopentadiene complex. Oxidative coupling of alkynes to form metallacyclopentadienes is well documented for Co [9], Rh [10], and Ir [11,12*]. Finally, an additional equivalent of 2-ethynylpyridine enters the iridium coordination sphere and rearranges to a vinylidene ligand. A pendant pyridine on the metallacyclopentadiene can then attack the α carbon of the vinylidene ligand to form the final product. This last step in the formation of the bicyclic system is similar to that found by O'Connor for the production of his bicyclic iridium species [1]. These transformations are summarized in Fig. 3.

The reaction between mer-$(Me_3P)_3Ir(H)(Ph)(Cl)$, 1, and 2-ethynylpyridine probably follows a similar path past the formation of the iridium(I) species, "Ir$(PMe_3)_3^+$", but differs in the prior steps. Following chloride removal by $Tl[PF_6]$, we speculate that the pyridine group binds to the iridium via the nitrogen lone pair. This species is unstable with respect to reductive elimination of benzene to form an iridium(I) species, "$[Ir(PMe_3)_3]^+$". From this point on, the reaction between 1 and 2-ethynylpyridine is the same as shown in Fig. 3. Supporting evidence for this initial step in the reaction with 1 is found in two observations. First, monitoring the reaction between 1 and 2-ethynylpyridine in CD_2Cl_2 showed, in addition to the resonances expected for 3, a resonance attributable to free benzene. Second, reaction between 1, pyridine, and $Tl[PF_6]$ produces the cationic phenyl(hydrido)-(pyridine)iridium complex shown in eqn. (4), but this complex is unstable with respect to reductive elimination of benzene [13]. So, in this case, coordination of the pyridyl group in ethynylpyridine may occur first inducing reductive elimination of benzene.

What is particularly intriguing in this work is that this metallacyclic system forms readily in aqueous solution. Milstein [14] and we [7] have shown that iridium(I) with PMe_3 ligands will react with water to form a hydroxy iridium hydride complex. Yet, in the chemistry leading to the formation of complex 3, water does not interfere with the reaction. We are continuing to investigate the aqueous chemistry of these iridium complexes to help understand this point.

Finally, we can speculate that other alkynes with groups capable of acting as nucleophiles should also form bicyclic iridium complexes via similar pathways. To date, the only bicyclic system that we have been able to isolate and characterize is complex 3. Some

other alkynes have produced materials whose NMR spectroscopy would indicate similarities with complex 3, but none have been isolated in pure form. Our studies on other alkynes which may undergo similar metallacycle formation are ongoing.

4. Conclusion

In this paper, we report on a very unusual trimerization of 2-ethynylpyridine to spontaneously form a bicyclic system on iridium. The sequence of alkyne coupling, alkyne to vinylidene rearrangement, and nucleophilic attack on the α carbon of the vinylidene is a unique one. To date, the only system for which this sequence has been confirmed is the one involving 2-ethynylpyridine but there is evidence that other systems may follow the same reaction path. The fact that this reaction path is followed even in aqueous solution is especially intriguing and points to other possibilities for organometallic chemistry in water for this system. We will continue to investigate the chemistry of the whole series of E–Ir–H complexes with alkenes and alkynes.

5. Supplementary material available

Complete data concerning the crystal structure of 3 are available from the corresponding author.

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