# Alkyne-to-Vinylidene Tautomerism Mediated by Two Adjacent Metal Centers. Structures of [Ir₂I₂(CO)₂(μ-CC(H)R)(Ph₂PCH₂PPh₂)₂] (R = H, Ph)

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The compound [Ir₂I₂(CO)(μ-CO)(dppm)₂] (1) (dppm = Ph₂PCH₂PPh₂) reacts with acetylene and phenylacetylene to give the vinylidene-bridged complexes [Ir₂I₂(CO)₂(μ-CC(H)R)(dppm)₂] (R = H (5), Ph (7)). With acetylene the first species observed is proposed to be the alkyne-bridged [Ir₂I₂(CO)₂(μ-HC₂H)(dppm)₂] (3), in which the alkyne is bound parallel to the Ir–Ir vector. This compound transforms to [Ir₂I(CO)₂(μ-HC₂H)(dppm)₂][I] (4), in which it is proposed, on the basis of $^{1}$H, $^{1}$H{$^{31}$P}, $^{13}$C and $^{13}$C{$^{31}$P} NMR experiments, that the alkyne is unsymmetrically bound, allowing it to π bond with one metal while still remaining σ bound to both. Compound 4 transforms to the vinylidene-bridged product 5 within ca. 20 h at ambient temperature. When the reaction of 1 with phenylacetylene is carried out at −40 °C, the only species detected is the acetylide-bridged hydrido complex [Ir₂(H)(I)(CO)₂(μ-C₂Ph)(dppm)₂][I] (6). However, at temperatures above 0 °C, only compound 7 is observed. A mechanism is proposed for the acetylene-to-vinylidene transformation. Compound 5 reacts with additional acetylene to give the products [Ir₂I(CO)₂(μ-CCH₂)(μ-HC₂H)(dppm)₂][I] (8) and [Ir₂(CO)₂(μ-CCH₂)(μ-HC₂H)-(dppm)₂][I]₂ (9a), in which the metals are bridged by a vinylidene unit and an alkyne group. These cationic complexes are also obtained in the reaction of [Ir₂(CO)₂(μ-I)(dppm)₂]⁺ (2) with acetylene. The structures of 5 and 7 have been determined by X-ray crystallography. Compound 5 crystallizes with 0.75 equiv of CH₂Cl₂ in the orthorhombic space group *Pbca* with $a$ = 16.474 (3) Å, $b$ = 18.289 (3) Å, $c$ = 37.642 (9) Å, $V$ = 11 341 (6) Å³, and $Z$ = 8, and is refined to $R$ = 0.064 and $R_w$ = 0.087 based on 319 parameters varied and 3759 observations. Compound 7 crystallizes in the orthorhombic space group $P2_12_12_1$ with $a$ = 13.093 (3) Å, $b$ = 18.177 (3) Å, $c$ = 22.784 (4) Å, $V$ = 5423 (1) Å, and $Z$ = 4, and is refined to $R$ = 0.046 and $R_w$ = 0.050 based on 331 parameters varied and 2985 unique observations. In both compounds the vinylidene moieties bridge the two Ir centers which are separated by 2.828 (1) Å (5) and 2.783 (1) Å (7). Both vinylidene C–C separations (1.25 (3) Å (5), 1.35 (3) Å (7)) are typical of double bonds. The phenyl substituent on the vinylidene unit of 7 causes significant skewing of the structure owing to repulsions involving the dppm phenyl groups.

## Introduction

Transition-metal vinylidene complexes are key species in the chemistry of two-carbon ligands[1] and continue to attract considerable interest.[1,2] It has been suggested that vinylidene species play an important role in Fischer–Tropsch chemistry,[3] in alkyne polymerization,[4] and in C–C bond formation in the condensation of alkynes with other substrates.[5] Vinylidene complexes have also proven useful in the synthesis of novel organic compounds.[6]

Although the majority of vinylidene complexes involve only a single metal center,[1] binuclear vinylidene-bridged complexes are attracting recent interest. One route to such species, involving the tautomerism of 1-alkynes, is demonstrated in the treatment of a dirhodium complex with phenylacetylene[7] and in related reactions involving dihaloacetylenes.[8] This tautomerism, mediated by a single metal center, can proceed via a concerted 1,2-hydrogen shift of an $\eta^2$-alkyne group[1,9] or via an oxidative addition yielding an acetylide–hydride intermediate.[1,2h] The acetylene-to-vinylidene tautomerism involving binuclear species has been much less studied and is not well understood. On the model alkyne-bridged compound [Pt₂H₄(μ-C₂H₂)]⁴⁻, calculations by Silvestre and Hoffmann showed that direct isomerization of the bridging alkyne to a bridging vinylidene moiety was energetically unlikely, although this

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## Table I. Spectroscopic Data[a]

| compd | IR, cm⁻¹ [b] | δ($^{31}$P{$^1$H})[d] | δ($^{13}$C{$^1$H})[e] | δ($^1$H)[e] |
|---|---|---|---|---|
| [Ir$_2$I$_2$(CO)$_2$(μ-HC$_2$H)(dppm)$_2$] (3) | 1998 (vs) | −32.1 (s) | 180.5 (m, CO)<br>113.9 (dt, $^2J_{CC}$ = 14 Hz, $^2J_{CP}$ = 6 Hz, HCCH) | 8.48 (br, 2H)<br>5.52 (m, 2H)<br>4.01 (m, 2H) |
| [Ir$_2$I(CO)$_2$(μ-HC$_2$H)(dppm)$_2$][I] (4) | 2000 (st)<br>1968 (vs) | −28.2 (m)<br>−36.3 (m) | 181.8 (dt, $^2J_{CC}$ = 25 Hz, $^2J_{CP}$ = 9 Hz, C⁴)<br>159.2 (t, $^2J_{CP}$ = 10 Hz, C³)<br>106.6 (m, C¹, $^2J_{CP^1}$ = 3.3 Hz,<br> $J_{CP^2}$ = 2.5 Hz, $^1J_{CC}$ = 59 Hz)<br>105.6 (m, C², $^3J_{CP^1}$ = 2.5 Hz, $^2J_{CP^2}$ = 6.5 Hz) | 8.52 (m, 1 H, H²)<br>8.06 (m, 1H, H¹,<br> $^3J_{H^1H^2}$ = 3.3 Hz)<br>5.79 (m, 2H)<br>4.91 (m, 2H) |
| [Ir$_2$I$_2$(CO)$_2$(μ-CCH$_2$)(dppm)$_2$] (5) | 1985 (med)<br>1960 (vs) | −20.2 (m)<br>−38.0 (m) | 194.3 (dm, Cα)<br>129.8 (d, $^1J_{C_\alpha C_\beta}$ = 67 Hz, C$_β$)<br>181.9 (t, $^2J_{CP}$ = 13 Hz)<br>169.5 (t, $^2J_{CP}$ = 12 Hz, CO) | 5.34 (m, 2H)<br>4.62 (m, 2H) |
| [Ir$_2$(H)I(CO)$_2$(μ-CCPh)(dppm)$_2$][I] (6) | 2028 (w)<br>1996 (w) | −9.0 (m)<br>−25.3 (m) | | 4.55 (m, 2H)<br>3.46 (m, 2H)<br>−11.55 (t, 1H,<br> $^2J_{PH}$ = 12.4 Hz) |
| [Ir$_2$I$_2$(CO)$_2$(μ-CC(H)Ph)(dppm)$_2$] (7) | 1998 (med)<br>1984 (vs) | −23.3 (m)<br>−24.1 (m)<br>−32.5 (m)<br>−33.0 (m) | 192.6 (q, $^2J_{CP}$ = 5 Hz, Cα)<br>184.8 (CO)<br>166.6 (CO)<br>135.6 (s, C$_β$) | 8.48 (br, 1H)<br>5.50 (m, 1H)<br>5.02 (m, 1H)<br>3.60 (m, 1H)<br>3.34 (m, 1H) |
| [Ir$_2$I(CO)$_2$(μ-HC$_2$H)(μ-CCH$_2$)(dppm)$_2$][I] (8) | 2018 (st)<br>2009 (med) | −18.3 (m)<br>−29.2 (m) | 174.1 (t, $^2J_{CP}$ = 7 Hz, CO)<br>172.9 (t, CO)<br>154.7 (dm, C$_α$), 139.5 (d, C$_β$, $^1J_{C_\alpha C_\beta}$ = 57 Hz),<br>141.2 (dm), 133.0 (dq, HC$_2$H, $^1J_{CC}$ = 57 Hz) | 9.18 (dt, 1 H,<br> $^1J_{HH}$ = 6 Hz,<br> $^3J_{PH}$ = 3 Hz)<br>8.84 (br, s, 1H)<br>8.02 (dm, 1H)<br>7.96 (br s, 1H)<br>4.46 (m, 2H)<br>3.00 (m, 2H) |
| [Ir$_2$(CO)$_2$(μ-HC$_2$H)(μ-CCH$_2$)(dppm)$_2$][I]$_2$ (9a) | 2027 (med) | −33.5 (s) | 172.8 (s, CO)<br>152.0 (dq, $^1J_{CC}$ = 57 Hz, $^2J_{CP}$ = 8 Hz, C$_α$)<br>147.3 (s)<br>129.1 (d, $^1J_{CC}$ = 57 Hz, C$_β$) | 9.34 (br s, 2H)<br>5.16 (m, 2H)<br>2.62 (m, 2H) |
| [Ir$_2$(CO)$_2$(μ-HC$_2$H)(μ-CCH$_2$)(dppm)$_2$][BF$_4$]$_2$ (9b) | 2028 (st) | −33.4 (s) | | 9.32 (br, s, 2H)<br>5.18 (m, 2H)<br>2.62 (m, 2H) |

[a] Abbreviations used: w = weak, med = medium, st = strong, vs = very strong, s = singlet, d = doublet, t = triplet, q = quintet, m = multiplet, dt = doublet of triplets, dq = doublet of quintets, dm = doublets of multiplets, br = broad. [b] Nujol mull $\nu$(CO). [c] In CD$_2$Cl$_2$ solvent except compound 9b (THF-$d_8$). [d] Vs 85% H$_3$PO$_4$ at 25 °C except compounds 6 and 7 (−80 °C). [e] Vs TMS at 25 °C except compounds 6 and 7 (−80 °C). [f] $\nu$(CO).

transformation via a hydrido–acetylide intermediate appeared to be feasible.[9]

In previous studies involving the binuclear iodo complex [Ir$_2$I$_2$(CO)(μ-CO)(dppm)$_2$] (1), we discovered unusual reactivity toward ethylene[10] and dioxygen.[11] An extension of this chemistry to terminal alkynes has again shown atypical chemistry; rather than the conventional μ,η²-alkynes usually obtained, as in the reactions of 1 with internal alkynes[10] or in reactions of the dichloro analogue [Ir$_2$Cl$_2$(CO)$_2$(dppm)$_2$], with internal or terminal alkynes,[12] complex 1 yielded vinylidene-bridged products with both acetylene and phenylacetylene. Herein we report the details of these reactions, in which we have attempted to spectroscopically monitor intermediates in these transformations in hopes of establishing the functions of the adjacent metals in the acetylene-to-vinylidene tautomerization.

## Experimental Section

All solvents were dried and distilled before use and were stored under argon. Reactions were conducted at room temperature by

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using standard Schlenk procedures unless otherwise noted. Dinitrogen was passed through columns of Ridox and 4-Å molecular sieves to remove traces of oxygen and water, respectively. Hydrated iridium trichloride was purchased from Johnson-Matthey, bis(diphenylphosphino)methane was obtained from Strem Chemicals, acetylene and phenylacetylene were purchased from Matheson and Aldrich, respectively, and acetylene (98.9% $^{13}$C enriched) was obtained from MSD Isotopes. These and all other reagents were used as received. The compounds [Ir$_2$I$_2$-(CO)(μ-CO)(dppm)$_2$] (1) and [Ir$_2$(CO)$_2$(μ-I)(dppm)$_2$][BF$_4$] (2) were prepared as previously reported.[10]

The NMR spectra were recorded on a Bruker AM-400 spectrometer operating at 161.9 MHz for $^{31}$P{$^1$H} and 100.6 MHz for $^{13}$C{$^1$H}. The $^{13}$C{$^1$H,$^{31}$P} NMR spectra were performed on a Bruker WH-200 spectrometer operating at 50.32 MHz. Infrared spectra were run on either a Nicolet 7199 Fourier transform interferometer or a Perkin-Elmer 883 spectrophotometer, as either solids (Nujol mulls on KBr disks) or solutions (KCl cell with 0.5 mm window path lengths). Spectroscopic parameters for the compounds are found in Table I. Elemental analyses were conducted by the microanalytical service within the department. Conductivity measurements were made on 10⁻³ M solutions by using a Yellow Springs Instrument Co. Model 31 conductivity bridge.

**Preparation of Compounds. (a) [Ir$_2$I$_2$(CO)$_2$(μ-CCH$_2$)-(dppm)$_2$] (5).** To a CH$_2$Cl$_2$ solution of [Ir$_2$I$_2$(CO)(μ-CO)(dppm)$_2$] (1) (200.0 mg, 0.14 mmol, in 15 mL) was added 3.6 mL of acetylene (0.14 mmol), by a gastight syringe, resulting in an immediate color change from dark to light orange. After the mixture was

stirred for ca. 20 h, the solvent was removed in vacuo. The yellow residue was recrystallized from CH₂Cl₂/Et₂O to give 5 as dark orange crystals in 50% yield. Anal. Calcd for Ir₂I₂O₂P₄C₅₄H₄₆: C, 43.55; H, 3.12. Found: C, 43.52; H, 3.22.

(b) [Ir₂I₂(CO)₂(μ-HC₂H)(dppm)₂] (3) and [Ir₂I(CO)₂(μ-HC₂H)(dppm)₂][I] (4). These compounds were characterized spectroscopically. Their formation was monitored by using NMR and IR spectroscopy. Compound 3 appeared immediately after addition of either excess or 1 equiv of HC≡CH to 1 and was stable at –40 °C. At room temperature, it transformed to 4 in ca. 20 min. Compound 5 was the only product after the solution was stirred for ca. 20 h at 20 °C.

(c) [Ir₂I₂(CO)₂(μ-CC(H)Ph)(dppm)₂] (7). To a CH₂Cl₂ solution of 1 (200.0 mg, 0.14 mmol, in 15 mL) was added 15.0 μL of phenylacetylene (0.14 mmol), causing a color change to light orange almost immediately. After the mixture was stirred for ca. 2 h, the solvent was removed. Redissolution of the residue in 2 mL of CH₂Cl₂ followed by addition of 15 mL of Et₂O precipitated a yellow-orange solid, which was washed with Et₂O and dried to give 7 in ca. 80% yield. The same compound was also obtained when excess phenylacetylene was used. Anal. Calcd for Ir₂I₂O₂P₄C₆₀H₅₀: C, 46.03; H, 3.32. Found: C, 46.01; H, 3.22.

(d) [Ir₂I(H)(CO)₂(μ-CCPh)(dppm)₂][I] (6). Compound 6 was characterized spectroscopically at temperatures below –40 °C. In a typical experiment, 1 equiv or more of phenylacetylene was syringed into an NMR tube containing 30.0 mg of compound 1 (0.020 mmol, in 0.50 mL of CD₂Cl₂) at –78 °C. NMR spectra, recorded at temperatures below –40 °C, showed only one product, identified as 6. At temperatures from 0 to 25 °C, 7 was the only product. To obtain an IR spectrum of 6, the reaction was conducted at –78 °C, and after the mixture was stirred for 0.5 h, Et₂O was added at the same temperature to the solution. The precipitated solid contained both 6 and 7.

(e) [Ir₂I(CO)₂(μ-HC₂H)(μ-CCH₂)(dppm)₂][I] (8) and [Ir₂(CO)₂(μ-HC₂H)(μ-CCH₂)(dppm)₂][I]₂ (9a). Acetylene was passed through a CH₂Cl₂ solution of 3 (60.0 mg, 0.040 mmol, in 10 mL), at a rate of 0.3 mL s⁻¹, causing an immediate color change to yellow. The solution was stirred for 0.5 h followed by concentration to ca. 2 mL and addition of Et₂O. The precipitated yellow solid contained two products, identified as complexes 8 and 9a in a typical ratio of ca. 1.8:1 (by NMR).

**X-ray Data Collection.** Suitable crystals of [Ir₂I₂(CO)₂(μ-CC(H)R)(dppm)₂] (R = H (5), Ph (7)) were grown from CH₂Cl₂/ether at 22 °C. Data for both compounds were collected on an Enraf-Nonius CAD4 diffractometer with use of Mo Kα radiation. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections in the range 21.3° ≤ 2θ ≤ 23.6° (5) and 20.0° ≤ 2θ ≤ 23.9° (7). The diffraction symmetry and the systematic absences 0kl, k = odd; h0l, l = odd; hk0, h = odd for 5 and h00, h = odd; 0k0, k = odd; 00l, l = odd for 7 are consistent with the space groups Pbca and P2₁2₁2₁, respectively. Data were collected to a maximum 2θ = 50°, and background counts were obtained by extending the scan 25% on each side of the peaks. Three reflections were chosen as intensity standards and were remeasured at 120-min intervals of X-ray exposure. There was no significant variation in the intensities of either set of standards, so no correction was applied. The data were processed in the usual way with a value of 0.04 used for $p$ to downweigh intense reflections,[13] and absorption corrections were applied by the method of Walker and Stuart.[14] See Table II for a summary of crystal data and X-ray collection information.

**Structure Solution and Refinement.** Both structures were solved by direct methods, using MULTAN[15] to locate the Ir, I, and P atoms. All other atoms were located after subsequent least-squares cycles and difference Fourier syntheses. Atomic scattering factors[16,17] and anomalous dispersion terms[18] were taken

**Table II. Crystallographic Data for [Ir₂I₂(CO)₂(μ-CCH₂)(dppm)₂]·0.75CH₂Cl₂ (5) and [Ir₂I₂(CO)₂(μ-CC(H)Ph)(dppm)₂] (7)**

| compd | 5 | 7 |
|---|---|---|
| formula | C₅₄H₄₆I₂Ir₂O₂P₄· 0.75CH₂Cl₂ | C₆₀H₅₀I₂Ir₂O₂P₄ |
| fw | 1553.31 | 1565.24 |
| space group | Pbca | P2₁2₁2₁ |
| temp, °C | 22 | 22 |
| radiation (λ, Å) | graphite-monochromated Mo Kα (0.710 69) | |
| cell params | | |
| $a$, Å | 16.474 (3) | 13.093 (3) |
| $b$, Å | 18.289 (3) | 18.177 (3) |
| $c$, Å | 37.642 (9) | 22.784 (4) |
| $\rho$(calcd), g cm⁻³ | 1.819 | 1.902 |
| $V$, Å³ | 11341 (6) | 5423 (1) |
| $Z$ | 8 | 4 |
| no. of unique data collcd | 10 808 | 4457 |
| no. of unique data used ($F_o^2 \geq 3\sigma(F_o^2)$) | 3759 | 2985 |
| linear abs coeff $\mu$, cm⁻¹ | 60.112 | 61.689 |
| range of transm factors | 0.8597–1.1952 | 0.8753–1.5266 |
| final no. of params refined | 319 | 331 |
| $R^a$ | 0.064 | 0.046 |
| $R_w^b$ | 0.087 | 0.050 |

$^a R = \sum||F_o| - |F_c||/\sum|F_o|.$ $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, where $w = 4F_o^2/\sigma^2(F_o^2)$.

from the usual sources. All hydrogen atoms of the complexes were included as fixed contributions; their idealized positions were generated from the geometries of the attached carbon atoms and their thermal parameters set at 20% greater than the isotropic thermal parameter of these carbons. In compound 5 a CH₂Cl₂ molecule was located and refined to 75% occupancy. Several other regions of electron density, remote from the complex, were located in the cell but could not unambiguously be assigned as solvent. This unassigned electron density and the poorer quality of the crystals of 5 prevented a better refinement. On the final Fourier map the maximum electron density (3.60 e/Å³) was associated with the assumed disordered solvent in 5; for compound 7 the maximum residual density was 1.06 e/Å³. Refinement of the other enantiomer of 7 resulted in significantly poorer values for $R$ and $R_w$, so the original choice was assumed correct.

For compound 5 the positional and thermal parameters of the non-hydrogen atoms, except for the dppm phenyl groups, are given in Table III; the equivalent parameters for compound 7 are given in Table IV.

## Description of Structures

To a first approximation the structures of both complexes [Ir₂I₂(CO)₂(μ-CC(H)R)(dppm)₂] (R = H (5), Ph (7)) are quite similar. These are shown in Figures 1 and 2, and relevant parameters are given in Tables V–VIII for the two compounds. Compound 5 crystallizes with CH₂Cl₂ in the lattice; however, there are no unusual contacts involving the solvent molecule, and its parameters are normal. Both compounds have an "A-frame" geometry in which the dppm groups bridge the metals in a trans arrangement, with the vinylidene units also bridging the metals in the equatorial plane perpendicular to the metal-phosphine bonds. The parameters within both species are remarkably similar, and both resemble the related dichloro tricarbonyl compound [Ir₂Cl₂(CO)₂(μ-CO)-(dppm)₂],[19] in which a carbonyl bridges the metals instead of a vinylidene unit. In both vinylidene-bridged compounds the metals have distorted-octahedral geometries in which the two Ir(II) centers are joined by an Ir–Ir single

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**Table III. Parameters for Selected Atoms[a] in Compound 5**

| atom | x | y | z | B (Å²) |
|---|---|---|---|---|
| Ir(1) | 0.42094 (7) | 0.07445 (7) | 0.35945 (3) | 2.84 (3)* |
| Ir(2) | 0.53413 (8) | 0.17778 (7) | 0.38531 (3) | 3.15 (3)* |
| I(1) | 0.4513 (1) | 0.0913 (1) | 0.28720 (6) | 5.08 (7)* |
| I(2) | 0.6062 (2) | 0.2444 (1) | 0.44436 (7) | 5.86 (8)* |
| P(1) | 0.5176 (4) | –0.0185 (4) | 0.3607 (2) | 3.0 (2)* |
| P(2) | 0.6405 (5) | 0.0929 (4) | 0.3827 (2) | 3.4 (2)* |
| P(3) | 0.3200 (5) | 0.1635 (5) | 0.3542 (2) | 3.4 (2)* |
| P(4) | 0.4395 (5) | 0.2740 (5) | 0.3843 (2) | 3.6 (2)* |
| O(1) | 0.292 (1) | –0.040 (1) | 0.3606 (5) | 3.6 (4) |
| O(2) | 0.606 (2) | 0.245 (2) | 0.3175 (8) | 9.4 (8) |
| C(1) | 0.340 (2) | 0.001 (2) | 0.3633 (9) | 6 (1) |
| C(2) | 0.585 (2) | 0.222 (2) | 0.3460 (9) | 5.8 (9) |
| C(3) | 0.456 (2) | 0.103 (1) | 0.4110 (7) | 2.8 (6) |
| C(4) | 0.427 (2) | 0.090 (2) | 0.4412 (8) | 5.1 (8) |
| C(5) | 0.617 (2) | 0.018 (1) | 0.3523 (7) | 2.3 (6) |
| C(6) | 0.363 (2) | 0.252 (2) | 0.3497 (8) | 4.8 (8) |

[a] Numbers in parentheses are estimated standard deviations in the least significant digits in this and all subsequent tables. Starred values denote atoms refined anisotropically. Thermal parameters for the anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameters, defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

**Table IV. Parameters for Selected Atoms[a] in Compound 7**

| atom | x | y | z | B (Å²) |
|---|---|---|---|---|
| Ir(1) | –0.16740 (7) | 0.05064 (6) | 0.04302 (4) | 1.98 (2)* |
| Ir(2) | –0.09097 (7) | –0.01468 (5) | –0.05833 (4) | 1.95 (2)* |
| I(1) | –0.3582 (1) | 0.1097 (1) | 0.01189 (8) | 3.53 (4)* |
| I(2) | 0.0341 (1) | –0.1160 (1) | –0.11805 (8) | 4.24 (4)* |
| P(1) | –0.0931 (5) | 0.1603 (3) | 0.0132 (3) | 2.1 (1)* |
| P(2) | 0.0383 (5) | 0.0776 (3) | –0.0692 (3) | 2.2 (1)* |
| P(3) | –0.2633 (5) | –0.0521 (4) | 0.0724 (3) | 2.5 (1)* |
| P(4) | –0.2012 (4) | –0.1145 (4) | –0.0443 (3) | 2.5 (1)* |
| O(1) | –0.155 (2) | 0.101 (1) | 0.1674 (7) | 6.3 (5)* |
| O(2) | –0.213 (1) | 0.024 (1) | –0.1666 (7) | 4.8 (5)* |
| C(1) | –0.167 (2) | 0.086 (1) | 0.120 (1) | 3.9 (6) |
| C(2) | –0.164 (2) | 0.010 (1) | –0.1273 (9) | 2.9 (5) |
| C(3) | –0.040 (2) | –0.009 (1) | 0.027 (1) | 3.4 (5) |
| C(4) | 0.049 (1) | –0.030 (1) | 0.0520 (9) | 2.1 (4) |
| C(5) | 0.037 (2) | 0.143 (1) | –0.012 (1) | 3.6 (6) |
| C(6) | –0.307 (2) | –0.097 (1) | 0.0066 (9) | 2.5 (5) |

[a] See footnote a in Table III.



**Figure 1.** Perspective view of [Ir₂I₂(CO)₂(μ-CCH₂)(dppm)₂] (5). Thermal ellipsoids are shown at the 20% level, except for methylene and vinylidene hydrogens, which are shown arbitrarily small; phenyl hydrogens are omitted.



**Figure 2.** Perspective view of [Ir₂I₂(CO)₂(μ-CC(H)Ph)-(dppm)₂] (7). Thermal ellipsoids are shown at the 20% level, except for methylene and vinylidene hydrogens, which are shown arbitrarily small; phenyl hydrogens are omitted.

**Table V. Selected Bond Distances (Å) in Compound 5**

| | | | |
|---|---|---|---|
| Ir(1)–Ir(2) | 2.828 (1) | Ir(2)–P(2) | 2.343 (6) |
| Ir(1)–I(1) | 2.782 (2) | Ir(2)–P(4) | 2.351 (6) |
| Ir(1)–P(1) | 2.330 (5) | Ir(2)–C(2) | 1.88 (3) |
| Ir(1)–P(3) | 2.336 (6) | Ir(2)–C(3) | 2.11 (2) |
| Ir(1)–C(1) | 1.90 (3) | O(1)–C(1) | 1.09 (3) |
| Ir(1)–C(3) | 2.09 (2) | O(2)–C(2) | 1.21 (3) |
| Ir(2)–I(2) | 2.799 (2) | C(3)–C(4) | 1.25 (3) |

distances are consistent with normal single bonds. The major distortions from octahedral geometry in both 5 and 7 result from the strain imposed by the bridging vinylidene groups and the accompanying metal–metal bonds. Therefore, the angles at each metal subtended by the vinylidene α-carbon and the adjacent metal are very acute (near 47°) while all the other angles between adjacent ligands in the equatorial plane are greater than 90°. All parameters involving the iodo and carbonyl ligands compare very closely between 5 and 7 and are also closely comparable to those in one isomer of the dichloro tricarbonyl compound.[19] In both 5 and 7 the iodo ligand is almost trans to the Ir–Ir bond on one metal while the other is cis to it on the adjacent metal. There are no significant differences in the Ir–I distances opposite the Ir–Ir bonds (2.799 (2) Å (5), 2.815 (2) Å (7)) and those opposite the vinylidene unit (2.782 (2) Å (5), 2.810 (2) Å (7)).

In both cases the vinylidene groups bridge the metals symmetrically, with the Ir–C(3) distances (av 2.08 Å) involving these groups, and the Ir(1)–C(3)–Ir(2) angles (84.6 (7)° (5), 86.0 (9)° (7)) agreeing surprisingly well with the related parameters involving the bridging carbonyl ligand in [Ir₂Cl₂(CO)₂(μ-CO)(dppm)₂].[19] The Ir–C distances in 5 and 7 are considerably longer than that observed in the related mononuclear species *trans*-[IrCl(C₂(H)CO₂-Me)(PPr₃ⁱ)₂] (1.868 (9) Å),[20] in line with a formal Ir=C double bond in the latter and Ir—C single bonds in the vinylidene-bridged complexes. Such differences are common in related terminal and bridging carbonyl complexes. Although the two vinylidene units are symmetrically bound

bond. Although the Ir–Ir separation in 7 (2.783 (1) Å) is very close to that in the carbonyl-bridged analogue (2.779 (1) Å),[19] the distance observed in 5 (2.828 (1) Å) is somewhat longer; however, this difference is not large, and all
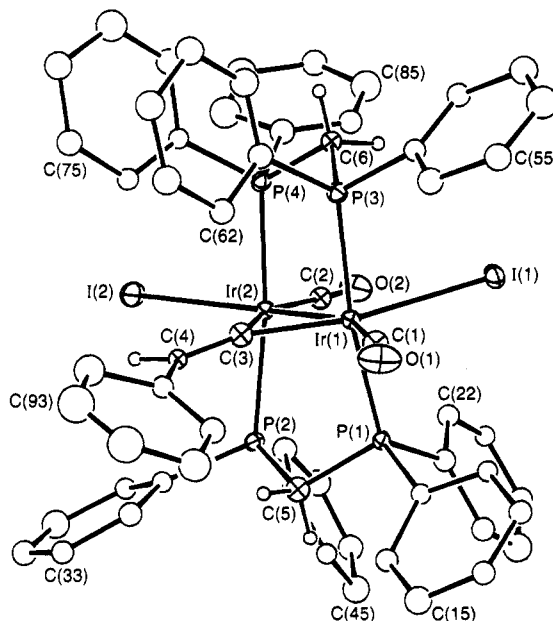
(20) Höhn, A.; Otto, H.; Dziallas, M.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1987**, 852.

**Table VI. Selected Angles (deg) in Compound 5**

(a) Bond Angles

| | | | | | |
|---|---|---|---|---|---|
| Ir(2)–Ir(1)–I(1) | 98.28 (5) | P(3)–Ir(1)–C(3) | 95.7 (5) | P(2)–Ir(2)–C(3) | 92.7 (5) |
| Ir(2)–Ir(1)–P(1) | 91.7 (1) | C(1)–Ir(1)–C(3) | 107 (1) | P(4)–Ir(2)–C(2) | 87.6 (8) |
| Ir(2)–Ir(1)–P(3) | 91.9 (1) | Ir(1)–Ir(2)–I(2) | 147.55 (6) | P(4)–Ir(2)–C(3) | 94.9 (5) |
| I(2)–Ir(1)–C(1) | 155.5 (8) | Ir(1)–Ir(2)–P(2) | 92.0 (1) | C(2)–Ir(2)–C(3) | 155.4 (9) |
| Ir(2)–Ir(1)–C(3) | 48.1 (5) | Ir(1)–Ir(2)–P(4) | 93.3 (1) | Ir(1)–P(1)–C(5) | 110.5 (6) |
| I(1)–Ir(1)–P(1) | 88.7 (2) | Ir(1)–Ir(2)–C(2) | 108.1 (8) | Ir(1)–C(1)–O(1) | 170 (2) |
| I(1)–Ir(1)–P(3) | 88.2 (1) | Ir(1)–Ir(2)–C(3) | 47.3 (5) | Ir(2)–C(2)–O(2) | 168 (2) |
| I(1)–Ir(1)–C(1) | 106.2 (8) | I(2)–Ir(2)–P(2) | 90.3 (1) | Ir(1)–C(3)–Ir(2) | 84.6 (7) |
| I(1)–Ir(1)–C(3) | 146.1 (5) | I(2)–Ir(2)–P(4) | 88.2 (2) | Ir(1)–C(3)–C(4) | 134 (2) |
| P(1)–Ir(1)–P(3) | 175.6 (2) | I(2)–Ir(2)–C(2) | 104.3 (8) | Ir(2)–C(3)–C(4) | 140 (2) |
| P(1)–Ir(1)–C(1) | 87.9 (8) | I(2)–Ir(2)–C(3) | 100.2 (5) | P(1)–C(5)–P(2) | 111 (1) |
| P(1)–Ir(1)–C(3) | 88.6 (6) | P(2)–Ir(2)–P(4) | 172.3 (2) | P(3)–C(6)–P(4) | 114 (1) |
| P(3)–Ir(1)–C(1) | 89.9 (8) | P(2)–Ir(2)–C(2) | 85.5 (8) | | |

(b) Torsion Angles

| | | | | | |
|---|---|---|---|---|---|
| P(1)–Ir(1)–Ir(2)–P(2) | 5.2 (3) | P(3)–Ir(1)–Ir(2)–P(4) | 2.3 (3) | I(1)–Ir(1)–Ir(2)–C(2) | 2 (1) |

**Table VII. Selected Bond Distances (Å) in Compound 7**

| | | | |
|---|---|---|---|
| Ir(1)–Ir(2) | 2.783 (1) | Ir(2)–P(4) | 2.341 (6) |
| Ir(1)–I(1) | 2.810 (2) | Ir(2)–C(2) | 1.89 (2) |
| Ir(1)–P(1) | 2.320 (6) | Ir(2)–C(3) | 2.06 (2) |
| Ir(1)–P(3) | 2.349 (6) | O(1)–C(1) | 1.12 (3) |
| Ir(1)–C(1) | 1.88 (3) | O(2)–C(2) | 1.13 (2) |
| Ir(1)–C(3) | 2.03 (2) | C(3)–C(4) | 1.35 (3) |
| Ir(2)–I(2) | 2.815 (2) | C(4)–C(91) | 1.49 (3) |
| Ir(2)–P(2) | 2.396 (6) | | |

at the α-carbon, they are tilted somewhat, in opposite directions. In both cases the tilts appear to result from nonbonded contacts within each complex, although the natures of these contacts differ because of the differing substituents on the vinylidene units of 5 and 7. In 5 the slightly larger Ir(2)–C(3)–C(4) angle (140 (2)°) compared to Ir(1)–C(3)–C(4) (134 (2)°) shows that the vinylidene group is tilted slightly towards Ir(1), probably to minimize repulsions with the adjacent iodo ligand I(2). In 7 the respective angles (132 (2)°, 142 (2)°) show that the phenylvinylidene unit is tipped toward Ir(2) and I(2); in this case it appears that this distortion minimizes the more severe contacts between the phenyl substituent on C(4) and the carbonyl group C(1)O(1). Other subtle differences in angles involving the iodo and carbonyl ligands also appear to result from the above nonbonded contacts in 5 and 7.

Although the contact between the vinylidene–phenyl substituent (group 9) and the carbonyl C(1)O(1) is potentially severe, the vinylidene unit is not significantly skewed about the olefin bond (the Ir(1)–C(3)–C(4)–C(91) torsion angle is only 2 (4)°). Instead, the phenyl substituent twists about the C(4)–C(91) bond, resulting in an average C(3)–C(4)–C(91)–C(ortho) torsion angle of 35°. As a result this phenyl substituent points in the direction of the phenyl groups on P(1), causing a twisting of the ligand framework on Ir(1) compared to that on Ir(2) (see Figure 2). This twisting is most severe for P(1), as seen by the P(1)–Ir(1)–Ir(2)–P(2) torsion angle of 21.8 (2)° in 7 compared with only 5.2 (3)° in 5. The other ligands on Ir(1) show a similar trend, so the I(1)–Ir(1)–Ir(2)–C(2) torsion angle is 12.0 (8)° in 7, but only 2 (1)° in 5 and the P(3)–Ir(1)–Ir(2)–P(4) angle is 8.5 (2)° in 7 compared to 2.3 (3)° in 5.

The C(3)–C(4) bonds of the vinylidene units (1.25 (3) Å (5), 1.35 (3) Å (7)) do not differ significantly and are normal for a double bond in an olefinic unit.[21]

## Discussion

The reactions of [Ir₂I₂(CO)(μ-CO)(dppm)₂] (1) with 1 equiv of either acetylene or phenylacetylene at ambient

temperature yield the vinylidene complex 5 after ca. 20 h or the phenylvinylidene complex 7 after ca. 2 h. These products, [Ir₂I₂(CO)₂(μ-CC(H)R)(dppm)₂] (R = H (5), Ph (7)) have the structures shown, as described in the previous section. For both compounds the bands in the IR spectra
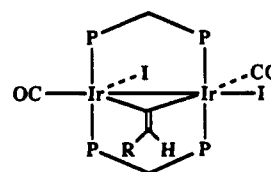


R = H (5), Ph (7)

indicate terminal carbonyls, with those of 7 (1998, 1984 cm⁻¹) being higher than those of 5 (1985, 1960 cm⁻¹), consistent with the phenyl-substituted vinylidene being a better π-acceptor.[1] The ³¹P{¹H} NMR spectrum of 5 displays an AA'BB' pattern, indicating an unsymmetrical arrangement of ligands, as found in the solid-state structure, in which the iodo ligand is opposite the metal–metal bond on one metal and cis to it on the other. In the ¹H NMR spectrum the vinylic protons of 5 are not obvious, presumably being obscured by the phenyl resonances. In a related dirhodium complex these proton resonances were also not observed,[7] whereas in the phenylvinylidene-bridged product 7 the vinylic proton is observed as a broad signal at δ 8.48.

The ¹³C{¹H} NMR spectrum of 5, prepared by using acetylene which was ¹³C-enriched at both positions, displays a doublet of multiplets at δ 194.3, assigned to Cα, and a doublet at δ 129.8, attributed to Cβ. The multiplet results from coupling to the four phosphorus nuclei, and the doublet results from coupling between the Cα and Cβ nuclei. This latter coupling of 67 Hz compares well to the value of 67.2 Hz in ethylene and shows the apparent insensitivity of this coupling to substituents on ethylene.[22] Although the chemical shift for Cβ is typical, that for Cα is at unusually high field, since generally these resonances appear in the region δ 250–380.[1]

Unlike compound 5, which has temperature-invariant ³¹P{¹H} and ¹H NMR spectra, compound 7 displays temperature-dependent spectra. At ambient temperature the ³¹P{¹H} NMR spectrum is typical of an AA'BB' spin system, as observed for 5, and the ¹H NMR spectrum displays two resonances for the dppm methylene groups. At –80 °C, however, the spectra become consistent with the solid-state structure, displaying four different phos-

(21) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. II* 1987, S1.

(22) Wehrli, F. W.; Marchand, A. P.; Wehrli, S. *Interpretation of Carbon-13 NMR Spectra*, 2nd ed.; Wiley: New York, 1988.

## Table VIII. Selected Angles (deg) in Compound 7

### (a) Bond Angles

| | | | | | |
|---|---|---|---|---|---|
| Ir(2)–Ir(1)–I(1) | 105.86 (5) | P(3)–Ir(1)–C(3) | 94.0 (7) | P(2)–Ir(2)–C(3) | 80.2 (7) |
| Ir(2)–Ir(1)–P(1) | 88.4 (1) | C(1)–Ir(1)–C(3) | 111 (1) | P(4)–Ir(2)–C(2) | 89.2 (7) |
| Ir(2)–Ir(1)–P(3) | 95.1 (1) | Ir(1)–Ir(2)–I(2) | 152.80 (5) | P(4)–Ir(2)–C(3) | 96.5 (7) |
| Ir(2)–Ir(1)–C(1) | 157.7 (8) | Ir(1)–Ir(2)–P(2) | 92.4 (1) | C(2)–Ir(2)–C(3) | 159.5 (9) |
| Ir(2)–Ir(1)–C(3) | 47.5 (6) | Ir(1)–Ir(2)–P(4) | 89.7 (1) | Ir(1)–C(1)–O(1) | 170 (3) |
| I(1)–Ir(1)–P(1) | 88.4 (1) | Ir(1)–Ir(2)–C(2) | 114.1 (6) | Ir(2)–C(2)–O(2) | 176 (2) |
| I(1)–Ir(1)–P(3) | 84.3 (1) | Ir(1)–Ir(2)–C(3) | 46.6 (6) | Ir(1)–C(3)–Ir(2) | 86.0 (9) |
| I(1)–Ir(1)–C(1) | 96.2 (8) | I(2)–Ir(2)–P(2) | 89.8 (1) | Ir(1)–C(3)–C(4) | 142 (2) |
| I(1)–Ir(1)–C(3) | 153.1 (6) | I(2)–Ir(2)–P(4) | 85.3 (1) | Ir(2)–C(3)–C(4) | 132 (2) |
| P(1)–Ir(1)–P(3) | 172.4 (2) | I(2)–Ir(2)–C(2) | 92.6 (6) | C(3)–C(4)–C(91) | 131 (2) |
| P(1)–Ir(1)–C(1) | 88.7 (8) | I(2)–Ir(2)–C(3) | 107.5 (7) | P(1)–C(5)–P(2) | 111 (1) |
| P(1)–Ir(1)–C(3) | 93.4 (7) | P(2)–Ir(2)–P(4) | 173.0 (2) | P(3)–C(6)–P(4) | 111 (1) |
| P(3)–Ir(1)–C(1) | 90.6 (8) | P(2)–Ir(2)–C(2) | 96.1 (7) | | |

### (b) Torsion Angles

| | | | | | |
|---|---|---|---|---|---|
| P(1)–Ir(1)–Ir(2)–P(2) | 21.8 (2) | I(1)–Ir(1)–Ir(2)–C(2) | 12.0 (8) | C(3)–C(4)–C(91)–C(96) | –38 (4) |
| P(3)–Ir(1)–Ir(2)–P(4) | 8.5 (2) | C(3)–C(4)–C(91)–C(92) | 148 (3) | Ir(1)–C(3)–C(4)–C(91) | 2 (4) |

## Scheme I
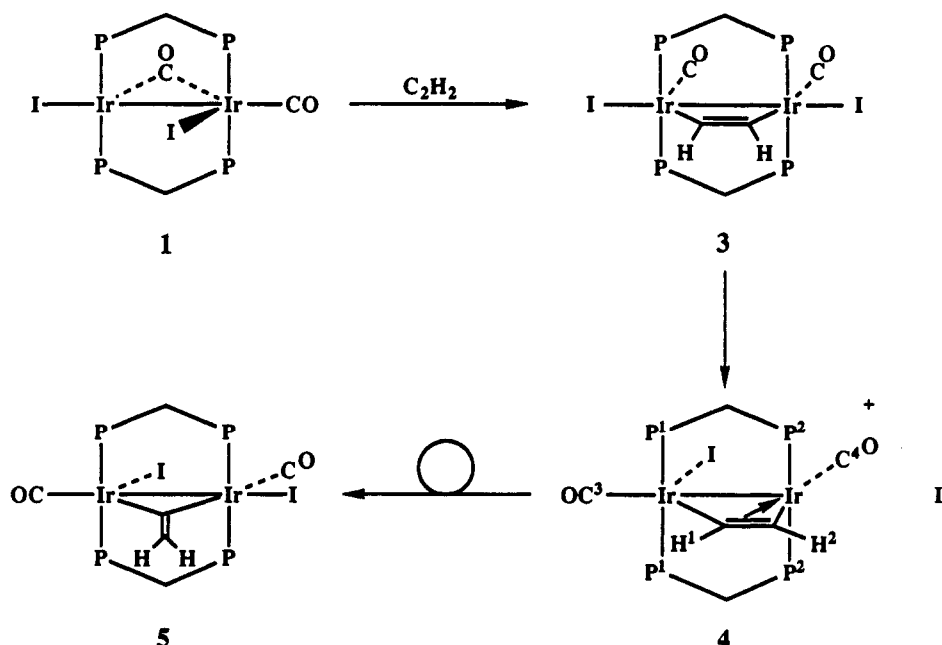


phorus resonances and four resonances for the methylene protons. In the low-temperature limiting structure the molecule has "left–right" asymmetry owing to the arrangement of the I and CO ligands, whereas "top–bottom" asymmetry apparently results from the orientation of the phenyl substituent on the vinylidene unit. We suggest that the temperature dependence results from a fluxional process in which the vinylidene phenyl group twists about the C(4)–C(91) bond, causing an accompanying twist of the ligand framework on Ir(1) in order to minimize nonbonded contacts between the vinylidene phenyl group and those on P(1) and P(3) (vide supra).

Although the reaction of 1 with acetylene is fast, compound 5 is not the first species observed; the first species observed, both at ambient temperature and at –80 °C, is compound 3 (shown in Scheme I), which transforms readily to 4 at ambient temperature. The $^{31}P\{^1H\}$ NMR spectrum of 3 appears as a singlet, indicating that all phosphorus nuclei are chemically equivalent, and the $^1H$ NMR spectrum displays a broad signal for the acetylene protons at $\delta$ 8.48. In the IR spectrum of a mixture of 3 and 4 the only band attributable to 3 is at 1998 cm$^{-1}$. A $^{13}C\{^1H\}$ NMR spectrum of 3 ($^{13}C$-enriched at the carbonyl and acetylenic carbons) shows two resonances at $\delta$ 180.5 and 113.9, for the carbonyl and acetylenic carbons, respectively, displaying coupling of 14 Hz between these

nuclei. The resonance for the acetylenic carbons also shows additional coupling to two phosphorus nuclei, consistent with the structure shown for 3. An alternate structure, in which the alkyne is bound perpendicular to the Ir–Ir axis with an accompanying cis-phosphine arrangement, seems unlikely, since such a geometry has only previously been observed for dppm-bridged Rh or Ir complexes having the metals in the zero oxidation state.[7,23] In addition, the perpendicular mode would be expected to show coupling of the acetylenic carbons to all four phosphorus nuclei, which is not observed. Although the $^{13}C$ chemical shift of the acetylenic carbons has previously been used to establish the alkyne binding mode, the observed value is intermediate between the normal ranges for parallel ($\delta$ 120–150) and perpendicular ($\delta$ 60–100) binding modes and so is inconclusive in this case. The structure proposed for 3 is based on the spectral similarities of 3 with those of the DMAD analogue.[10] An alternate structure, III, in which both iodo ligands are adjacent is also possible; however, it appears to be less likely, since the cis arrangement of the carbonyls and the acetylene ligand in this geometry would be expected to give rise to much smaller $^{13}C$–$^{13}C$ coupling than the 14 Hz observed. In addition this

(23) McDonald, R. Ph.D. Thesis, University of Alberta, 1991, Chapter 5.

III
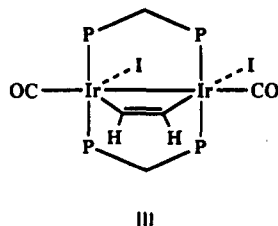
structure would result in unfavorable contacts between the two iodide groups. The structure shown for **3** is also consistent with initial attack of acetylene at the vacant site on the unsaturated Ir center, opposite the bridging carbonyl of **1**.

Conversion of **3** to **4**, shown in Scheme I, is rapid at ambient temperature. The $^{31}P\{^1H\}$ NMR spectrum of **4** is typical of an AA'BB' spin system having two different chemical environments at each Ir center. Compound **4** shows the acetylenic proton resonances at $\delta$ 8.52 and 8.06 as unresolved multiplets in the $^1H$ NMR spectrum. With broad-band $^{31}P$ decoupling these resonances collapse to a pair of doublets displaying vicinal H–H coupling of only 3.3 Hz. This coupling is unexpectedly smaller than values of between 6 and 12 Hz in substituted ethylenes[24] and in coordinated acetylene.[25] Selective $^{31}P$-decoupling experiments indicate that the low-field acetylenic proton resonance ($H^2$) is coupled to only one set of phosphorus nuclei (labeled $P^2$ in Scheme I), having a coupling constant of ca. 1.5 Hz, whereas the higher field resonance ($H^1$) is coupled to all four phosphorus nuclei, with a coupling of again ca. 1.5 Hz. The $^{13}C\{^1H\}$ NMR spectrum of **4** (using $^{13}C$-enriched acetylene) displays an AB quartet at ca. $\delta$ 106 for the two acetylene carbons, with additional coupling to the phosphorus nuclei, as shown in Figure 3. It is significant that the higher field branches of this spectrum are somewhat more complicated than the lower field ones, showing additional phosphorus coupling. The selective $^{31}P$ decoupling experiments show that the high-field carbon ($C^2$, attached to $H^2$) couples with two phosphorus nuclei ($P^2$) more strongly than with the others (6.5 vs 2.5 Hz), whereas the low-field carbon $C^1$ couples to $P^2$ with a 2.5-Hz coupling constant and to $P^1$ with a 3.3-Hz constant. This latter observation is reminiscent of the coupling noted between $H^1$ and the four phosphorus nuclei, suggesting that the acetylenic carbon ($C^1$) may be close to a bridging position. In a sample of **4** in which all the acetylenic and carbonyl carbons were $^{13}C$-enriched, a strong coupling (25 Hz) is observed between $C^2$ and the carbonyl carbon at $\delta$ 181.8 ($C^4$), suggesting a trans arrangement, whereas no coupling involving $C^1$ and the carbonyl carbon at $\delta$ 159.2 ($C^3$) is observed. On the basis of these data we propose the structure shown for **4** in Scheme I. In this formulation the symmetrically bound acetylene of **3** has slid toward $Ir^2$ (attached to $P^2$) to yield an unsymmetrically bound acetylene in which $C^1$ is now closer to $Ir^2$ than in **3**. It is also significant that the chemical shifts of the acetylenic carbon nuclei ($\delta$ 106.6, 105.6) are at higher field than those of **3** ($\delta$ 113.9), and the coupling constant between these carbons (ca. 59 Hz) is smaller than noted earlier for **5** and substituted ethylenes. In the complex [Rh$_2$(CO)$_2$($\mu$-HC$_2$-Ph)(dppm)$_2$], which contains a normal parallel acetylene,



**Figure 3.** $^{13}C\{^1H\}$ NMR spectrum of complex **4**, showing the acetylenic region. $^{13}C$-enriched acetylene was used in the preparation of **4**.

such coupling is ca. 70 Hz.[26] Both observations suggest a lowering of the C–C bond order in **4** and a change in hybridization toward sp$^3$.[27,28] It may also be that this lowering of the C–C bond order may be responsible for the small vicinal H–H coupling noted earlier. These data suggest that in complex **4** the $\pi^*$ or $\pi$ orbital of the dimetallo-olefin unit might also interact with $Ir^2$, although it is not clear which orbital of $Ir^2$ is involved. The structure shown for **4** is unusual but is not totally without precedent; the structure of [Rh$_2$Cl(CNMe)$_2$($\mu$-CF$_3$C$_2$CF$_3$)(dppm)$_2$]-[BF$_4$] showed an unsymmetrical binding mode of the alkyne in which one carbon was shifted significantly toward the other metal, giving rise to substantially different, nominally nonbonded Rh–C contacts of 2.660 (7) and 2.902 (7) Å.[29] It was suggested at the time that a weak interaction, of the type proposed here, was involved. Unsymmetrically coordinated alkynes have also been noted for other dppm-bridged complexes,[12] and theoretical studies on alkyne-bridged complexes have suggested distortions involving twisting of the alkyne group,[30] although interaction involving the $\pi$ bond was not suggested in these studies. It is also noteworthy that the structure proposed for **4** is not unlike that proposed as one possible intermediate in the calculations by Silvestre and Hoffmann on a Pt$_2$ model complex,[7] in which $C_\alpha$ has moved to a bridging site with cleavage of the bond between the $C_\beta$ and one metal, to yield a $\mu,\eta^1$-alkyne species. Although this intermediate was found to be at an unfavorable energy, it would appear that our proposed intermediate **4** is more favorable than a $\mu,\eta^1$-alkyne alternative owing to coordination of the C–C multiple bond to the second metal. It does not seem reasonable to us to ignore this rather conventional $\pi$ interaction, and certainly the NMR spectroscopy supports such an interaction.

(24) Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. *High Resolution Nuclear Magnetic Resonance Spectroscopy*; Pergamon: Oxford, 1966; Vol. 2.

(25) (a) Burn, M. J.; Kiel, G.-Y.; Seils, F.; Takats, J.; Washington, J. *J. Am. Chem. Soc.* **1989**, *111*, 6850. (b) Hogarth, G.; Kayser, F.; Knox, S. A. R.; Morton, D. A. V.; Orpen, A. G.; Turner, M. L. *J. Chem. Soc., Chem. Commun.* **1989**, 358. (c) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, *1297*.
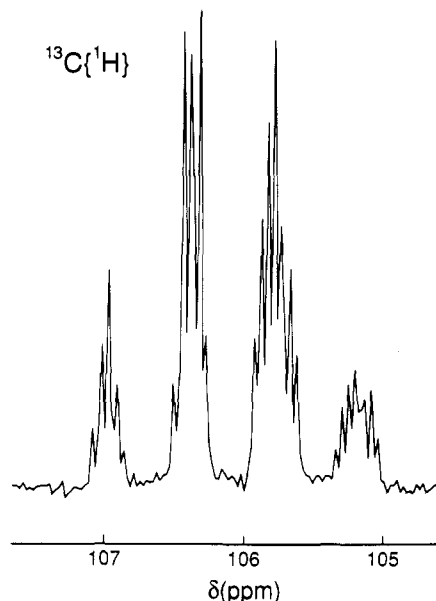
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The proposal that 4 is a cationic complex having an iodine counterion is based on its conductivity in nitromethane (79.8 $\Omega^{-1}$ cm$^2$ mol$^{-1}$) and on the need to generate coordinative unsaturation to allow the proposed $\pi$ interaction to occur. In addition the transformation from a mutually adjacent arrangement of iodo ligands in 1 to the arrangement in 5, in which they are no longer adjacent, requires reversible dissociation of I$^-$ or CO; the former seems more likely. In CH$_2$Cl$_2$ the low conductivity (12 $\Omega^{-1}$ cm$^2$ mol$^{-1}$) suggests ion pairing in this solvent. In fact, the iodide counterion appears to hinder the transformation of 4 to 5, possibly owing to the reversibility of the dissociation (vide infra). No other intermediate, in the transformation of 1 to 5, was observed. The hydrogen migration step (or steps) to yield 5 is much slower than the facile transformation of 3 to 4, requiring ca. 20 h at room temperature.

The possibility that C–H activation and the 1,2-hydrogen shift had already taken place in the transformation of 3 to 4, making 4 a vinylidene-bridged species, was considered and rejected. This conclusion is based in part on the facile conversion of 3 to 4 and on the very slow conversion of 4 to 5; it seems reasonable to assume that the C–H activation and H-transfer steps will be rate-determining. More importantly, $^{13}$C gated-decoupling experiments reveal no triplet which would be expected for this hypothetical species. Instead these experiments show that the acetylenic carbons of 4 each bear one hydrogen, being further split into doublets compared to the fully H-decoupled spectrum, consistent with the formulation suggested in Scheme I. The $^{13}$C NMR spectra of the gated decoupling experiments also reveal $^1J_{C^1H^1} \approx 160$ Hz and $^1J_{C^2H^2} \approx 175$ Hz, indicating that the C$^1$–H$^1$ bond might have been slightly weakened.

As noted earlier, the reaction of 1 with phenylacetylene at ambient temperature yields only 7, with no evidence of intermediates being observed. However, at –40 °C the additional species 6 is observed, which transforms slowly
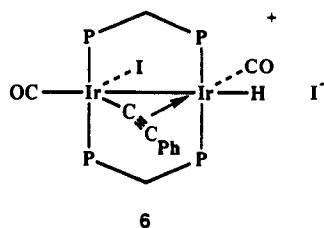


6

to 7 at this temperature or rapidly at temperatures above 0 °C. The $^{31}$P{$^1$H} NMR spectrum of 6 displays a pattern typical of an AA′BB′ spin system, and the $^1$H NMR shows a high-field triplet at $\delta$ –11.55 ($^2J_{P-H}$ = 12.4 Hz). The presence of the hydride signal suggests that 6 is an acetylide complex; however, confirmation by IR spectroscopy is not possible since 6 is only ever present in small amounts, resulting in the clear identification of only two new weak shoulders at 2028 and 1996 cm$^{-1}$, superimposed on the dominant bands of compounds 1 and 7. The structure shown for 6, in which the acetylide is bound in a $\sigma,\pi$ fashion, is based on analogies with related species.[31] In spite of the uncertainty in the structure of 6, it is clearly an acetylide–hydride complex, an observation that has sig-

nificant implications regarding the proposed mechanism of the acetylene-to-vinylidene tautomerism (vide infra). This is of course based on the assumption that both acetylene and phenylacetylene react with 1 by the same mechanism.

The conversion of the acetylene-bridged species 3 to the vinylidene-bridged product 5 is the first such transformation reported. Although both classes of species were obtained for a related dirhodium species, it was shown in that study that the acetylene adduct observed was not a necessary intermediate in the formation of the vinylidene-bridged product.[7] It is also significant that the alkyne adduct observed in the dirhodium complex was bound perpendicular to the metal–metal bond and *not* parallel to it as proposed for our intermediate in the hydrogen-transfer reaction.

On the basis of the species observed in both the acetylene and phenylacetylene reactions, we propose a scheme for the acetylene-to-vinylidene transformation, much as shown in Scheme I, with the exception that species 4 (and its phenyl analogue) is followed by an acetylide–hydride species such as 6. We propose that transfer of the hydrogen from the $\alpha$- to $\beta$-carbons occurs through an acetylide–hydride intermediate analogous to 6. This proposal supports previous studies that suggested that a concerted mechanism was unlikely for a binuclear complex, although a transformation via an acetylide–hydride intermediate was feasible.[9] Strong support for such a mechanism comes from a study in which a vinylidene-bridged diplatinum species was obtained upon reaction of a mononuclear platinum–hydride complex with a mononuclear platinum–acetylide species.[32] It is also noteworthy that the transformations of alkyne to vinylidene complexes, via acetylide–hydride intermediates, have been observed on single-metal fragments.[2h,20,33,34] The transformation of 4 to an acetylide–hydride species, analogous to 6, might be envisaged as resulting from oxidative addition of the acetylenic C–H bond to Ir$^1$, brought about by H$^1$ being brought into proximity with this metal center through slippage of the acetylene toward Ir$^2$. This would require some rearrangement of the hydride and acetylide groups; however, such rearrangements are known to be facile in such systems.[31,35]

In the acetylene-to-vinylidene rearrangements, mediated by a single metal center, two mechanisms appear to have been established. The first involves a 1,2-hydrogen shift via initial slippage of the alkyne to give an $\eta^1$-alkyne binding mode,[1,9] whereas the second involves oxidative addition of the acetylene to give an acetylide–hydrido intermediate.[2h] We note that our proposal contains features of both above extremes, except that whereas alkyne slippage occurs to give an $\eta^1$ binding mode in mononuclear species, the free multiple bond in a binuclear species can be stabilized through coordination to the second metal. Movement of the alkyne toward this second metal brings the C–H bond into proximity of the first metal, allowing subsequent oxidative addition.

In an attempt to induce carbon–carbon coupling in the vinylidene products 5 and 7, these complexes were exposed to additional acetylene and phenylacetylene. While no reaction was detected between phenylacetylene and either

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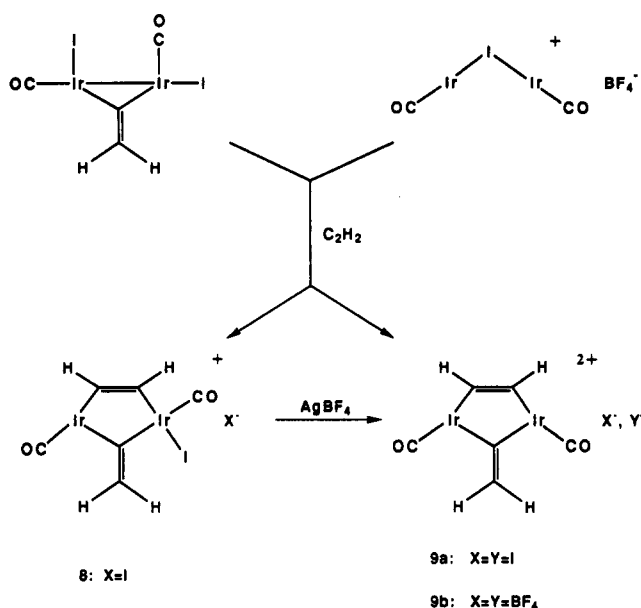
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**Scheme II**





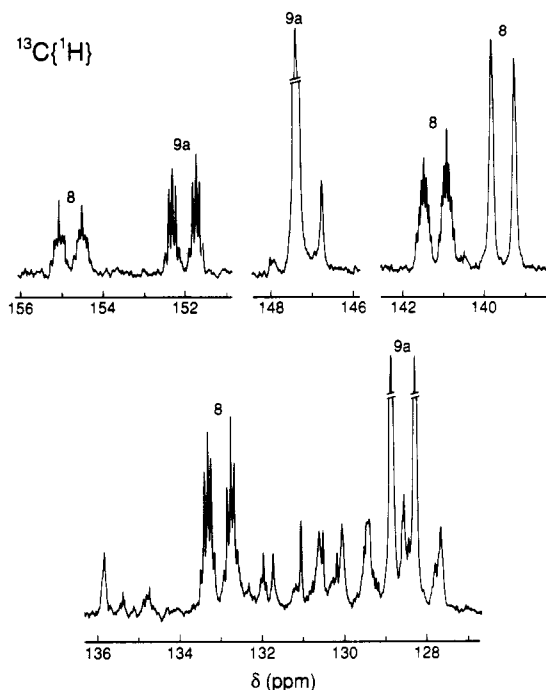**Figure 4.** $^{13}C\{^1H\}$ NMR spectrum of a mixture of 8 and 9a, prepared from $^{13}C$-enriched acetylene. The high background between $\delta$ 127 and 136 is due to phenyl resonances.

5 or 7, or between acetylene and 7, compound 5 *did* react instantly with acetylene to give the two products 8 and 9a in ca. 1.8:1 ratio, respectively. These products have been identified spectroscopically as the vinylidene- and acetylene-bridged complexes $[Ir_2I(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}HC_2H)\text{-}(dppm)_2][I]$ (8) and $[Ir_2(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}HC_2H)(dppm)_2]\text{-}[I]_2$ (9a), as shown in Scheme II (dppm ligands perpendicular to the plane of the drawings are not shown). The $^{31}P\{^1H\}$ NMR spectrum of this mixture showed that 8 is unsymmetrical, displaying an AA′BB′ pattern at $\delta$ -18.3 and $\delta$ -29.2, while 9a is symmetrical, displaying a singlet at $\delta$ -33.5. The $^{13}C\{^1H\}$ NMR spectrum of the mixture displays two equal-intensity carbonyl resonances (triplets) at $\delta$ 174.1 and 172.9 and another (a broad singlet) at $\delta$ 172.8. On the basis of selective $^{31}P$-decoupling experiments and on the integrations of these signals, the two triplets are assigned to 8 and the singlet to 9a. The IR spectrum of a mixture of these species shows three carbonyl bands; the two at 2018 and 2009 cm$^{-1}$ are assigned to 8, while the one at 2027 cm$^{-1}$ is assigned to 9a on the basis of a comparison with the IR spectrum of its BF$_4^-$ analogue 9b (vide infra). Additional information about the natures of these products was obtained from $^{13}C$ NMR experiments in which $^{13}C$-enriched acetylene was used in the preparation of 5 and in the subsequent formation of the final products. The $^{13}C\{^1H\}$ NMR spectrum of the product mixture, shown in Figure 4, displays seven resonances in the range $\delta$ 128–156, and their assignments are made possible by selective heteronuclear decoupling experiments. On the basis of these experiments the doublet of quintets at $\delta$ 152.0, the broad singlet at $\delta$ 147.3, and the doublet at $\delta$ 129.1 were shown to arise from 9a. For the low-field signal the quintet results from coupling to all four phosphorus nuclei, and the doublet results from coupling to the carbon at $\delta$ 129.1 ($^1J_{CC}$ = 57 Hz); these two signals clearly result from the $\alpha$- and $\beta$-carbons of the bridging vinylidene moiety. Gated-decoupling experiments confirm the assignment, establishing that the high-field carbon bears two protons while the low-field carbon is quaternary. As was the case for 5, no proton resonance was observed for this vinylidene unit. Each acetylenic carbon, corresponding to the $^{13}C$ resonance at $\delta$ 147.3, has one proton attached, the resonance for which is located at $\delta$ 9.34 in the $^1H$ NMR spectrum (integrated as 2H). The

assignment of the proton resonance is in agreement with both the gated experiment and the $^1H$ NMR spectrum, with both showing carbon–hydrogen coupling of 142 Hz, and further confirmed by heteronuclear carbon–hydrogen decoupling. The structure shown for compounds 9, having the carbonyl ligands opposite the acetylenic unit, is based on the structures of analogous dppm-bridged compounds in which the alkyne bridge is accompanied by a bridging methylene[36] or carbonyl group.[37,38] It must be, however, that the alkyne–Ir–CO angles deviate significantly from linearity in this case since a sample of 9a, in which the vinylidene, acetylene, and carbonyl groups were all $^{13}C$ enriched, showed coupling between the acetylene carbons and the carbonyls of only 4 Hz; no coupling between $C_\alpha$ of the vinylidene moiety and the carbonyls was observed. The $^{13}C$ resonances for the vinylidene moiety of 8 appear as a doublet of multiplets at $\delta$ 154.7 for $C_\alpha$ and a doublet at $\delta$ 139.5 for $C_\beta$ ($^1J_{CC}$ = 57 Hz), while those for the alkyne appear as two doublets of multiplets at $\delta$ 141.2 and 133.0. In this case when the compound is also enriched in $^{13}CO$, one carbonyl (at $\delta$ 174.1) displays strong coupling (29 Hz) with $C_\alpha$ of the vinylidene unit while the other ($\delta$ 172.9) displays coupling of the same magnitude with one of the acetylenic carbons. These carbon–carbon coupling constants are quite substantial and support a structure as shown in which one carbonyl is opposite the vinylidene unit while the other is opposite the acetylene ligand. Clearly, on the basis of substantial coupling observed, the arrangements must be closer to trans than in 9a.

Reaction of the cationic, iodo-bridged A-frame $[Ir_2(CO)_2\text{-}(\mu\text{-}I)(dppm)_2][BF_4]$ (2) with acetylene yields the analogous mono- and dicationic species 8 and 9 except with a BF$_4^-$ anion, in approximately the same mole ratio as obtained in the previous reaction of 5. In addition, this solution can be converted completely to 9b, in which both anions

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are $BF_4^-$, by reaction with $AgBF_4$, supporting the mono- and dicationic nature of the respective species. Compound **9b** is unstable, slowly transforming to two unidentified species, and is only spectroscopically characterized. Surprisingly the addition of iodide ion to **9b** does not regenerate the monocationic species **8** but instead results in no reaction. It appears therefore that species **8** and **9** are not in equilibrium but are generated by two competing pathways, probably resulting from alkyne attack at two different sites in some cationic vinylidene-bridged precursor.

The $^1H$ NMR spectra of **8** and its $BF_4^-$ salt are essentially superimposable and show the presence of all four protons on the vinylidene and acetylene groups. The vinylidene protons appear at $\delta$ 8.84 and 7.96, whereas the acetylene protons are observed at $\delta$ 9.18 and 8.02. The gated $^{13}C$ NMR spectrum reveals carbon–hydrogen coupling constants of 143–153 Hz for these protons. In addition to phosphorus coupling, the acetylenic protons show vicinal coupling of 6.4 Hz to each other.

It is noteworthy that the $^{13}C$ chemical shifts for the $\alpha$-carbons of the vinylidene units of **8** and **9a** are at unusually high field ($\delta$ 154.7, 152.0, respectively). Generally such resonances appear downfield of $\delta$ 230. These shifts are even at higher field than those noted for **5** and **7** (ca. $\delta$ 193). The vinylidene unit is isoelectronic with a carbonyl, and a parallel high-field shift in the carbonyl resonances (by ca. 40 ppm) also occurred upon insertion of alkynes into the carbonyl-bridged metal–metal bond in some related dirhodium complexes.[37] In both cases expansion of a three-membered metallocycle ring to a five-membered ring occurred upon alkyne insertion.

The reaction of **2** with acetylene to give the acetylene- and vinylidene-bridged species is unexpectedly fast, completed almost immediately after the introduction of acetylene, in sharp contrast to the reaction of **1** with acetylene to produce **5**, which takes ca. 20 h to complete. When **1** is treated with excess acetylene, the final products are the same as obtained in the reaction of **5** with excess acetylene, and it can be easily shown by NMR monitoring that the former reaction proceeds via the initial formation of **5**. Keeping in mind that the formation of **8** and **9a** from **5** and acetylene is instant, it appears that the reaction of **2** with acetylene either is via a different mechanism from the one between **1** and acetylene, or the rate for the formation of **5** is affected by the iodo ligand, which might hinder the reaction through recoordination. The latter seems more plausible, since the reaction of **1** with excess acetylene, leading to complexes **8** and **9a**, is completed within 1 or 2 h, when conducted in a polar solvent mix such as $CH_2Cl_2/CH_3CN$ or $CH_2Cl_2/MeOH$. However, the same reaction, when carried out in $CH_2Cl_2$, takes about the same time as required for the generation of **5**.

## Conclusions

This study, in which the diiodo species $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ reacts with acetylene and phenylacetylene, to give the respective vinylidene-bridged products $[Ir_2I_2$-

$(CO)_2(\mu\text{-}CC(H)R)(dppm)_2]$, is the first in which several binuclear intermediates have been observed, allowing a mechanism to be proposed for the 1,2-hydrogen shift. For the first time in a binuclear species evidence for an acetylide–hydride intermediate has been obtained. The precursor to this acetylide–hydride species, in which a parallel-bound alkyne shifts toward one metal to allow the additional interaction of the C–C $\pi$ bond with the other metal, is also a pivotal intermediate in the acetylene-to-vinylidene transformation.

Although the phenylvinylidene-bridged species does not react further with alkynes, the vinylidene-bridged compound does react with acetylene to give the unusual products $[Ir_2I(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}HCCH)(dppm)_2][I]$ and $[Ir_2(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}HCCH)(dppm)_2][I]_2$ in which the metals are simultaneously bridged by a vinylidene *and* an acetylene group. Analogous mono- and dicationic species can also be obtained in the direct reaction of $[Ir_2(CO)_2\text{-}(\mu\text{-}I)(dppm)_2][BF_4]$ with acetylene. In these compounds the vinylidene and the acetylene groups that may potentially condense are on opposite faces of the binuclear framework and cannot come together; consequently, carbon–carbon bond forming was not observed. Coordinated vinylidenes are known to condense with free alkynes, presumably via an intermediate in which alkyne precoordination to the metal has occurred.[1] The formation of these vinylidene- and alkyne-bridged products indicates that vinylidene and alkyne units can coexist, although if the two units are disposed on opposite faces of the dimer, condensation is inhibited. It is also noteworthy that alkyne-bridged units in related, diphosphine-bridged complexes are notoriously unreactive.[29,36] The formation of **5** and **7** is possibly promoted by the enhanced basicity of the metal centers in **1**, brought about by the good $\pi$-donor iodide ligand. This may not be surprising, since the reaction leading to these vinylidene complexes appears to be controlled by the oxidative addition of the C–H bond to form the acetylide–hydride species.

Although C–C bond formation involving the bridging vinylidene units was not observed in this study, it is hoped that further work on these systems can lead to such reactivity, which should shed light on the involvement of two adjacent metals in C–C bond-forming reactions.