3040 *Organometallics* **1995,** *14,* 3040−3057

Cationic Vinylidene-Bridged Complexes and Their Reactions with Alkynes To Yield Either Alkyne- and Vinylidene-Bridged or Bis(vinylidene) Products. Facile Interconversion between Terminal and Bridging Vinylidene Bonding Modes

Li-Sheng Wang and Martin Cowie*

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Received December 23, 1994[⊗]

Reaction of the cationic A-frame complex $[Ir_2(CO)_2(\mu\text{-}I)(dppm)_2][SO_3CF_3]$ (**2**) (dppm = $Ph_2PCH_2PPh_2$) with either acetylene or phenylacetylene at −78 °C yields the respective species $[Ir_2(CO)(HCCR)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][SO_3CF_3]$ (R = H, Ph), in which the alkyne is terminally bound to one metal. At ambient temperature these alkyne adducts slowly rearrange to the vinylidene-bridged species $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CC(H)R)(dppm)_2][SO_3CF_3]$. An analogous allene adduct is obtained in the reaction of **2** with allene. Reaction of the neutral, vinylidene-bridged complexes $[Ir_2I_2(CO)_2(\mu\text{-}CC(H)R)(dppm)_2]$ (R = H, Ph) with methyl triflate yields the same cationic vinylidene-bridged species through loss of CH_3I. Protonation of this neutral vinylidene-bridged species (R = H) at −40 °C yields an ethylidyne-bridged product which rearranges to a vinylidene- and hydride-bridged product at ambient temperature. Reaction of $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CC(H)Ph)(dppm)_2][SO_3CF_3]$ with either acetylene or phenylacetylene yields alkyne- and phenylvinylidene-bridged products $[Ir_2I(CO)_2(\mu\text{-}CC(H)Ph)(\mu\text{-}HCCR)(dppm)_2][SO_3CF_3]$ (R = H, Ph), and the X-ray structure of a derivative, $[Ir_2I_2(CO)_2(\mu\text{-}CC(H)Ph)(\mu\text{-}HCCH)(dppm)_2]$ (**15**), has been carried out. The reaction of $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CCH_2)(dppm)_2][SO_3CF_3]$ with phenylacetylene yields an unusual bis(vinylidene) product, $[Ir_2I(CO)_2(CCH_2)(CC(H)Ph)(dppm)_2][SO_3CF_3]$ (**19**), in which each vinylidene is terminally bound to a different metal. Reaction of **19** with either I^- or CO converts the terminal vinylidenes to bridging groups yielding $[Ir_2I(L)(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}CC(H)Ph)(dppm)_2]^{n+}$ (L = I, $n = 0$; L = CO, $n = 1$). The structure of the diiodo species (**20b**) has been determined by X-ray techniques. Compound **15**, as the CH_2Cl_2 solvate, crystallizes in the monoclinic space group $P2_1/c$ with $a = 15.799(3)$ Å, $b = 18.029(2)$ Å, $c = 21.126(5)$ Å, $\beta = 99.48(2)°$, $V = 5935(4)$ Å^3 ($T = -65$ °C), and $Z = 4$. On the basis of 7406 unique observations and 441 parameters varied, the structure refined to $R = 0.034$ and $R_w = 0.040$. This complex has a bridging phenylvinylidene and a bridging acetylene group with the iodo ligands bound cis to the alkyne bridge. Compound **20b** crystallizes in the tetragonal space group $I4_1/a$ with $a = 30.407(5)$ Å, $c = 13.065(6)$ Å, $V = 12079(6)$ Å^3, and $Z = 8$ ($T = 22$ °C). On the basis of 3730 unique observations and 305 parameters varied, the structure refined to $R = 0.045$ and $R_w = 0.050$. In this product both the vinylidene and the phenylvinylidene groups are bridging, with the iodo ligands having an anti arrangement on adjacent metals.

Introduction

Vinylidene (:C=CH_2) is an unstable isomer of acetylene, which can be stabilized by coordination to one or more metal centers.[1,2] Since the first vinylidene complex was established, only 28 years ago,[3] interest in this fascinating group has grown dramatically, and its close analogy to the ubiquitous carbonyl ligand[2] suggests that a rich chemistry will continue to develop for vinylidene and its derivatives. Parallels between the two groups show up clearly in their coordination chemistry, in which vinylidene can function as either a terminal or a bridging group;[1,2] in addition the bridged vinylidene can be either symmetrically bridging or bound in a side-on manner (μ-σ,η^2),[4] much as is observed for carbonyls.[5] This ability to function as either a terminal or bridging group has led to a strategy in which vinylidene-bridged heterobinuclear complexes are prepared through the reaction of a terminal-vinylidene complex with an unsaturated metal fragment.[6]

Much of the recent interest in vinylidene ligands focuses on their involvement in C−C bond-forming reactions.[1,7−18] On the basis of evidence of vinylidene

---

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1995.

(1) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197 and references therein.

(2) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1077 and references therein.

(3) (a) Mills, O. S.; Redhouse, A. D. *J. Chem. Soc., Chem. Commun.* **1966**, 444. (b) Mills, O. S.; Redhouse, A. D. *J. Chem. Soc. A* **1968**, 1282.

(4) (a) Doherty, N. M.; Elschenbroich, C.; Kneuper, H.-J.; Knox, S. A. R. *J. Chem. Soc., Chem. Commun.* **1985**, 170. (b) Mercer, R. J.; Green, M.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1986**, 567.

(5) (a) Cotton, F. A. *Prog. Inorg. Chem.* **1976**, *21*, 1. (b) Commons, C. J.; Hoskins, B. F. *Aust. J. Chem.* **1975**, *28*, 1663.

(6) Werner, H.; Garcia Alonso, F. J.; Otto, H.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1988**, *121*, 1565.

(7) Hoel, E. L.; Answll, G. B.; Leta, S. *Organometallics* **1984**, *3*, 1633.

(8) Casey, C. P.; Miles, W. H.; Fagan, P. J.; Haller, K. J. *Organometallics* **1985**, *4*, 559.

(9) Casey, C. P.; Austin, E. A. *Organometallics* **1986**, *5*, 584.

0276-7333/95/2314-3040$09.00/0

species on the surface of Fischer–Tropsch catalysts,[19] a mechanism for hydrocarbon chain lengthening, resulting from surface-bound vinylidene species, has been presented.[20] Vinylidene groups have also been attracting attention for applications in organic synthesis[21,22] and in alkyne polymerization, for which vinylidenes are suggested as polymerization initiators.[10]

The idea that binuclear complexes could function as effective models for processes occurring on metal surfaces, by allowing the substrate of interest to interact with more than one metal, led us to investigate binuclear vinylidene complexes. In a recent paper[23] we reported that the vinylidene-bridged species $[Ir_2I_2(CO)_2(\mu\text{-}CCH_2)(dppm)_2]$ reacted with excess acetylene to yield products which were proposed to have a bridging vinylidene and a bridging acetylene group on opposite faces of the complex. Since the vinylidene-bridged precursor is coordinatively saturated, it appeared that removal of I^- should lead to unsaturation which might make preparation of these mixed alkyne–vinylidene species more facile. It also appeared that the preparation of bis(vinylidene) species should be possible starting from coordinatively unsaturated mono(vinylidene) precursors. In this paper we report the preparation of cationic vinylidene-bridged species starting from either $[Ir_2(CO)_2(\mu\text{-}I)(dppm)_2][X]$ or $[Ir_2I_2(CO)_2(\mu\text{-}CC(H)R)(dppm)_2]$ and some subsequent reactions of these products.

Experimental Section

General Procedures. Purified argon and carbon monoxide were obtained from Linde, and allene was from Matheson. The 99% carbon-13-enriched carbon monoxide was purchased from Isotec Inc., and the 99% carbon-13-enriched acetylene, from Cambridge Isotope Laboratories. All gases were used as received. Diethyl ether, THF, and hexane were dried over Na–benzophenone ketyl whereas CH_2Cl_2 was dried by P_2O_5 and MeOH by magnesium metal; all solvents were distilled under argon before use. The perdeuterated methylene chloride was dried over molecular sieves and deoxygenated by repeated freeze–pump–thaw cycles. The compounds phenylacetylene, silver tetrafluoroborate, methyllithium, tetrafluoroboric acid–dimethyl etherate, triflic acid, methyl triflate, and *tert*-butyl isocyanide were used as received from Aldrich; potassium iodide was purchased from BDH Chemicals. Reactions were routinely conducted under Schlenk conditions. Ammonium hexachloroiridate(IV) was purchased from Victoria Precious Metals. Compounds $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$) (**1**)[24] and $[Ir_2I_2(CO)_2(\mu\text{-}CC(H)R)(dppm)_2]$ (R = H (**8**), Ph (**9**))[23] were prepared as previously reported.

All routine NMR experiments were conducted on a Bruker AM-400 spectrometer, whereas the $^{13}C\{^{31}P\}$ NMR experiments were conducted on a Bruker AM-200 spectrometer (this capability is not available on the AM-400 instrument). For all NMR experiments CD_2Cl_2 was used as solvent. IR spectra were recorded either on a Nicolet 7199 Fourier transform interferometer or a Perkin-Elmer 883 spectrophotometer as solids (Nujol mull or CH_2Cl_2 cast) or CH_2Cl_2 solutions. Elemental analyses were performed by the microanalytical service within the department. The spectral data for all compounds are given in Table 1.

Preparation of Compounds. (a) $[Ir_2(CO)_2(\mu\text{-}I)(dppm)_2][SO_3CF_3]$ (2). To a CH_2Cl_2 solution of compound **1** (100 mg in 5 mL, 68 μmol) was added 7.8 μL of methyl triflate (68 μmol) causing the color of the solution to change from orange to burgundy immediately. Removal of the solvent and recrystallization from CH_2Cl_2/hexane gave a burgundy solid (yield 86%). The compound was very air sensitive, and the elemental analysis was not attempted.

(b) $[Ir_2(\eta^2\text{-}HCCH)(CO)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][SO_3CF_3]$ (3). To a CH_2Cl_2 solution of compound **2** (100 mg in 5 mL, 67 μmol) was added 5 mL of acetylene (0.2 mmol) at −78 °C causing the color of the solution to change from burgundy to yellow immediately. The solution was partially evacuated to remove excess acetylene, and 30 mL of hexane was slowly added to the solution to precipitate the pale yellow solid (80%). The solid was found to be stable for short periods at room temperature; however, the CH_2Cl_2 solution was not stable at ambient temperature and therefore the NMR sample was prepared at −78 °C. Characterization was by NMR and IR spectroscopies.

(c) $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CCH_2)(dppm)_2][SO_3CF_3]$ (4·SO_3CF_3). To a CH_2Cl_2 solution of compound **8** (100 mg, 67 μmol in 10 mL) was added 7.6 μL of $CF_3SO_3CH_3$ (67 μmol), and the solution was stirred for 1 h. Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave a yellow crystalline solid (yield 90%). Anal. Calcd for $Ir_2ISP_4F_3O_5C_{55}H_{46}$: C, 43.70; H, 3.05; I, 8.40. Found: C, 43.48; H, 2.91; I, 8.40.

(d) $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CCH_2)(dppm)_2][BF_4]$ (4·BF_4). To a CH_2Cl_2 solution of compound **8** (50 mg, 34 μmol in 5 mL) was added 6.6 mg of $AgBF_4$ (34 μmol), and the solution was stirred for 15 min and filtered to remove AgI. Removal of the solvent from the yellow filtrate and recrystallization from CH_2Cl_2/Et_2O gave a yellow crystalline solid (yield 84%). Anal. Calcd for $Ir_2IP_4F_4O_2BC_{54}H_{46}$: C, 44.75; H, 3.18. Found: C, 44.43; H, 3.12.

(e) $[Ir_2(\eta^2\text{-}HCCPh)(CO)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][SO_3CF_3]$ (5a,b). To a CD_2Cl_2 solution of compound **2** (10 mg in 0.5 mL in an NMR tube, 7 μmol) was added 3 μL of phenylacetylene (27 μmol) at −78 °C. The solution turned to yellow from burgundy, and the variable-temperature NMR experiments were undertaken. These species were characterized by NMR and IR techniques, showing two isomers (**5a,b**).

(f) $[Ir_2(\eta^2\text{-}HCCPh)(CO)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][SO_3CF_3]$ (5b). To a CH_2Cl_2 solution of compound **2** (50 mg in 5 mL, 34 μmol) was added 6 μL of phenylacetylene (54 μmol) at −78 °C. The solution turned to yellow from burgundy, and 30 mL of hexane was slowly added to the solution to precipitate the pale yellow solid (80%). The solid was found to be stable for short periods at room temperature; however the CH_2Cl_2 solution was not stable at ambient temperature and therefore the NMR sample was prepared at −78 °C. Characterization was by NMR and IR spectroscopies, showing only **5b**.

---

(10) Alt, H. G.; Engelhardt, H. E.; Rausch, M. D.; Kool, L. B. *J. Organomet. Chem.* **1987**, *329*, 61.

(11) Berry, D. H.; Eisenberg, R. *Organometallics* **1987**, *6*, 1796.

(12) Gamble, A. S.; Birdwhistell, K. R.; Templeton, J. L. *Organometallics* **1988**, *7*, 1046.

(13) Etienne, M.; Guerchais, J. E. *J. Chem. Soc., Dalton Trans.* **1989**, 2187.

(14) Gibson, V. C.; Parkin, G.; Bercaw, J. E. *Organometallics* **1991**, *10*, 220.

(15) Selnau, H. E.; Merola, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 4008.

(16) Etienne, M.; Talarmin, J.; Toupet, L. *Organometallics* **1992**, *11*, 2058.

(17) Fryzuk, M. D.; Huang, L.; McManus, N. T.; Paglia, P.; Rettig, S. J.; White, G. S. *Organometallics* **1992**, *11*, 2979.

(18) Wiedemann, R.; Steinert, P.; Schäfer, M.; Werner, H. *J. Am. Chem. Soc.* **1993**, *115*, 9864.

(19) (a) Ibach, H.; Lehwald, S. J. *J. Vac. Sci. Technol.* **1978**, *15*, 407. (b) Demuth, J. E. *Surf. Sci.* **1979**, *80*, 367. (c) Kesmodel, L. L.; Gates, J. A. *J. Electron. Spectrosc. Relat. Phenom.* **1983**, *29*, 307. (d) Koestner, R. J.; Frost, J. C.; Stair, P. C.; Van Hove, M. A.; Somorjai, G. A. *Surf. Sci.* **1982**, *116*, 85. (e) Hills, M. M.; Parmenter, J. E.; Weinberg, W. H. *J. Am. Chem. Soc.* **1987**, *109*, 597.

(20) McCandlish, L. E. *J. Catal.* **1983**, *83*, 362.

(21) Buchwald, S. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 5490.

(22) Trost, B. M.; Dyker, G.; Kulawiec, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 7809.

(23) Xiao, J.; Cowie, M. *Organometallics* **1993**, *12*, 463.

(24) Vaartstra, B. A.; Xiao, J.; Jenkins, J. A.; Verhagen, R.; Cowie, M. *Organometallics* **1991**, *10*, 2708.

Table 1. Spectroscopic Data for the Compounds[a]

compd	IR ($\mathrm{cm^{-1}}$)	NMR		
		$\delta(^{31}\mathrm{P}\{^1\mathrm{H}\})$	$\delta(^1\mathrm{H})$	$\delta(^{13}\mathrm{C}\{^1\mathrm{H}\})$
$[\mathrm{Ir_2(CO)_2(\mu\text{-}I)(dppm)_2}][\mathrm{SO_3CF_3}]$ (**2**)	1971 (st)[c]	10.4 (t, $^2J_{\mathrm{P(Ir)C}} = 5$ Hz)[d]	4.67 (m, 4H, $\mathrm{PCH_2P}$)[d]	166.8 (qui, CO, $^2J_{\mathrm{P(Ir)C}} = 5$ Hz)[d]
$[\mathrm{Ir_2(\eta^2\text{-}C_2H_2)(CO)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2}][\mathrm{SO_3CF_3}]$ (**3**)	1966 (vs),[b] 1824 (m), 1660 (w)	−4.4 (ddm, $\mathrm{P^1}$, $^2J_{\mathrm{P^1(Ir)C^1}} = 14$ Hz, $^2J_{\mathrm{P^1(Ir)C^{bri}}} = 4$ Hz),[g] −13.2 (dm, $\mathrm{P^2}$, $^2J_{\mathrm{P^2(Ir)C^{bri}}} = 4$ Hz)	4.98 (dd, $1\mathrm{H_b}$, $^1J_{\mathrm{CH_b}} = 234$ Hz, $^2J_{\mathrm{CCH_b}} = 24$ Hz, $H_\mathrm{b}\mathrm{CCH_a}$),[g] 4.11 (m, 2H, $\mathrm{PCH_2P}$), 3.90 (m, 2H, $\mathrm{PCH_2P}$), 3.42 (dd, $1\mathrm{H_a}$, $^1J_{\mathrm{CH_a}} = 237$ Hz, $^2J_{\mathrm{CCH_a}} = 26$ Hz, $\mathrm{H_bCC}H_\mathrm{a}$)	187.7 (ddm, $\mathrm{C^{bri}O}$, $^2J_{\mathrm{C^{bri}(Ir)C^1}} = 10$ Hz, $^2J_{\mathrm{C^{bri}(Ir)C_a}} = 7.5$ Hz),[g] 179.0 (dt, $\mathrm{C^1O}$, $^2J_{\mathrm{C^{bri}(Ir)C^1}} = 10$ Hz, $^2J_{\mathrm{P^1(Ir)C^1}} = 14$ Hz), 75.2 (dd, $\mathrm{C_a}$, $^1J_{\mathrm{C_aC_b}} = 102$ Hz, $^2J_{\mathrm{C^{bri}(Ir)C_a}} = 7.5$ Hz), 62.0 (d, $\mathrm{C_b}$, $^1J_{\mathrm{C_aC_b}} = 102$ Hz)
$[\mathrm{Ir_2(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}I)(dppm)_2}][\mathrm{SO_3CF_3}]$ (**4·SO$_3$CF$_3$**)	1949 (st),[b] 1588 (w); 1963 (st),[c] 1587 (w)	−7.9 (dt, $^2J_{\mathrm{Ca(Ir)P}} = 7$ Hz, $^2J_{\mathrm{C(Ir)P}} = 7$ Hz)[d]	4.63 (m, 2H, $\mathrm{PCH_2P}$),[d] 3.92 (m, 2H, $\mathrm{PCH_2P}$), 3.72 (d, $^1J_{\mathrm{C_\beta H}} = 161$ Hz, $\mathrm{CCH_2}$)	219.6 (dtm, $^1J_{\mathrm{C_\alpha C_\beta}} = 65$ Hz, $^2J_{\mathrm{C_\alpha(Ir)C}} = 9$ Hz, $\mathrm{CCH_2}$),[d] 181.7 (dquin, $^2J_{\mathrm{C_\alpha(Ir)C}} = 9$ Hz, $^2J_{\mathrm{P(Ir)C}} = 8$ Hz, CO), 129.9 (d, $^1J_{\mathrm{C_\alpha C_\beta}} =$ 65 Hz, $\mathrm{CCH_2}$)
$[\mathrm{Ir_2(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}I)(dppm)_2}][\mathrm{BF_4}]$ (**4·BF$_4$**)		−7.9 (d, $^2J_{\mathrm{Ca(Ir)P}} = 7$ Hz)[d]	4.60 (m, 2H, $\mathrm{PCH_2P}$),[d] 3.92 (m, 2H), $\mathrm{PCH_2P}$), 3.72 (d, $^1J_{\mathrm{C_\beta H}} = 161$ Hz, $\mathrm{CCH_2}$)	219.6 (dqui, $^1J_{\mathrm{C_\alpha C_\beta}} = 65$ Hz, $^2J_{\mathrm{P(Ir)C_\alpha}} =$ 7 Hz, $\mathrm{CCH_2}$),[d] 129.9 (d, $^1J_{\mathrm{C_\alpha C_\beta}} = 65$ Hz, $\mathrm{CCH_2}$)
$[\mathrm{Ir_2(\eta^2\text{-}PhCCH)(CO)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2}][\mathrm{SO_3CF_3}]$ (**5a**)		−2.7 (ddm, $\mathrm{P^1}$, $^2J_{\mathrm{P^1(Ir)C^1}} = 14$ Hz, $^2J_{\mathrm{P^1(Ir)C^{bri}}} = 4$ Hz),[h] −10.8 (dm, $\mathrm{P^2}$, $^2J_{\mathrm{P^2(Ir)C^{bri}}} = 4$ Hz)	4.30 (s, 1H, $\mathrm{PhCC}H$),[h] 3.92 (m, 2H, $\mathrm{PCH_2P}$), 3.81 (m, 2H, $\mathrm{PCH_2P}$)	190.2 (dquin, $1\mathrm{C^{bri}O}$, $^2J_{\mathrm{C^{bri}(Ir)C^1}} = 8$ Hz, $^2J_{\mathrm{P^1(Ir)C^{bri}}} = {}^2J_{\mathrm{P^2(Ir)C^{bri}}} = 4$ Hz),[h] 179.2 (dt, $1\mathrm{C^1O}$, $^2J_{\mathrm{C^{bri}(Ir)C^1}} = 8$ Hz, $^2J_{\mathrm{P^1(Ir)C^1}} =$ 14 Hz)
$[\mathrm{Ir_2(\eta^2\text{-}PhCCH)(CO)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2}][\mathrm{SO_3CF_3}]$ (**5b**)	1977 (w),[b] 1965 (vs), 1810 (st)	−4.7 (ddm, $\mathrm{P^1}$, $^2J_{\mathrm{P^1(Ir)C^1}} = 15$ Hz, $^2J_{\mathrm{P^1(Ir)C^{bri}}} = 4$ Hz),[d] −19.1 (dm, $\mathrm{P^2}$, $^2J_{\mathrm{P^2(Ir)C^{bri}}} = 4$ Hz)	5.39 (s, 1H, $\mathrm{PhCC}H$),[d] 4.20 (m, 2H, $\mathrm{PCH_2P}$), 3.88 (m, 2H, $\mathrm{PCH_2P}$)	188.3 (dquin, $1\mathrm{C^{bri}O}$, $^2J_{\mathrm{C^{bri}(Ir)C^1}} = 11$ Hz, $^2J_{\mathrm{P^1(Ir)C^{bri}}} = {}^2J_{\mathrm{P^2(Ir)C^{bri}}} = 4$ Hz),[d] 179.2 (dt, $1\mathrm{C^1O}$, $^2J_{\mathrm{C^{bri}(Ir)C^1}} = 11$ Hz, $^2J_{\mathrm{P^1(Ir)C^1}} = 15$ Hz)
$[\mathrm{Ir_2(CO)_2(\mu\text{-}CC(H)Ph)(\mu\text{-}I)(dppm)_2}][\mathrm{SO_3CF_3}]$ (**6**)	1972 (vs),[b] 1589 (w); 1968 (vs),[c] 1590 (w)	−5.2 (m),[d] −8.5 (m)	5.08 (s, 1H, $\mathrm{CC(}H\mathrm{)Ph}$),[d] 4.54 (m, 2H, $\mathrm{PCH_2P}$), 3.90 (m, 2H, $\mathrm{PCH_2P}$)	220.7 (m, $C\mathrm{C(H)Ph}$),[d] 182.5 (t, $^2J_{\mathrm{P(Ir)C}} =$ 15 Hz, CO), 181.5 (t, $^2J_{\mathrm{P(Ir)C}} = 15$ Hz, CO), 129.2 (s, $\mathrm{C}C\mathrm{(H)Ph}$)
$[\mathrm{Ir_2(\eta^2\text{-}H_2CCCH_2)(CO)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2}][\mathrm{SO_3CF_3}]$ (**7a·SO$_3$CF$_3$**)	1965 (st),[b] 1801 (st); 1978 (st),[c] 1815 (m)	−7.1 (m),[d] −10.5 (m)	5.95 (m, 1H),[d] 5.34 (m, 1H), 4.30 (m, 2H), 4.01 (m, 2H), 1.33 (m, 2H)	189.9 (dquin, 1CO),[d] 179.9 (dt, 1CO)
$[\mathrm{Ir_2(\eta^2\text{-}H_2CCCH_2)(CO)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2}][\mathrm{I}]$ (**7a·I**)	1963 (st),[b] 1801 (m); 1983 (st),[c] 1819 (m)	−6.9 (m, $\mathrm{P^1}$),[d] −10.4 (m, $\mathrm{P^2}$)	5.93 (dt, $1\mathrm{H_a}$, $^2J_{\mathrm{gem}} = 2.4$ Hz, $^4J_{\mathrm{H_aH_c}} = 3.4$ Hz, $\mathrm{(H_c)_2CCC}H_\mathrm{a}\mathrm{H_b}$),[d] 5.33 (dt, $1\mathrm{H_b}$, $^2J_{\mathrm{gem}} = 2.4$ Hz, $^4J_{\mathrm{H_bH_c}} =$ 3.4 Hz, $\mathrm{(H_c)_2CCCH_a}H_\mathrm{b}$), 4.29 (m, 2H, $\mathrm{PCH_2P}$), 4.08 (m, 2H, $\mathrm{PCH_2P}$), 1.31 (ddt, $2\mathrm{H_c}$, $^3J_{\mathrm{P^2(Ir)CH_c}} = 7$ Hz, $(H_\mathrm{c})_2\mathrm{CCCH_aH_b}$)	189.9 (dquin, $\mathrm{C^{bri}O}$, $^2J_{\mathrm{C^1(Ir)C^{bri}}} = 8$ Hz),[d] $^2J_{\mathrm{P(Ir)C^{bri}}} = 6.5$ Hz), 179.9 (dt, $\mathrm{C^1O}$, $^2J_{\mathrm{C^1(Ir)C^{bri}}} = 8$ Hz, $^2J_{\mathrm{P^1(Ir)C^1}} = 14$ Hz)
$[\mathrm{Ir_2(\eta^2\text{-}H_2CCCH_2)(CO)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2}][\mathrm{SO_3CF_3}]$ (**7b·SO$_3$CF$_3$**)	1921 (st),[b] 1760 (st)	−7.2 (m),[d] −8.2 (m)	5.26 (m, 1H, $\mathrm{(H_c)_2CCC}H_\mathrm{a}\mathrm{H_b}$),[d] 4.27 (m, 2H, $\mathrm{PCH_2P}$), 4.05 (m, 2H, $\mathrm{PCH_2P}$), 2.70 (m, 2H, $(H_\mathrm{c})_2\mathrm{CCCH_aH_b}$)	190.4 (dquin, $\mathrm{C^{bri}O}$, $^2J_{\mathrm{C^1(Ir)C^{bri}}} = 10$ Hz, $^2J_{\mathrm{P(Ir)C^{bri}}} = 6$ Hz),[d] 179.9 (dt, $\mathrm{C^1O}$, $^2J_{\mathrm{C^1(Ir)C^{bri}}} = 10$ Hz, $^2J_{\mathrm{P(Ir)C^1}} = 12$ Hz)
$[\mathrm{Ir_2(\eta^2\text{-}H_2CCCH_2)(CO)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2}][\mathrm{I}]$ (**7b·I**)		−7.1 (m),[d] −8.1 (m)	5.25 (m, 1H, $\mathrm{(H_c)_2CCC}H_\mathrm{a}\mathrm{H_b}$),[d] 4.28 (m, 2H, $\mathrm{PCH_2P}$), 4.10 (m, 2H, $\mathrm{PCH_2P}$), 2.67 (m, 2H, $(H_\mathrm{c})_2\mathrm{CCCH_aH_b}$)	
$[\mathrm{Ir_2I_2(CO)_2(\mu\text{-}CCH_3)(dppm)_2}][\mathrm{SO_3CF_3}]$ (**10·SO$_3$CF$_3$**)		−14.7 (m),[g] −20.3 (m)	4.78 (m, 2H),[g] 4.56 (m, 2H), 4.00 (d, 3H, $^1J_{\mathrm{C_\beta H}} = 128$ Hz)	
$[\mathrm{Ir_2I_2(CO)_2(\mu\text{-}CCH_3)(dppm)_2}][\mathrm{BF_4}]$ (**10·BF$_4$**)		−14.9 (m, $\mathrm{P^1}$),[g] −20.3 (m, $\mathrm{P^2}$)	4.73 (m, 2H, $\mathrm{PCH_2P}$),[g] 4.51 (m, 2H, $\mathrm{PCH_2P}$), 3.99 (d, 3H, $^1J_{\mathrm{C_\beta H}} = 128$ Hz, $\mathrm{CCH_3}$)	409.1 (dd, $^1J_{\mathrm{C_\alpha C_\beta}} = 23$ Hz, $^2J_{\mathrm{C_\alpha(Ir)C^2}} = 23$ Hz, $C_\alpha\mathrm{C_\beta H_3}$),[g] 179.0 (dt, $^2J_{\mathrm{C_\alpha(Ir)C^2}} = 23$ Hz, $^2J_{\mathrm{P^2(Ir)C^2}} = 15$ Hz, $\mathrm{C_2O}$), 166.5 (t, $^2J_{\mathrm{P^1(Ir)C^1}} =$ 10 Hz, $\mathrm{C_1O}$), 68.5 (d, $^1J_{\mathrm{C_\alpha C_\beta}} = 23$ Hz, $\mathrm{C_\alpha}C_\beta\mathrm{H_3}$)

[Ir$_2$I$_2$(CO)$_2$(μ-CCH$_2$)(μ-H)(dppm)$_2$][SO$_3$CF$_3$] (**11·SO$_3$CF$_3$**)	2066 (st),[b] 2020 (st), 1605 (w); 2081 (st),[c] 2028 (st), 1594 (w)	−21.2 (m),[d] −48.2 (m)	8.18 (d, 1H, $^2J_{\text{gem}}$ = 7 Hz),[d] 5.02 (m, 2H), 4.13 (m, 2H), −12.47 (b, 1H)	
[Ir$_2$I$_2$(CO)$_2$(μ-CCH$_2$)(μ-H)(dppm)$_2$][BF$_4$] (**11·BF$_4$**)		−21.3 (m),[d] −48.2 (m)	8.17 (dd, 1H, $^1J_{C\beta H}$ = 156 Hz, $^2J_{\text{gem}}$ = 7 Hz, CCH$_2$),[d] 5.01 (m, 2H, PCH$_2$P), 4.12 (m, 2H, PCH$_2$P), −12.48 (b, 1H, hydrido)	187.5 (ddqui, C$_\alpha$ $^1J_{C\alpha C\beta}$ = 70 Hz, $^2J_{C\alpha(Ir)C}$ = 26 Hz, $^2J_{P(Ir)C}$ = 7 Hz, *C*CH$_2$),[d] 167.9 (t, $^2J_{P(Ir)C}$ = 12 Hz, CO), 166.3 (dt, $^2J_{C\alpha(Ir)C}$ = 26 Hz, $^2J_{P(Ir)C}$ = 9 Hz, CO), 132.3 (d, $^1J_{C\alpha C\beta}$ = 70 Hz, C$_\beta$, C*C*H$_2$)
[Ir$_2$I(CN-*t*-Bu)(CO)$_2$(μ-CCH$_2$)(dppm)$_2$][SO$_3$CF$_3$] (**12**)	2184 (st),[c] 1990 (sh), 1976 (vs), 1585 (w)	−20.4 (m, P^1),[d] −22.8 (m, P^2)	6.75 (d, 2H, $^1J_{C\beta H}$ = 157 Hz, CCH$_2$),[d] 6.05 (m, 2H, PCH$_2$P), 4.49 (m, 2H, PCH$_2$P), 0.89 (s, 9H, CN-*t*-Bu)	188.3 (ddqui, C$_\alpha$ $^1J_{C\alpha C\beta}$ = 67 Hz, $^2J_{C\alpha(Ir)C^1}$ = 3 Hz, $^2J_{P(Ir)C\alpha}$ = 5 Hz, *C*CH$_2$),[d] 172.9 (ddt, C^{1}O, $^3J_{C^1C^2}$ = 8 Hz, $^2J_{C\alpha(Ir)C^1}$ = 3 Hz, $^2J_{P^1(Ir)C^1}$ = 8 Hz), 166.3 (dt, C^{2}O, $^3J_{C^1C^2}$ = 8 Hz, $^2J_{P^2(Ir)C^2}$ = 8 Hz), 132.0 (d, $^1J_{C\alpha C\beta}$ = 67 Hz, C$_\beta$, C*C*H$_2$)
[Ir$_2$I(CO)$_3$(μ-CCH$_2$)(dppm)$_2$][SO$_3$CF$_3$] (**13**)	2060 (st),[c] 2015 (vs), 1985 (vs), 1586 (w)	−21.2 (m),[d] −23.5 (m)	6.88 (dd, 1H, $^1J_{C\beta H}$ = 158 Hz, $^2J_{\text{gem}}$ = 6 Hz, CCH$_2$),[d] 6.77 (dd, 1H, $^1J_{C\beta H}$ = 158 Hz, $^2J_{\text{gem}}$ = 6 Hz, CCH$_2$), 5.56 (m, 2H, PCH$_2$P), 4.43 (m, 2H, PCH$_2$P)	188.3 (ddm(dd), C$_\alpha$, $^1J_{C\alpha C\beta}$ = 67 Hz, $^2J_{C\alpha(Ir)C}$ = 15 Hz, $^2J_{P(Ir)C\alpha}$ = 7 Hz, *C*CH$_2$),[d] 174.1 (dt(dd), CO, $^2J_{C\alpha(Ir)C}$ = 15 Hz, $^2J_{P(Ir)C}$ = 9 Hz), 170.0 (t(ddd), CO, $^2J_{P(Ir)C}$ = 9 Hz), 162.4 (t(ddd), CO, $^2J_{P(Ir)C}$ = 8 Hz), 131.4 (d, C*C*H$_2$, $^1J_{C\alpha C\beta}$ = 67 Hz)
[Ir$_2$I(CO)$_2$(μ-HCCH)(μ-CC(H)Ph)(dppm)$_2$][SO$_3$CF$_3$] (**14·SO$_3$CF$_3$**)	2054 (sh),[b] 2040 (st), 1592 (w); 2051 (sh),[c] 2034 (st), 1598 (w)	−9.4 (m, P^1),[d] −33.0 (m, P^2)	8.60 (d, 1H, $^1J_{CbH}$ = 146 Hz, HC*CH*),[d] 8.53 (s, 1H, CC(*H*)Ph), 4.46 (m, 2H, PCH$_2$P), 2.87 (m, 2H), PCH$_2$P)	177.3 (t, $^2J_{P^1(Ir)C^1}$ = 6 Hz, C^{1}O),[d] 169.2 (dt, $^2J_{Cb(Ir)C^2}$ = 30 Hz, $^2J_{P^2(Ir)C^2}$ = 9 Hz, C^{2}O), 133.8 (ddtt, $^1J_{CaCb}$ = 60 Hz, $^2J_{Cb(Ir)C^2}$ = 30 Hz, $^2J_{P^2(Ir)Cb}$ = 11 Hz, $^2J_{P^1(Ir)Cb}$ = 6.5 Hz, HC$_a$*C*$_b$H), 120.8 (dqui, $^1J_{CaCb}$ = 60 Hz, $^2J_{P^1(Ir)Ca}$ = $^2J_{P^2(Ir)Ca}$ = 7.5 Hz, H*C*$_a$C$_b$H)
[Ir$_2$I(CO)$_2$(μ-HCCH)(μ-CC(H)Ph)(dppm)$_2$][BPh$_4$] (**14·BPh$_4$**)		−9.4 (m),[d] −33.0 (m)	8.61 (s),[d] 8.54 (s, 1H), 4.46 (m, 2H), 2.81 (m, 2H)	
[Ir$_2$I$_2$(CO)$_2$(μ-HCCH)(μ-CC(H)Ph)(dppm)$_2$] (**15**)	2027 (vs),[b] 1587 (w); 2023 (vs),[c] 1590 (w)	−29.9 (m, P^1),[d] −33.6 (m, P^2)	9.55 (dm, 1H, $^1J_{CH}$ = 146 Hz, *H*CCH),[d] 9.00 (dm, 1H, $^1J_{CH}$ = 146 Hz, HCC*H*), 8.41 (s, 1H, CC(H)Ph), 4.83 (m, 2H, PCH$_2$P), 2.87 (m, 2H, PCH$_2$P)	173.0 (dt, $^2J_{Ca(Ir)C^1}$ = 29 Hz, $^2J_{P^1(Ir)C^1}$ = 5 Hz, C^{1}O),[d] 172.5 (dt, $^2J_{Cb(Ir)C^2}$ = 28 Hz, $^2J_{P^2(Ir)C^2}$ = 5 Hz, C^{2}O), 147.7 (ddtt, $^1J_{CaCb}$ = 53 Hz, $^2J_{C^2(Ir)Cb}$ = 29 Hz, $^2J_{P^2(Ir)Cb}$ = 9 Hz, $^2J_{P^1(Ir)Cb}$ = 6.5 Hz, HC$_a$*C*$_b$H), 144.1 (ddtt, $^1J_{CaCb}$ = 53 Hz, $^2J_{C^1(Ir)Ca}$ = 29 Hz, $^2J_{P^1(Ir)Ca}$ = 9 Hz, $^2J_{P^2(Ir)Ca}$ = 6 Hz, H*C*$_a$C$_b$H)
[Ir$_2$I(CO)$_3$(μ-HCCH)(μ-CC(H)Ph)(dppm)$_2$]-[SO$_3$CF$_3$] (**16**)	2092 (st),[c] 2052 (st), 2046 (st)	−20.3 (m),[d] −30.0 (m)	9.91 (m, 1H, HCC*H*),[d] 8.57 (m, 1H, HCC*H*), 4.73 (m, 2H), PCH$_2$P), 3.03 (m, 2H, PCH$_2$P)	171.6 (t, $^2J_{P(Ir)C}$ = 5 Hz, 1CO),[d] 164.6 (t, $^2J_{P(Ir)C}$ = 6 Hz, 1CO), 162.8 (t, $^2J_{P(Ir)C}$ = 5 Hz, 1CO)
[Ir$_2$(CO)$_4$(μ-HCCH)(μ-CC(H)Ph)(dppm)$_2$]-[SO$_3$CF$_3$]$_2$ (**17**)	2101 (st),[c] 2067 (st)	−19.8 (m),[d] −20.6 (m)	9.06 (m, 1H, HCC*H*),[d] 8.70 (b, 1H, CC(*H*)Ph), 8.31 (m, 1H, HCC*H*), 4.43 (m, 2H, PCH$_2$P), 3.79 (m, 2H, PCH$_2$P)	164.6 (t, $^2J_{P(Ir)C}$ = 5 Hz, 1CO),[d] 163.4 (t, $^2J_{P(Ir)C}$ = 6 Hz, 1CO), 162.9 (t, $^2J_{P(Ir)C}$ = 5 Hz, 1CO), 162.6 (t, $^2J_{P(Ir)C}$ = 5 Hz, 1CO)
[Ir$_2$I(CO)$_2$(μ-HCCPh)(μ-CC(H)Ph)(dppm)$_2$]-[SO$_3$CF$_3$] (**18**)	2071 (m),[c] 1967 (st)	−7.9 (m),[d] −36.1 (m)	8.60 (s, 1H, CC(*H*)Ph),[d] 7.95 (s, 1H, *H*CCPh), 4.12 (m, 2H, PCH$_2$P), 3.12 (m, 2H, PCH$_2$P)	181.1 (t, $^2J_{P(Ir)C}$ = 11 Hz, CO),[d] 162.9 (t, $^2J_{P(Ir)C}$ = 8 Hz, CO)
[Ir$_2$I(CCH$_2$)(CC(H)Ph)(CO)$_2$(dppm)$_2$][SO$_3$CF$_3$] (**19·SO$_3$CF$_3$**)	2065 (m),[b] 1991 (st), 1580 (w); 2064 (m),[c] 1989 (st), 1577 (w)	−7.8 (dm, P^1, $^2J_{P^1(Ir)C^1}$ = 10 Hz),[g] −34.8 (ddm, P^2, $^2J_{P^2(Ir)C\alpha}$ = 9 Hz, $^2J_{P^2(Ir)C^2}$ = 9 Hz)	8.20 (d, 1H, $^4J_{C^1(Ir)CCH}$ = 4 Hz, CC(*H*)Ph),[d] 6.54 (ddt, 1H, $^1J_{C\beta H}$ = 157 Hz, $^2J_{\text{gem}}$ = 10 Hz, $^4J_{P(Ir)CCH}$ = 2 Hz, CCH$_2$), 6.04 (ddt, 1H, $^1J_{C\beta H}$ = 157 Hz, $^2J_{\text{gem}}$ = 10 Hz, $^4J_{P(Ir)CCH}$ = 2 Hz, CCH$_2$), 4.40 (m, 2H, PCH$_2$P), 3.02 (m, 2H, PCH$_2$P)	179.9 (t, $^2J_{P^1(Ir)C^1}$ = 10 Hz, C^{1}O),[d] 174.6 (ddt, $^1J_{C\alpha C\beta}$ = 64 Hz, $^2J_{C\alpha(Ir)C^2}$ = 35 Hz, $^2J_{P^2IrC\alpha}$ = 10 Hz, *C*CH$_2$), 174.3 (m, *C*C(H)Ph), 163.8 (dt, $^2J_{C\alpha(Ir)C^2}$ = 35 Hz, $^2J_{P^2(Ir)C^2}$ = 9 Hz, C^{2}O), 143.9 (s, C*C*(H)Ph), 133.6 (d, $^1J_{C\alpha C\beta}$ = 64 Hz, C*C*H$_2$)

Table 1 (Continued)

		NMR		
compd	IR ($\mathrm{cm^{-1}}$)	$\delta(^{31}\mathrm{P}\{^1\mathrm{H}\})$	$\delta(^1\mathrm{H})$	$\delta(^{13}\mathrm{C}\{^1\mathrm{H}\})$
$\mathrm{[Ir_2I(CCH_2)(CC(H)Ph)(CO)_2(dppm)_2]\text{-}[BF_4]}$ (**19·BF$_4$**)		-8.0 (m, $\mathrm{P^1}$),[d] -34.8 (dm, $\mathrm{P^2}$, $^2J_{\mathrm{P^2(Ir)C\alpha}} = 10$ Hz)	8.20 (s, 1H, $\mathrm{CC(\mathit{H})Ph}$),[d] 6.54 (ddt, 1H, $\mathrm{CCH_2}$), 6.04 (ddt, 1H, $\mathrm{CCH_2}$), 4.39 (m, 2H, $\mathrm{PCH_2P}$), 2.98 (m, 2H, $\mathrm{PCH_2P}$)	174.6 (dt, $^1J_{\mathrm{C\alpha C\beta}} = 64$ Hz, $^2J_{\mathrm{P^2IrC\alpha}} = 10$ Hz, $\mathit{C}\mathrm{CH_2}$),[d] 133.7 (d, $^1J_{\mathrm{C\alpha C\beta}} = 64$ Hz, $\mathrm{C}\mathit{C}\mathrm{H_2}$)
$\mathrm{[Ir_2I_2(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}CC(H)Ph)(dppm)_2]}$ (**20a**)	2027 (st),[c]	-32.3 (m),[d] -37.7 (m)	9.19 (d, 1H, $^1J_{\mathrm{C\beta H}} = 153$ Hz, $\mathrm{CCH_2}$),[d] 9.16 (d, 1H, $^1J_{\mathrm{C\beta H}} = 153$ Hz, $\mathrm{CCH_2}$), 4.65 (m, 2H, $\mathrm{PCH_2P}$), 2.45 (m, 2H, $\mathrm{PCH_2P}$)	171.9 (dt, $^2J_{\mathrm{C\alpha(Ir)C}} = 27$ Hz, $^2J_{\mathrm{P(Ir)C}} = 7$ Hz, CO),[g] 170.4 (dt, $^2J_{\mathrm{C\alpha(Ir)C}} = 27$ Hz, $^2J_{\mathrm{P(Ir)C}} = 5$ Hz, CO), 143.3 (d, $^1J_{\mathrm{C\alpha C\beta}} = 61$ Hz, $\mathit{C}\mathrm{CH_2}$), 102.2 (dtm, $^1J_{\mathrm{C\alpha C\beta}} = 61$ Hz, $^2J_{\mathrm{Ca(Ir)C}} = 27$ Hz, $\mathrm{C}\mathit{C}\mathrm{H_2}$)
$\mathrm{[Ir_2I_2(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}CC(H)(Ph)(dppm)_2]}$ (**20b**)	2009 (st),[b]	-9.6 (m),[i] -10.3 (m), -31.3 (m), -36.5 (m)		174.7 (dt, $^2J_{\mathrm{C\alpha(Ir)C}} = 30$ Hz, $^2J_{\mathrm{P(Ir)C}} = 8$ Hz, CO),[g] 172.7 (t, $^2J_{\mathrm{P(Ir)C}} = 8$ Hz, CO), 133.0 (d, $^1J_{\mathrm{C\alpha C\beta}} = 61$ Hz, $\mathit{C}\mathrm{CH_2}$), 102.2 (m, $\mathrm{C}\mathit{C}\mathrm{H_2}$)
$\mathrm{[Ir_2I(CO)_3(\mu\text{-}CCH_2)(\mu\text{-}CC(H)Ph)(dppm)_2]\text{-}[SO_3CF_3]}$ (**21a**)	2094 (st),[c] 2050 (st), 2034 (sh)	-19.4 (m, $\mathrm{P^1}$),[e] -33.3 (m, $\mathrm{P^2}$)	8.81 (d, 1H, $^1J_{\mathrm{CbH}} = 157$ Hz, $\mathrm{CCH_2}$),[g] 8.14 (d, 1H, $^1J_{\mathrm{CbH}} = 157$ Hz, $\mathrm{CCH_2}$), 4.01 (m, 2H, $\mathrm{PCH_2P}$), 3.26 (m, 2H, $\mathrm{PCH_2P}$)	171.4 (dt, $^2J_{\mathrm{C\alpha(Ir)C^2}} = 31$ Hz, $^2J_{\mathrm{P^2(Ir)C^2}} = 7$ Hz, $\mathrm{C^2O}$),[g] 166.7 (t, $^2J_{\mathrm{P^1(Ir)C^1}} = 6$ Hz, $\mathrm{C^1O}$), 164.4 (dt, $^2J_{\mathrm{C\alpha(Ir)C^1}} = 21$ Hz, $^2J_{\mathrm{P^1(Ir)C^1}} = 5$ Hz, $\mathrm{C^1O}$), 141.9 (d, $^1J_{\mathrm{C\alpha C\beta}} = 60$ Hz, $\mathit{C}\mathrm{CH_2}$), 101.0 (m, $\mathrm{C}\mathit{C}\mathrm{H_2}$)
$\mathrm{[Ir_2I(CO)_3(\mu\text{-}CCH_2)(\mu\text{-}CC(H)Ph)(dppm)_2]\text{-}[SO_3CF_3]_2}$ (**21b**)		-20.7 (m, $\mathrm{P^1}$),[e] -30.7 (m, $\mathrm{P^2}$)	8.72 (d, 1H, $^1J_{\mathrm{C\beta H}} = 152$ Hz, $\mathrm{CCH_2}$),[g] 8.18 (d, 1H, $^1J_{\mathrm{C\beta H}} = 152$ Hz, $\mathrm{CCH_2}$), 4.26 (m, 2H, $\mathrm{PCH_2P}$), 3.26 (m, 2H, $\mathrm{PCH_2P}$)	170.0 (dt, $^2J_{\mathrm{C\alpha(Ir)C^2}} = 32$ Hz, $^2J_{\mathrm{P^2(Ir)C^2}} = 7$ Hz, $\mathrm{C^2O}$),[g] 166.2 (t, $^2J_{\mathrm{P(Ir)C^1}} = 9$ Hz, $\mathrm{C^1O}$), 164.0 (dt, $^2J_{\mathrm{C\alpha(Ir)C^3}} = 22$ Hz, $^2J_{\mathrm{P^1(Ir)C^3}} = 5$ Hz, $\mathrm{C^3O}$), 142.8 (d, $^1J_{\mathrm{C\alpha C\beta}} = 60$ Hz, $\mathit{C}\mathrm{CH_2}$), 99.8 (m, $\mathrm{C}\mathit{C}\mathrm{H_2}$)
$\mathrm{[Ir_2(CO)_4(\mu\text{-}CCH_2)(\mu\text{-}CC(H)Ph)(dppm)_2]\text{-}[SO_3CF_3]}$ (**22**)	2102 (st),[c] 2066 (st)	-17.4 (m),[d] -19.1 (m)	8.19 (t, 1H, $^4J_{\mathrm{C(Ir)CCH}} = 5.5$ Hz, $\mathrm{CC(\mathit{H})Ph}$),[d] 7.94 (dd, 1H, $^1J_{\mathrm{CH}} = 148$ Hz, $^2J_{\mathrm{gem}} = 2.5$ Hz, $\mathrm{CCH_2}$), 7.82 (dd, 1H, $^1J_{\mathrm{CH}} = 148$ Hz, $^2J_{\mathrm{gem}} = 2.5$ Hz, $\mathrm{CCH_2}$), 4.60 (m, 2H), $\mathrm{PCH_2P}$), 3.90 (m, 2H, $\mathrm{PCH_2P}$)	165.8 (dt, $^2J_{\mathrm{C\alpha(Ir)C}} = 26$ Hz, $^2J_{\mathrm{P(Ir)C}} = 6$ Hz, 1CO),[d] 165.7 (dt, $^2J_{\mathrm{Ca(Ir)C}} = 26$ Hz, $^2J_{\mathrm{P(Ir)C}} = 6$ Hz, 1CO), 164.7 (t, $^2J_{\mathrm{P(Ir)C}} = 6$ Hz, CO), 164.1 (t, $^2J_{\mathrm{P(Ir)C}} = 7$ Hz, CO), 142.6 (d, $^1J_{\mathrm{C\alpha C\beta}} = 61$ Hz, $\mathit{C}\mathrm{CH_2}$), 98.2 (dtqui, $^1J_{\mathrm{C\alpha C\beta}} = 61$ Hz, $^2J_{\mathrm{C\alpha(Ir)C}} = 26$ Hz, $^2J_{\mathrm{P(Ir)C\alpha}} = 8$ Hz, $\mathrm{C}\mathit{C}\mathrm{H_2}$)
$\mathrm{[Ir_2(CH_3)_2(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}CC(H)Ph)\text{-}(dppm)_2]}$ (**23**)		-10.7 (m, $\mathrm{P^1}$),[d] -12.8 (m, $\mathrm{P^2}$)	-0.45 (t, 3H, $^3J_{\mathrm{P^2(Ir)CH}} = 4.5$ Hz, $\mathrm{CH_3}$),[d] -0.92 (t, 3H, $^3J_{\mathrm{P^1(Ir)CH}} = 4.5$ Hz, $\mathrm{CH_3}$)	177.9 (dt, $^2J_{\mathrm{C\alpha(Ir)C}} = 26$ Hz, $^2J_{\mathrm{P(Ir)C}} = 9$ Hz, 1CO),[d] 177.5 (t, 1CO, $^2J_{\mathrm{P(Ir)C}} = 6$ Hz), 133.4 (d, $^1J_{\mathrm{C\alpha C\beta}} = 59$Hz, $\mathit{C}\mathrm{CH_2}$), 106.0 (m, $\mathrm{C}\mathit{C}\mathrm{H_2}$)

[a] Abbreviations used are as follows. IR: w = weak; m = medium; st = strong; vs = very strong. NMR: s = singlet; d = doublet; t = triplet; q = quartet; qui = quintet; m = multiplet; b = broad; or any combination; bri = bridging. In all samples, except where noted in the text, the NMR data are for $^{13}\mathrm{CO}$, $^{13}\mathrm{C{=}^{13}CH_2}$, and $\mathrm{H^{13}C{\equiv}^{13}CH}$ groups; however, IR results are for the natural abundance samples. [b] Nujol mull. [c] $\mathrm{CH_2Cl_2}$ solution. [d] 22 °C. [e] 0 °C. [f] −20 °C. [g] −40 °C. [h] −60 °C. [i] −80 °C.

(g) $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CC(H)Ph)(dppm)_2][SO_3CF_3]$ (6). To a CH_2Cl_2 solution of compound **9** (100 mg, 64 μmol of 5 mL) was added 15 μL of $CF_3SO_3CH_3$ (128 μmol), and the solution was stirred for 0.5 h, resulting in a color change from yellow to orange. Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave a yellow crystalline solid (yield 85%). Anal. Calcd for $Ir_2ISP_4F_3O_5C_{61}H_{50}$: C, 46.15; H, 3.15. Found: C, 45.76; H, 3.03.

(h) $[Ir_2(\eta^2\text{-}H_2CCCH_2)(CO)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][SO_3CF_3]$ (7a·SO_3CF_3 and 7b·SO_3CF_3). To a CH_2Cl_2 solution of compound **2** (50 mg in 5 mL, 34 μmol) was added 5 mL of allene (0.2 mmol). The color of the solution changed from burgundy to light yellow immediately. Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave a pale yellow solid (yield 90%). The ^{31}P NMR showed a ratio of *ca* 2:1 of **7a·SO_3CF_3** and **7b·SO_3CF_3**, respectively. Elemental analyses were not carried out on this species but were done instead for the iodide salts which have essentially identical spectroscopic parameters.

(i) $[Ir_2(\eta^2\text{-}H_2CCCH_2)(CO)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][I]$ (7a·I and 7b·I). To a CH_2Cl_2 solution of compound **1** (50 mg in 5 mL, 34 μmol) was added 5 mL of allene (0.2 mmol). The solution was stirred for 1 h, during which time the yellow color of the solution lightened. Removal of the solvent and recrystallization from THF/Et_2O gave a pale yellow solid (yield 84%). The ^{31}P NMR showed a ratio of *ca* 10:1 of **7a·I** and **7b·I**, respectively. Anal. Calcd for $Ir_2I_2P_4O_2C_{55}H_{48}$: C, 43.94; H, 3.20. Found: C, 44.58; H, 3.36.

(j) $[Ir_2I_2(CO)_2(\mu\text{-}CCH_3)(dppm)_2][SO_3CF_3]$ (10·SO_3CF_3). To a CD_2Cl_2 solution of compound **8** (10 mg in 0.5 mL in an NMR tube, 7 μmol) was added 1 μL of CF_3SO_3H (11 μmol at −78 °C. The compound was characterized by NMR experiments at −40 °C.

(k) $[Ir_2I_2(CO)_2(\mu\text{-}CCH_3)(dppm)_2][BF_4]$ (10·BF_4). To a CD_2Cl_2 solution of compound **1** (5 mg in 0.5 mL in an NMR tube, 3.4 μmol) was added 1 μL of $HBF_4{\cdot}Me_2O$ (8 μmol) at −78 °C. The NMR characterization was undertaken at −40 °C.

(l) $[Ir_2I_2(CO)_2(\mu\text{-}CCH_2)(dppm)_2][SO_3CF_3]$ (11·SO_3CF_3). To a CH_2Cl_2 solution of compound **8** (50 mg in 0.5 mL, 34 μmol) was added 3 μL of CF_3SO_3H (34 μmol). Removal of the solvent and recrystallization from THF/Et_2O gave a yellow solid (yield 90%). Anal. Calcd for $Ir_2I_2P_4SF_3O_5C_{55}H_{47}{\cdot}C_4H_8O$: C, 41.40; H, 3.22. Found: C, 41.27; H, 2.95. The 1 equiv of THF was verified from the ^1H NMR spectrum.

(m) $[Ir_2I_2(CO)_2(\mu\text{-}H)(\mu\text{-}CCH_2)(dppm)_2][BF_4]$ (11·BF_4). To a CH_2Cl_2 solution of compound **8** (50 mg in 0.5 mL, 34 μmol) was added 4.2 μL of $HBF_4{\cdot}Me_2O$ (34 μmol). Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave a yellow solid (yield 82%).

(n) $[Ir_2I(t\text{-}BuNC)(CO)_2(\mu\text{-}CCH_2)(dppm)_2][SO_3CF_3]$ (12). To a CH_2Cl_2 solution of compound **4a** (50 mg, 33 μmol in 5 mL) was added 5 μL of *tert*-butyl isocyanide (43 μmol), and the solution was stirred for 0.5 h, during which time the yellow color lightened. Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave a pale yellow solid (yield 96%). Anal. Calcd for $Ir_2ISP_4F_3O_5NC_{60}H_{55}$: C, 45.20; H, 3.45. Found: C, 45.12; H, 3.26.

(o) $[Ir_2I(CO)_3(\mu\text{-}CCH_2)(dppm)_2][SO_3CF_3]$ (13). A CH_2Cl_2 solution of compound **4·SO_3CF_3** (50 mg, 33 μmol in 5 mL) was put under CO (1 atm), and the solution was stirred for 0.5 h, during which time the yellow color lightened. Removal of the solvent under a stream of CO and recrystallization from CH_2Cl_2/Et_2O gave a pale yellow solid (yield 90%). An elemental analysis was not obtained for this compound owing to reversible CO loss regenerating **4·SO_3CF_3**.

(p) $[Ir_2I(CO)_2(\mu\text{-}HCCH)(\mu\text{-}CC(H)Ph)(dppm)_2][SO_3CF_3]$ (14·SO_3CF_3). To a CH_2Cl_2 solution of compound **6** (100 mg, 63 μmol in 5 mL) was added 10 mL of C_2H_2 (0.4 mmol). The solution was allowed to stir for 24 h causing a color change from orange to brown. Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave a pale yellow solid (yield 82%). Anal. Calcd for $Ir_2ISP_4F_3O_5C_{63}H_{52}$: C, 46.90; H, 3.23. Found: C, 46.88; H, 3.20.

(q) $[Ir_2I(CO)_2(\mu\text{-}HCCH)(\mu\text{-}CC(H)Ph)(dppm)_2][BPh_4]$ (14·BPh_4). To a CH_2Cl_2 solution of compound **14·SO_3CF_3** (50 mg, 31 μmol in 5 mL) was added 5 mL of an acetone solution of $NaBPh_4$ (106 mg in 5 mL, 310 μmol), and the solution was stirred for 1 h. The solvent was removed, the residue was dissolved in 5 mL of CH_2Cl_2, and the solution was filtered. Removal of the solvent of the filtrate and recrystallization of the residue gave a yellow powder (yield 70%).

(r) $[Ir_2I_2(CO)_2(\mu\text{-}HCCH)(\mu\text{-}CC(H)Ph)(dppm)_2]$ (15). To a CH_2Cl_2 solution of compound **14·SO_3CF_3** (100 mg, 63 μmol in 5 mL) was added a solution of KI (130 mg in a minimum volume of MeOH, 783 μmol) causing the color to change from light orange to light yellow immediately. The solution was stirred for 0.5 h, and then the solvent was removed. The residue was dissolved in 5 mL of CH_2Cl_2, and the solution was filtered. The filtrate was washed by 3 × 5 mL of degassed water. Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave a yellow solid (yield 76%). Anal. Calcd for $Ir_2I_2SP_4O_2C_{62}H_{52}{\cdot}CH_2Cl_2$: C, 45.13; H, 3.22. Found: C, 44.76; H, 3.03. One equivalent of CH_2Cl_2 was verified from crystal structure determination.

(s) $[Ir_2I(CO)_3(\mu\text{-}HCCH)(\mu\text{-}CC(H)Ph)(dppm)_2][SO_3CF_3]$ (16). A CD_2Cl_2 solution of compound **14·SO_3CF_3** (15 mg in 0.5 mL in an NMR tube, 10 μmol) was put under CO (10 psi), and the NMR experiments were carried out. Removal of the CO atmosphere reversed the reaction.

(t) $[Ir_2(CO)_4(\mu\text{-}HCCH)(\mu\text{-}CC(H)Ph)(dppm)_2][SO_3CF_3]_2$ (17). A CD_2Cl_2 solution of compound **14·SO_3CF_3** (15 mg in 0.5 mL in an NMR tube, 10 μmol) was put under CO (10 psi), and 2 μL of $CF_3SO_3CH_3$ (18 μmol) was added and the NMR experiments were undertaken. The iodomethane was observed in the ^1H NMR. Removal of CO caused the generation of unknown species at the cost of compound **17**.

(u) $[Ir_2I(CO)_2(\mu\text{-}HCCPh)(\mu\text{-}CC(H)Ph)(dppm)_2][SO_3CF_3]$ (18). To a CH_2Cl_2 solution of compound **6** (50 mg, 32 μmol in 5 mL) was added 1 mL of phenyl acetylene (8.92 mmol). The solution was allowed to stir for 3 days causing a color change from orange to burgundy. Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave a burgundy solid (yield 76%). The compound was not stable even in the solid owing to the slow loss of phenylacetylene.

(v) $[Ir_2I(CCH_2)(CC(H)Ph)(CO)_2(dppm)_2][SO_3CF_3]$ (19·SO_3CF_3). To a CH_2Cl_2 solution of compound **4·SO_3CF_3** (100 mg, 66 μmol in 10 mL) was added 500 μL of phenylacetylene (4.46 mmol), and the solution was stirred for 2 days. The color changed gradually from yellow to deep burgundy. Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave a burgundy solid (yield 92%). Anal. Calcd for $Ir_2ISP_4F_3O_5C_{63}H_{52}$: C, 46.90; H, 3.23. Found: C, 46.14; H, 3.12.

(w) $[Ir_2I(CCH_2)(CC(H)Ph)(CO)_2(dppm)_2][BF_4]$ (19·BF_4). To a CH_2Cl_2 solution of compound **4·BF_4** (50 mg, 35 μmol in 5 mL) was added 250 μL of phenylacetylene (2.23 mmol), and the solution was and stirred for 24 h. The color changed from yellow to deep burgundy. Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave a burgundy solid (yield 86%).

(x) $[Ir_2I_2(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}CC(H)Ph)(dppm)_2]$ (20a,b). To a CH_2Cl_2 solution of compound **19·SO_3CF_3** (50 mg, 33 μmol in 5 mL) was added a solution of KI (100 mg in a minimum volume of MeOH, 602 μmol) causing the color to change from burgundy to yellow. After the solution was stirred for 0.5 h, the solvent was removed, the residue was dissolved in 5 mL of CH_2Cl_2, and the solution was filtered. Removal of the solvent of the filtrate and recrystallization from CH_2Cl_2/Et_2O gave a yellow solid (yield 68%).

(y) $[Ir_2I(CO)_3(\mu\text{-}CCH_2)(\mu\text{-}CC(H)Ph)(dppm)_2][SO_3CF_3]$ (21a,b). A CD_2Cl_2 solution of compound **19·SO_3CF_3** (15 mg in 0.5 mL in an NMR tube, 10 μmol) was put under CO (10

Table 2. Crystallographic Data

compd	**15**	**20b**
formula	$C_{63}H_{54}Cl_2I_2Ir_2O_2P_4$	$C_{62}H_{52}I_2Ir_2O_2P_4$
fw	1676.14	1591.20
space group	$P2_1/c$ (No. 14)	$I4_1/a$ (No. 88)
unit cell parameters		
a (Å)	15.799(3)	30.407(5)
b (Å)	18.029(2)	
c (Å)	21.126(5)	13.065(6)
β (deg)	99.48(2)	
V (Å^3)	5935(4)	12079(6)
Z	4	8
ϱ(calcd) (g cm^{-3})	1.876	1.75
μ (cm^{-1})	57.3	55.8
diffractometer	Enraf-Nonius CAD4	Rigaku AFC7R
temperature (°C)	−65	22
radiation (λ (Å))	graphite-monochromated Mo Kα (0.710 69)	
take-off angle (deg)	3.0	6.0
detector aperture (mm)	(3.00 + tan θ) horiz × 4.00 vert	3.0 × 3.0
crystal-detector distance (mm)	173	235
scan type	$\omega-2\theta$	$\omega-2\theta$
scan rate (deg min^{-1})	6.71−1.73	4.00
scan width (deg)	0.80 + 0.344 tan θ	0.94 + 0.35 tan θ
max 2θ (deg)	50.0	55.0
tot. unique reflcns	10684 ($\pm h,+k,+l$)	7235 ($+h,+k,+l$)
tot. obsvns (NO)	7406 ($F_o^2 \geq 3.0\sigma(F_o^2)$)	3730
range of abs corr factors	0.85−1.21	0.83−1.20
final no. params varied (NV)	441	305
R^a	0.034	0.045
$R_w{}^b$	0.040	0.050
error in obs of unit weight (GOF)^c	1.274	1.80

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$. ^{c} GOF $= [\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$.

psi) for 1 h, and the NMR experiments were carried out. Removal of the CO atmosphere reversed the reaction.

(z) [$Ir_2(CO)_4(\mu$-$CCH_2)(\mu$-CC(H)Ph)(dppm)$_2$][SO_3CF_3]$_2$ (22). A CD_2Cl_2 solution of compound **19·SO$_3$CF$_3$** (10 mg in 0.5 mL in an NMR tube, 7 μmol) was put under CO (10 psi), 4 μL of $CF_3SO_3CH_3$ (36 μmol) was added, and the NMR experiments were undertaken. Iodomethane was found in the ^{1}H NMR spectra. Removal of CO caused the transformation of compound **14** to uknown species.

(aa) [$Ir_2(Me)_2(CO)_2(\mu$-$CCH_2)(\mu$-CC(H)Ph)(dppm)$_2$] (23). To a CD_2Cl_2 solution of compound **19·SO$_3$CF$_3$** (25 mg in 0.5 mL in an NMR tube, 17 μmol) was added 50 μL of LiMe (1.4 M in Et_2O, 70 μmol), and NMR experiments were carried out. The ^{31}P NMR showed that 1 equiv of compound **20** accompanies compound **23**.

X-ray Data Collection. (a) [$Ir_2I_2(CO)_2(\mu$-CC(H)Ph)(μ-HCCH)(dppm)$_2$] (15). Crystals were obtained, with 1 equiv of CH_2Cl_2 of crystallization, from CH_2Cl_2/Et_2O and mounted in capillaries. Unit cell parameters, at −65 °C, were obtained from a least-squares analysis of 25 reflections in the range 20.1° $\leqslant 2\theta \leqslant$ 23.9°, which were accurately centered on a CAD4 diffractometer. The systematic absences ($h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$) defined the space group as $P2_1/c$ (No. 14).

Intensity data were collected on the CAD4 diffractometer at −65 °C, employing the $\theta/2\theta$ scan technique in the bisecting mode up to $2\theta = 50°$. Peaks were collected using variable scan speeds (between 1.73 and 6.71 deg min^{-1}) with backgrounds scanned for 25% of the peak scan on either side of the peak. The intensities of three standard reflections were checked every 1 h of exposure time. No variation was observed so no correction was applied. A value of 0.04 was used for *p*,[25] and data were corrected for Lorentz and polarization effects and for absorption.[26] See Table 2 for additional information.

(b) [$Ir_2I_2(CO)_2(\mu$-$CCH_2)(\mu$-CC(H)Ph)(dppm)$_2$] (20b). Yellow crystals suitable for an X-ray diffraction study were grown from CH_2Cl_2/Et_2O, and one was wedged into a capillary which was flame sealed. Unit cell parameters were obtained from a least-squares analysis of the setting angles of 18 reflections in the range 14.1° $\leqslant 2\theta \leqslant$ 15.8°, which were accurately centered on a Rigaku AFC7R diffractometer with graphite-monochromated MoKα radiation and 12 kW rotating anode generator. The systematic absences (hkl, $h + k + l \neq 2n$; $hk0$, h (k), $\neq 2n$; $00l$, $l \neq 4n$) and the $4/m$ Laue symmetry defined the space group as $I4_1/a$ (No. 88).

Intensity data were collected on the Rigaku diffractometer at 22 °C, employing the $\theta/2\theta$ scan technique in the bisecting mode up to $2\theta = 55°$, at scan speeds of 4.0 deg min^{-1}; weak reflections ($I < 10\sigma(I)$) were rescanned up to three times and the counts accumulated. Stationary backgrounds were collected on each side of the reflection for a total duration of half of the time of the peak scan. The intensities of three standard reflections were measured every 150 reflections to monitor crystal and electronic stability; no significant variation was observed so no correction was applied. The data were processed in the usual manner assuming a value of 0.013 used for *p* to downweight intense reflections. Corrections for Lorenz and polarization effects and for absorption were made. See Table 2 for pertinent crystal data and details of intensity collection.

Structure Solution and Refinement. Both compounds were solved by a combination of Patterson and direct methods techniques to locate the Ir and I atoms, and all other atoms were located in subsequent difference Fourier maps. For compound **15** all hydrogens were located but were input in the idealized positions except for the phenylvinylidene hydrogen which was allowed to refine. Although they were located, the hydrogens on the acetylene ligand did not refine well so were fixed at the idealized positions. In compound **20b** the vinylidene groups were disordered about the inversion center at $^1/_2$, $^1/_2$, 0. Attempts to refine the two half-occupancy, inversion-related phenyl rings allowing the phenyl carbons to refine individually resulted in a slightly distorted geometry for this group. It was therefore refined as a rigid group with a single thermal parameter refined for all carbon atoms. All hydrogen atoms, except on the disordered phenylvinylidene, were located but were input in idealized coordinates and assigned thermal parameters of 1.2 times those of the attached carbon.

Refinements were carried out using full-matrix, least-squares techniques[27,28] minimizing the function $\sum w(|F_o| -$

---

(25) Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 204.

(26) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A.: Found. Crystallogr.* **1983**, *A39*, 158.

Table 3. Atomic Coordinates and Thermal Parameters for the Core Atoms of Compound 15[a]

atom	x	y	z	B^b (Å^2)
Ir(1)	0.34732(2)	0.03235(1)	0.26634(1)	1.808(6)
Ir(2)	0.20380(2)	−0.10432(2)	0.31382(1)	1.994(6)
I(1)	0.47655(3)	0.13735(3)	0.30735(3)	3.04(1)
I(2)	0.13086(4)	−0.17685(3)	0.40899(3)	4.27(1)
P(1)	0.4502(1)	−0.0617(1)	0.27880(9)	2.04(4)
P(2)	0.3159(1)	−0.1880(1)	0.3153(1)	2.39(5)
P(3)	0.2332(1)	0.1152(1)	0.26892(9)	2.01(4)
P(4)	0.1065(1)	−0.0065(1)	0.30832(9)	2.19(4)
O(1)	0.3707(4)	0.0919(3)	0.1350(3)	4.0(2)
O(2)	0.0741(4)	−0.2040(3)	0.2282(3)	4.3(2)
C(1)	0.3597(5)	0.0647(4)	0.1807(4)	2.3(2)
C(2)	0.1240(5)	−0.1656(4)	0.2576(4)	2.8(2)
C(3)	0.3428(5)	0.0045(4)	0.3612(3)	2.3(2)
C(4)	0.2885(5)	−0.0437(4)	0.3786(4)	2.4(2)
C(5)	0.2558(4)	−0.0508(4)	0.2403(3)	2.0(2)
C(6)	0.2277(5)	−0.0733(4)	0.1804(4)	2.8(2)
C(7)	0.4044(4)	−0.1557(4)	0.2754(4)	2.5(2)
C(8)	0.1295(4)	0.0681(4)	0.2550(3)	2.2(2)

[a] Parameters for solvent molecule and phenyl rings are given as supplementary material. [b] All atoms given were refined anisotropically. Displacement parameters for the anisotropically refined atoms are given in the form of the equivalent isotropic Gaussian displacement parameter, $B\{\mathrm{eq}\}$, 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 4. Atomic Coordinates and Thermal Parameters for the Inner Core Atoms of Compound 20b[a]

atom	x	y	z	B^b (Å^2)
Ir	0.46133(2)	0.51955(2)	0.07445(4)	2.38(1)
I	0.40802(4)	0.59642(3)	0.07318(9)	4.93(3)
P(1)	0.5175(1)	0.5542(1)	0.1700(3)	2.73(7)
P(2)	0.5904(1)	0.5164(1)	0.0306(3)	2.63(7)
O(1)	0.4115(3)	0.4966(4)	0.2661(8)	5.4(3)
C(1)	0.4283(4)	0.5047(5)	0.197(1)	4.4(4)
C(2)	0.5000(4)	0.4638(4)	0.0559(9)	2.3(3)
C(3)	0.4989(5)	0.4266(4)	0.103(1)	3.8(4)
C(4)	0.5671(4)	0.5649(4)	0.0955(10)	2.7(3)

[a] Phenyl carbons are given as supplementary material. [b] See Table 3 for definition of B.

$|F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$. The neutral atom scattering factors[29,30] and anomalous dispersion terms[31] used in structure solution were obtained from the usual sources. Both structures refined well as shown in Table 2. Positional parameters for the core atoms of compounds **15** and **20b** are given in Tables 3 and 4, respectively.

Results and Discussion

(a) Mono(vinylidene) Complexes. In our previous study of alkyne-to-vinylidene transformations at an "Ir_2" core[23] the majority of reactions carried out utilized the neutral diiodo species $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ (**1**) as precursor; only preliminary studies were done with the closely related cationic A-frame $[Ir_2(CO)_2(\mu\text{-}I)(dppm)_2][X]$ (**2**). In the current paper we extend our investigations of cationic vinylidene complexes, reasoning that the removal of an anionic ligand should generate a coordination site for additional substrate molecules. Using this strategy the reaction with additional alkynes should be capable of generating bis(vinylidene) complexes or, alternatively, monovinylidene−alkyne complexes.

The cationic precursor used (**2**) had been previously prepared by the reaction of **1** with 1 equiv of the appropriate silver salt.[24] We now find that a more convenient preparation involves the reaction of **1** with methyl triflate, yielding **2** as the triflate salt, together with methyl iodide.

The reaction of **2** (as the triflate salt) with a 3-fold excess of acetylene at −80 °C yields the cationic acetylene adduct $[Ir_2(CO)(HC_2H)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][SO_3CF_3]$ (**3**) as shown in Scheme 1 (note that in all schemes the dppm ligands above and below the plane of the drawing are omitted for clarity). This product can be isolated as a pale yellow solid at this temperature. The $^{13}C\{^1H\}$ NMR spectrum of **3** (at −40 °C) shows two carbonyl signals at δ 179.0 and 187.7, and selective and broad-band ^{31}P decoupling experiments demonstrate a 10 Hz coupling between these carbonyls as well as coupling of the high-field carbonyl to the ^{31}P nuclei on one metal and coupling of the low-field carbonyl to all four ^{31}P nuclei, identifying the former as terminal and the latter as bridging. The acetylenic carbons resonate at δ 75.2 and 62.0 with a mutual coupling of 102 Hz. This coupling is intermediate between those for ethylene (67.6 Hz) and acetylene (171.5 Hz),[32] consistent with the expected rehybridization upon coordination to a metal center. In the ^1H NMR spectrum the acetylenic protons resonate at δ 4.98 and 3.42 and, when $^{13}C_2H_2$ is used, display coupling to the attached carbons of 234 and 237 Hz, respectively. These values are close to that observed in acetylene (249 Hz)[32] suggesting little rehybridization of this group (although it appears that this parameter may not be as sensitive to changes at carbon as $^1J_{C-C}$). In the IR spectrum a stretch for the terminal carbonyl is observed at 1966 cm^{-1} while the bridging CO appears at 1824 cm^{-1}. A weak shoulder at 1660 cm^{-1} is identified as the alkyne C≡C stretch, which is significantly lower than that in the free acetylene (1974 cm^{-1}),[33] consistent with the significant change in C−C coupling constant noted above. This stretch is at higher frequency than values of *ca.* 1590 cm^{-1} reported later for vinylidene ligands in which rehybridization to sp^2 and bond-order reduction from three to two is complete. As expected for a low-valent, late transition metal, this alkyne, without electron-withdrawing substituents, is weakly bound,[34] as seen by the facile loss of acetylene from **3** under vacuum, even in the solid, which slowly develops a burgundy tinge, characteristic of **2**.

The structure proposed for compound **3** is analogous to that observed in the X-ray study of the hexafluorobutyne adduct $[Ir_2(CO)(CF_3C_2CF_3)(\mu\text{-}S)(\mu\text{-}CO)(dppm)_2]$.[35]

---

(27) For compound **15**, programs used were those of the Enraf-Nonius Structure Determination Package by B. A. Frenz, in addition to local programs by R. G. Ball.

(28) For compound **20b**, the teXsan Crystal Structure Analysis Package, by Molecular Structure Corp. (1985 and 1992), was used.

(29) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

(30) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(31) (a) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891. (b) Creagh, D. C.; McAuley, W. J. *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Boston, MA, 1992; Vol. C, Table 4.2.6.8, pp 219−222.

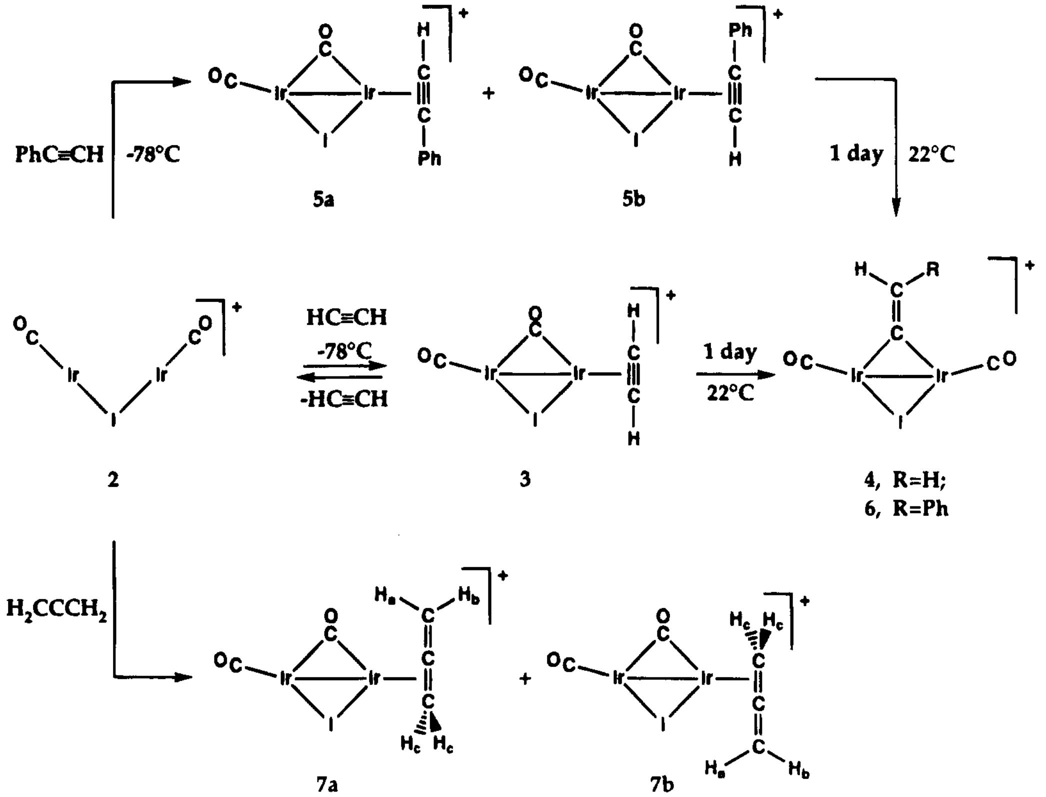
(32) Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*; VCH Verlagsgesellschaft Publishers: Weinheim, Federal Republic of Germany, 1991; Chapter 3.

(33) Jones, R. N.; Sandorfy, C. *Technique of Organic Chemistry*; West, W., Ed.; Interscience Publishers: New York, 1956; Vol. IX, p 385.

(34) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(35) Vaartstra, B. A.; Cowie, M. *Organometallics* **1989**, *8*, 2388.

Scheme 1



This is the structure expected for alkyne attack at the less sterically encumbered coordination site on the outside of the A-frame, remote from the adjacent metal. However, it is surprising that **3** has not rearranged to an alkyne-bridged product, since such rearrangements are usually extremely facile in these complexes.[36] It may be that rearrangement is unfavorable because of the large bulk of the iodo ligand. Compound **3** is also isoelectronic with the series of tricarbonyl A-frames derived from CO addition to **2** and its analogues,[24,37] in which the terminal alkyne has been replaced by a carbonyl.

In the absence of excess acetylene, compound **3** rearranges to the vinylidene-bridged $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CCH_2)(dppm)_2][SO_3CF_3]$ (**4**) after 24 h at ambient temperature. Although no intermediates were observed in this transformation, it appears that it is not a trivial process since the 1,2-hydrogen shift is accompanied by a reshuffling of the vinylidene and a carbonyl ligand to give the symmetric **4**. The $^{13}C\{^1H\}$ NMR spectrum shows the vinylidene C_α and C_β resonances at δ 219.6 and 129.9, and the coupling between these nuclei (65 Hz) is consistent with a C=C double bond between sp^2-hybridized carbons, comparing well to the value for ethylene (67.6 Hz).[32] C_α also displays coupling to all four phosphorus nuclei (7 Hz) and to both carbonyls (9 Hz, ^{13}CO-enriched), confirming its bridging nature. One resonance for both carbonyls is observed at δ 181.7, displaying coupling to C_α (^{13}C-enriched vinylidene) in addition to being virtually coupled to all four phosphorus nuclei. The ^{1}H NMR spectrum shows the vinylidene protons at δ 3.72, with coupling (in the $^{13}C_2H_2$ sample) to the β carbon of 161 Hz, which is again close to that in ethylene (156.4 Hz)[32] but substantially different from that noted in the acetylene adduct **3**. In the IR spectrum only one carbonyl stretch is observed (1949 cm^{-1}, Nujol) together with a weak band at 1588 cm^{-1} (1536 cm^{-1} in the $^{13}C{=}^{13}CH_2$ sample) corresponding to the vinylidene C=C stretch. Compound **4** was obtained as the $SO_3CF_3^-$ or the BF_4^- salt, starting from compound **2** having the appropriate anion, and both salts display identical spectroscopic parameters for the cations indicating that these anions behave as innocent, noncoordinating counterions.

Extending this chemistry to include unsymmetrical, termal alkynes, such as phenylacetylene, gives similar chemistry with **2**, yielding two isomers of $[Ir_2(CO)(HC{\equiv}CPh)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][SO_3CF_3]$ (**5a,b**) at −60 °C, as shown in Scheme 1. The existence of two isomers presumably results from the differing orientations of the unsymmetrical alkyne, in which the phenyl substituent faces the bridging iodo (**5a**) or carbonyl (**5b**) groups. All spectroscopic parameters for these isomers closely resemble those of **3**, supporting the structural assignments. At −60 °C **5a** is dominant (*ca.* 5:2 mole ratio); however, as the temperature is raised to ambient, this isomer disappears leaving only **5b**. It is assumed that this is the thermodynamically favored isomer on the basis of less repulsion of the phenyl substituent with the smaller carbonyl ligand, as opposed to the large iodo group. At ambient temperature compound **5b** slowly

---

(36) See for example: (a) Cowie, M.; Dickson, R. S. *Inorg. Chem.* **1981**, *20*, 2682. (b) Cowie, M.; Southern, T. G. *Inorg. Chem.* **1982**, *21*, 246. (c) Sutherland, B. R.; Cowie, M. *Organometallics* **1984**, *3*, 1869. (d) Vaartstra, B. A.; Xiao, J.; Jenkins, J. A.; Verhagen, R.; Cowie, M. *Organometallics* **1991**, *10*, 2708. (e) Jenkins, J. A.; Cowie, M. *Organometallics* **1992**, *11*, 2774. (f) Johnson, K. A.; Gladfelter, W. L. *Organometallics* **1989**, *8*, 2866. (g) Johnson, K. A.; Gladfelter, W. L. *Organometallics* **1992**, *11*, 2534. (h) Mague, J. T. *Organometallics* **1986**, *5*, 918. (i) Mague, J. T. *Polyhedron* **1990**, *9*, 2635.

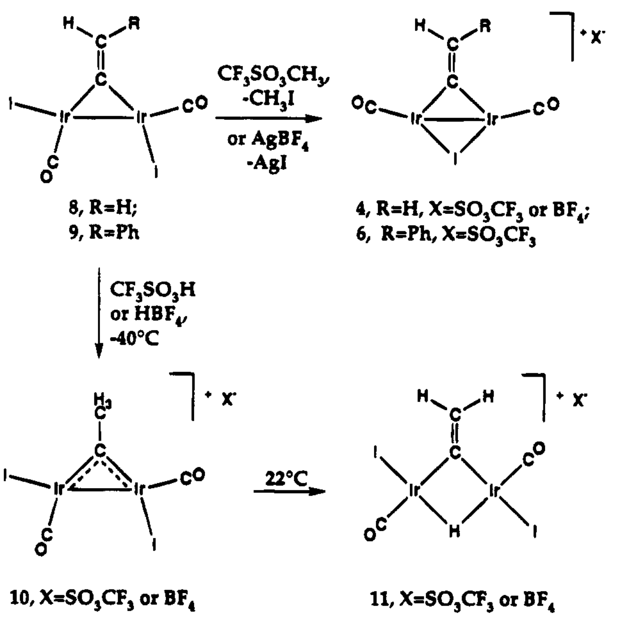
(37) (a) Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1980**, *19*, 2733. (b) Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1982**, *21*, 2119. (c) Cowie, M. *Inorg. Chem.* **1979**, *18*, 286. (d) Sutherland, B. R.; Cowie, M. *Inorg. Chem.* **1984**, *23*, 2324. (e) Sutherland, B. R.; Cowie, M. *Can. J. Chem.* **1986**, *64*, 464.

transforms into several (four or more) intermediates which in turn, after 24 h, transform into **6**, the phenylvinylidene-bridged analogue of **4**. Unfortunately, these intermediates were never present in large enough quantities and were always present as a complex mixture, so could not be identifed. However, at least one of these intermediates displays a high-field resonance in the ^{1}H NMR spectrum, suggesting the involvement of a hydride–acetylide species, as has been observed in other acetylene-to-vinylidene rearrangements.[23,38-41] The presence of several intermediates is consistent with our earlier hypothesis that this transformation from a terminally bound alkyne to a bridging vinylidene in **4** and **6** must require several steps.

An allene product, $[Ir_2(CO)(C_3H_4)(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][X]$ (**7**), analogous to the alkyne species **3** and **5**, is obtained in the reaction of **2** with allene at ambient temperature. As was observed with phenylacetylene, two isomers, **7a**,**b**, are obtained in *ca.* 5:1 ratio. It is proposed that the major isomer (**7a**) has the CH_2 moiety, which is not coordinated to the metal, aimed toward the smaller carbonyl rather than the iodo ligand, whereas this unit is closer to I in **7b**. For the major isomer (I^- salt) a terminal (δ 179.9) and a bridging (δ 189.9) carbonyl is identified in the $^{13}C\{^1H\}$ NMR spectra, based on their coupling to the appropriate ^{31}P nuclei, and this assignment is substantiated by the IR spectrum which shows a terminal and a bridging (1983, 1819 cm^{-1}, CH_2Cl_2) carbonyl stretch. The ^{1}H NMR spectrum shows the allene protons at δ 5.93, 5.33, and 1.31 in a 1:1:2 intensity ratio, respectively. The high-field signal corresponds to the protons on the coordinated CH_2 group, which display coupling to two phosphorus nuclei ($^3J_{PH}$ = 7 Hz) and to each of the other allene protons ($^4J_{H_aH_c} = {^4J_{H_bH_c}} = 3.4$ Hz). In addition the inequivalent protons on the unbound end of the allene (H_a, H_b) show geminal coupling of 2.4 Hz. For the less abundant isomer **7b** the spectroscopic data in Table 1 are very similar to those of **7a**. The subsequent chemistry of these allene products, with regards C–H activation or condensation reactions, has not yet been investigated.

In an attempt to probe the reactivity of the bridging vinylidene moiety in the previously reported complexes, $[Ir_2I_2(CO)_2(\mu\text{-}CC(H)R)(dppm)_2]$ (R = H (**8**), Ph (**9**)),[23] methyl triflate was added on the assumption that electrophilic attack at the vinylidene β-carbon would occur.[41] Instead, as shown in Scheme 2, loss of CH_3I occurs (as detected in the ^{1}H NMR by a resonance at δ 2.16) to generate the previously described cationic, vinylidene-bridged complexes **4** and **6**. No intermediates were detected, so whether initial CH_3^+ attack occurs at a metal or directly at an iodo ligand is not known. The same species, having BF_4^- anions instead of $CF_3SO_3^-$, can be obtained by the addition of 1 equiv of $AgBF_4$ to **8** or **9**. The vinylidene-bridged, cationic compounds **4** and **6** can therefore be prepared either by reaction of the appropriate alkyne with the cationic precursor **2** or by iodide removal from the preformed neutral vinylidene complexes **8** and **9**.

Scheme 2



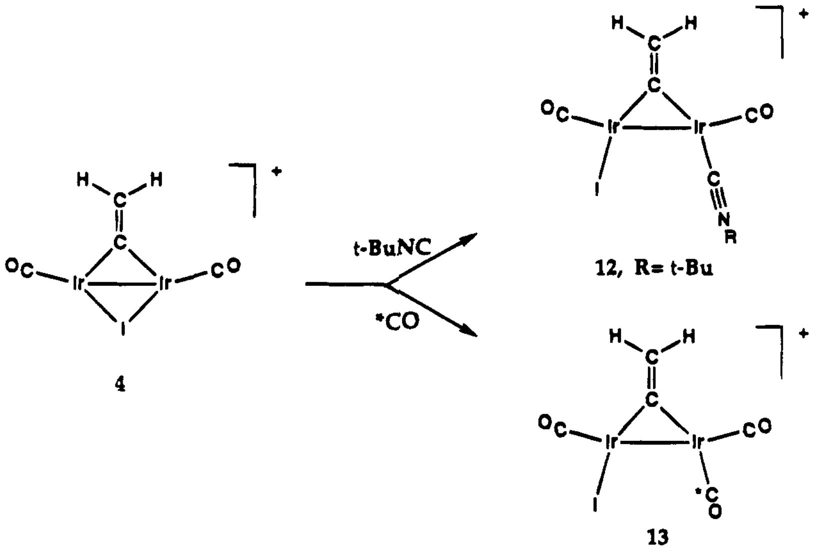
Although, as noted above, electrophilic attack by CH_3^+ apparently did not occur at the vinylidene β-carbon, protonation of **8** does yield the expected ethylidyne-bridged species **10** when protonation is carried out at −40 °C, as shown in Scheme 2. In the $^{13}C\{^1H\}$ NMR spectrum of **10** (BF_4 salt) two carbonyl resonances at δ 179.0 and 166.5 are observed and each shows coupling to a different pair of ^{31}P nuclei, indicating that these carbonyls are terminally bound to different metals. When the ethylidyne ligand is ^{13}C-enriched, the low-field ^{13}CO resonance of **10** also shows 23 Hz coupling to the α-carbon of the ethylidyne unit. The ethylidyne carbons resonate at δ 409.1 (C_α) and 68.5 (C_β), comparing closely to the values reported (δ 405–453, C_α; δ 58, C_β) in some ethylidyne-bridged heterobinuclear complexes,[6,43] and display a mutual coupling of 23 Hz. Although we were unable to find reports of C–C coupling in bridging ethylidyne groups, presumably because these groups were not ^{13}C enriched, the value observed for **10** is comparable to the value reported for ethane (34.6 Hz) and is consistent with a C–C single bond. In the ^{1}H NMR spectrum of ethylidyne methyl protons resonate as a singlet at δ 3.99 or as a doublet with 128 Hz coupling to C_β when the ethylidyne is ^{13}C enriched; again this coupling is in good agreement with that reported for ethane (124.9 Hz) consistent with sp^3 hybridization of the carbon.

Upon warming of **10** to ambient temperature an immediate and surprising rearrangement occurs in which an ethylidyne proton transfers to the metals to give the hydride- and vinylidene-bridged product $[Ir_2I_2(CO)_2(\mu\text{-}H)(\mu\text{-}CCH_2)(dppm)_2][X]$ (**11**). The $^{13}C\{^1H\}$ NMR spectrum of the BF_4^- salt shows the carbonyl ligands at δ 167.9 and 166.3 with the latter displaying 26 Hz coupling to the vinylidene C_α (^{13}C enriched). Resonances for the vinylidene group appear at δ 187.5 (C_α) and 132.3 (C_β) with a mutual coupling of 70 Hz; in addition the C_α resonance displays equal coupling to all four phosphorus nuclei, confirming the bridged arrange-

---

(38) Wolf, J.; Werner, H.; Sehadli, O.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 414.
(39) Garcia Alonso, F. J.; Höhn, A.; Wolf, J.; Otto, H.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 406.
(40) Höhn, A.; Otto, H.; Dziallas, M.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1987**, 852.
(41) Höhn, A.; Werner, H. *J. Organomet. Chem.* **1990**, *382*, 255.
(42) Kostic, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974.
(43) Awang, M. R.; Jeffery, J. C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 2091.

Scheme 3



4

12, R= t-Bu

13

ment, and to the carbonyl ligand. In the ^{1}H NMR spectrum only one resonance for a vinylidene hydrogen is observed at δ 8.17 with the other presumably being obscured by the phenyl protons. This resonance displays 7 Hz geminal coupling to the other vinylidene proton and 156 Hz coupling to C_β (^{13}C enriched). The hydride resonance appears as a multiplet at δ −12.48 and is shown to be bridging based on selective and broad-band ^{31}P decoupling experiments. Protonation of **8** to give **11** has resulted in a net oxidation of the metals, and this is mirrored by the change in carbonyl stretches from 1960 and 1985 cm^{-1} to 2020 and 2066 cm^{-1}. The vinylidene stretch appears at 1605 cm^{-1}.

This transformation is the opposite of what one intuitively expects, with protonation generally occurring first at the metals with subsequent transfer to the hydrocarbyl ligand, and certainly the opposite has been observed in related mononuclear vinylidene complexes in which protonation at Ir with subsequent transfer to the β-carbon occurred.[41,44] Apparently in **8** the most nucleophilic site is at the β-carbon yielding **10** as the kinetic product, but with the hydride- and vinylidene-bridged species being thermodynamically favored. In spite of the favorable C−H bond enthalpy in **10**, we assume that the delocalized Ir−C_α−Ir multiple bond is not sufficient to overcome the C=C bond and the Ir−H−Ir interaction that results in the final product **11**.

Although the cationic vinylidene-bridged complexes **4** and **6** are saturated, by virtue of the iodo ligand assuming a bridging position, they have incipient unsaturation, since movement of I$^-$ to a terminal site on one metal can generate unsaturation at the other. Consistent with this proposal, compound **4** (as the triflate salt) reacts readily at ambient temperature with ^{t}BuNC or CO, as shown in Scheme 3, to give the respective compounds $[Ir_2I(CO)_2(^tBuNC)(\mu\text{-}CCH_2)(dppm)_2][SO_3CF_3]$ (**12**) and $[Ir_2I(CO)_3(\mu\text{-}CCH_2)(dppm)_2][SO_3CF_3]$ (**13**). The $^{13}C\{^1H\}$ NMR spectrum of **12** shows the terminal carbonyls at δ 172.9 and 166.3, and selective ^{31}P decoupling shows that each CO is bound to a different metal. These carbonyls show 8 Hz mutual coupling which argues in favor of a structure in which the carbonyls are close to the trans position with respect to the Ir−Ir bond; large 3-bond coupling through a metal−metal bond has been previously noted.[45] An arrangement of ligands like that proposed for **12** has been observed in the X-ray structures of **8** and **9**.[23] The vinylidene carbons (^{13}C enriched) are observed at δ 188.3 (C_α) and 132.0 (C_β) and display the usual C_α−C_β coupling of 67 Hz. As expected, C_α displays additional coupling to all phosphorus nuclei, confirming its bridged arrangement, whereas C_β shows no additional coupling. C_α also shows coupling to one of the carbonyls, but this is only 3 Hz, indicating that the vinylidene is cis to both carbonyls. In the ^{1}H NMR the vinylidene protons appear as a singlet at δ 6.75 and the ^{t}BuNC protons also appear as a singlet; however cooling the sample shows that the chemical shifts of the vinylidene protons are temperature dependent since the singlet resolves into an AB quartet. At ambient temperature the use of ^{13}C-enriched vinylidene splits the vinylidene proton signal into a doublet ($^1J_{CH}$ = 157 Hz). The IR spectrum supports the structural assignment showing the terminal carbonyl bands at 1990 and 1976 cm^{-1}, the C≡N stretch of the isocyanide at 2184 cm^{-1}, and the vinylidene C=C stretch at 1585 cm^{-1}. The increase in the isocyanide stretch from *ca.* 2125 cm^{-1} in the free molecule indicates that this ligand functions mainly as a σ donor.[46]

For the carbonyl adduct **13** the spectroscopic data are closely comparable. In the $^{13}C\{^1H\}$ NMR three carbonyl resonances are now observed at δ 174.1, 170.0, and 162.4, and all are shown to correspond to terminally bound CO's, based on ^{31}P decoupling experiments. All carbonyls display weak coupling (<3 Hz) with each other, but only the low-field resonance displays substantial coupling (15 Hz) to C_α of the ^{13}C-enriched vinylidene. This coupling suggests an arrangement of this carbonyl and the vinylidene group which is close to trans. If the ^{13}CO-enriched sample of **4** is reacted with ^{12}CO, the $^{13}C\{^1H\}$ NMR of the product shows that the low-field carbonyl signal is substantially weaker (*ca.* 50%) than the other two, supporting the structural

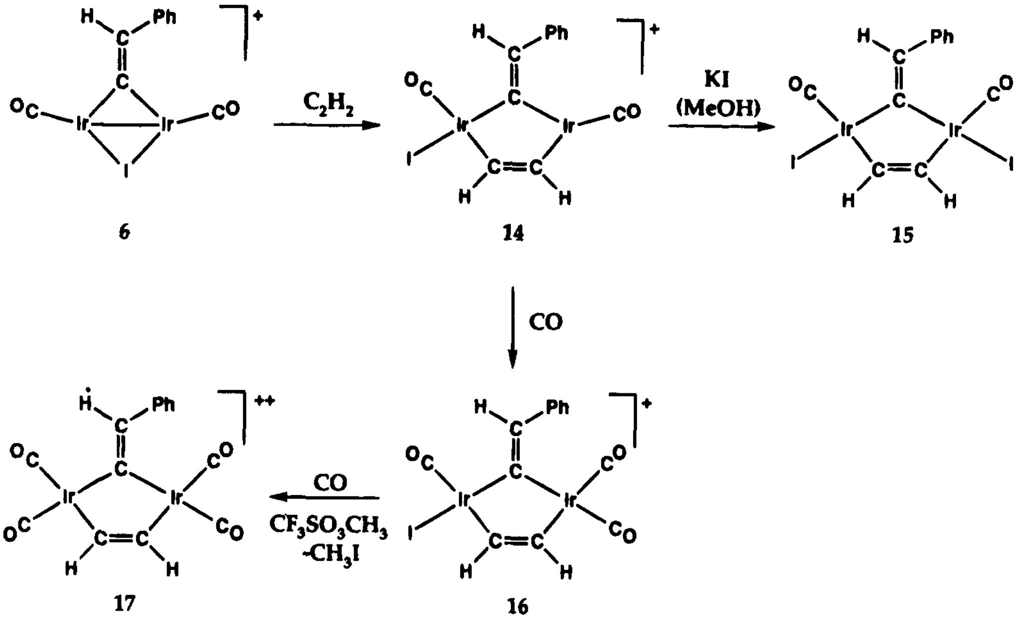
---

(44) Höhn, A.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 737.

(45) Brown, M. P.; Fisher, J. R.; Hill, R. H.; Puddephatt, R. J.; Seddon, K. R. *Inorg. Chem.* **1981**, *20*, 3516.

(46) Treichel, P. M. *Adv. Organomet. Chem.* **1973**, *11*, 21.

Scheme 4



assignment shown for **13** in which the attacking group binds at the site vacated by the bridging I^- ligand. The partial occupancy of this site by ^{13}CO in the latter experiment indicates either scrambling of the carbonyls on the metals or some attack by CO adjacent to the vinylidene group.

(b) Mixed Vinylidene–Acetylene-Bridged Complexes. In our previous study[23] we had reported that the neutral vinylidene-bridged complex **8** reacted with acetylene to give two cationic species containing both a bridging vinylidene and a bridging acetylene group,[47] and that the same two species could be obtained in the reaction of $[Ir_2(CO)_2(\mu\text{-}I)(ddpm)_2][BF_4]$ with excess acetylene. It appeared likely that a cationic monobridged vinylidene intermediate such as **4** was involved in this reaction. The previously described reactions of **4** with ^tBuNC and CO demonstrated ligand attack on the face of the complex opposite the vinylidene group. Similar reactivity of **4** with acetylene, followed by movement of acetylene to the bridging position, would give products analogous to those proposed in the earlier study. In agreement with these ideas the reaction of **4** with acetylene does give one of the two previously reported complexes, containing a bridged vinylidene and a bridged acetylene ligand (on the basis of a comparison of spectral parameters with those previously reported). However the present reaction is complex, yielding a large number of additional unidentified species. Owing to the complexity of this reaction we turned instead to the reaction of the analogous phenylvinylidene-bridged species **6** with acetylene. In this case the anticipated product, $[Ir_2I(CO)_2(\mu\text{-}CC(H)Ph)(\mu\text{-}HC_2H)(dppm)_2][SO_3CF_3]$ (**14**), containing a bridging phenylvinylidene and bridging acetylene group was obtained cleanly, as outlined in Scheme 4.

Since the phenylvinylidene ligand was not ^{13}C enriched, we do not have ^{13}C NMR parameters for it; however it is assumed to remain bridging on the basis of the subsequent structure determination of a derivative (**15**) (*vide infra*) and on the spectral data. The $^{13}C\{^1H\}$ NMR spectrum of **14** ($SO_3CF_3^-$ salt), in which the carbonyl and acetylene ligands are ^{13}C enriched, shows two resonances for the terminal carbonyls (δ 177.3, 169.2) and two acetylenic resonances at δ 133.8 and 120.8, with the latter two showing a mutual coupling of 60 Hz. Of the two CO resonances, only one displays strong coupling (30 Hz) to one of the acetylenic carbons indicating a trans arrangement at one metal—presumably at the saturated metal for which an octahedral geometry is proposed. Although the ^{13}C NMR parameters are not enough to differentiate between an acetylene and a vinylidene group, the ^{31}P coupling pattern strongly supports the acetylene-bridged formulation since *both* carbons show coupling to all ^{31}P nuclei; while one carbon shows 11 Hz coupling to one pair of ^{31}P nuclei and 6.5 Hz to the other, the adjacent carbon shows 7.5 Hz coupling to all ^{31}P nuclei. A similar coupling pattern is observed for the structurally characterized compound **15** (*vide infra*), and this coupling pattern is in contrast to that of bridging vinylidenes for which we find that only C_α generally displays coupling to the ^{31}P nuclei. In the ^1H NMR spectrum of **14** one acetylenic proton is observed at δ 8.60, with coupling to an acetylenic carbon ($^1J_{CH}$ = 146 Hz), and the phenylvinylidene hydrogen is observed at δ 8.53; the second acetylenic proton resonance is presumably obscured by phenyl resonances.

Reaction of **14** with KI yields the neutral diiodo product $[Ir_2I_2(CO)_2(\mu\text{-}CC(H)Ph)(\mu\text{-}HCCH)(dppm)_2]$ (**15**). Although the local geometries at both Ir centers in **15** are identical, the orientation of the bridging phenylvinylidene ligand renders the metals inequivalent. As a result two closely spaced ^{31}P resonances are observed. Significantly, these resonances appear close to that observed for the saturated end of complex **14**, suggesting that this metal center in **14** has a similar environment to both metals in **15**, as shown in Scheme 4. Most other spectroscopic parameters for **15** compare well with those of **14** apart from the strong coupling of *both* carbonyls to an acetylenic carbon (^{13}C enriched) in **15**, in line with

---

(47) It now appears that the compound previously reported in ref 23 as dicationic is in fact a neutral diiodo species analogous to **15** and should therefore be reformulated as $[Ir_2I(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}HCCH)(dppm)_2]$.

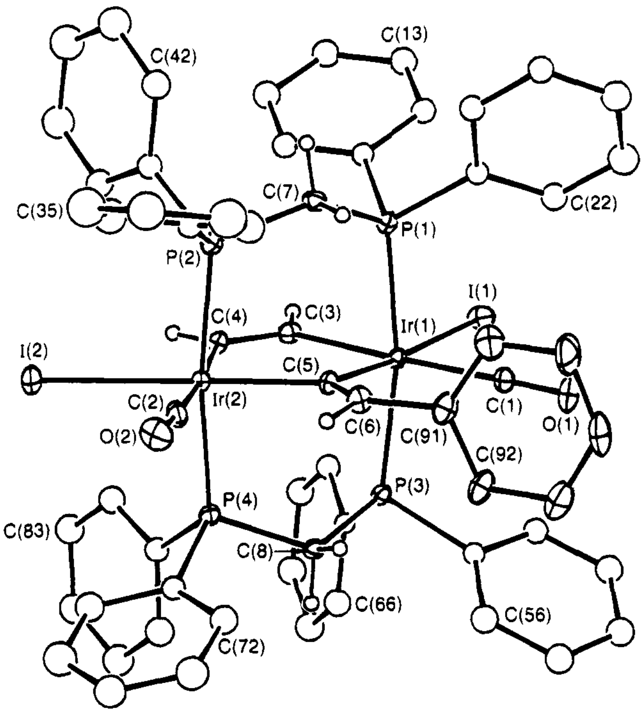


Figure 1. Perspective drawing of [$Ir_2I_2(CO)_2(\mu$-CC(H)Ph)(μ-HCCH)(dppm)$_2$] (**15**), showing the numbering scheme. Numbering on the phenyl carbons starts at the ipso position and proceeds sequentially around the ring. Thermal ellipsoids are shown at the 20% level except for methylene and vinylidene hydrogens which are shown arbitrarily small and phenyl hydrogens which are omitted.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Compound 15

Bond Lengths			
Ir(1)–I(1)	2.8144(7)	Ir(2)–C(2)	1.931(8)
Ir(1)–P(1)	2.333(2)	Ir(2)–C(4)	2.063(7)
Ir(1)–P(3)	2.349(2)	Ir(2)–C(5)	2.106(6)
Ir(1)–C(1)	1.942(7)	O(1)–C(1)	1.120(8)
Ir(1)–C(3)	2.078(7)	O(2)–C(2)	1.150(8)
Ir(1)–C(5)	2.092(6)	C(3)–C(4)	1.316(9)
Ir(2)–I(2)	2.8006(8)	C(5)–C(6)	1.335(9)
Ir(2)–P(2)	2.323(2)	C(6)–C(91)	1.48(1)
Ir(2)–P(4)	2.330(2)	C(6)–H(6)	1.08(8)
Bond Angles			
I(1)–Ir(1)–P(1)	89.87(5)	P(2)–Ir(2)–P(4)	171.00(6)
I(1)–Ir(1)–P(3)	94.93(4)	P(2)–Ir(2)–C(2)	93.2(2)
I(1)–Ir(1)–C(1)	84.6(2)	P(2)–Ir(2)–C(4)	85.7(2)
I(1)–Ir(1)–C(3)	90.2(2)	P(2)–Ir(2)–C(5)	85.3(2)
I(1)–Ir(1)–C(5)	176.1(2)	P(4)–Ir(2)–C(2)	92.5(2)
P(1)–Ir(1)–P(3)	169.26(6)	P(4)–Ir(2)–C(4)	89.0(2)
P(1)–Ir(1)–C(1)	98.5(2)	P(4)–Ir(2)–C(5)	87.2(2)
P(1)–Ir(1)–C(3)	81.3(2)	C(2)–Ir(2)–C(4)	176.2(3)
P(1)–Ir(1)–C(5)	87.0(2)	C(2)–Ir(2)–C(5)	95.9(3)
P(3)–Ir(1)–C(1)	91.5(2)	C(4)–Ir(2)–C(5)	87.5(2)
P(3)–Ir(1)–C(3)	89.0(2)	Ir(1)–C(1)–O(1)	170.9(6)
P(3)–Ir(1)–C(5)	87.8(2)	Ir(2)–C(2)–O(2)	174.8(6)
C(1)–Ir(1)–C(3)	174.8(3)	Ir(1)–C(3)–C(4)	123.8(5)
C(1)–Ir(1)–C(5)	98.2(3)	Ir(2)–C(4)–C(3)	123.1(5)
C(3)–Ir(1)–C(5)	87.0(3)	Ir(1)–C(5)–Ir(2)	118.1(3)
I(2)–Ir(2)–P(2)	95.18(5)	Ir(1)–C(5)–C(6)	125.0(5)
I(2)–Ir(2)–P(4)	92.46(5)	Ir(2)–C(5)–C(6)	116.9(5)
I(2)–Ir(2)–C(2)	82.5(2)	C(5)–C(6)–C(91)	131.5(7)
I(2)–Ir(2)–C(4)	94.0(2)	C(5)–C(6)–H(6)	128(5)
I(2)–Ir(2)–C(5)	178.4(2)	C(91)–C(6)–H(6)	100(5)

the trans arrangement between these groups as shown. This geometry is consistent with I^- attack at **14** being directed away from the bulky phenyl substituent on the vinylidene group and is confirmed by the X-ray structure determination.

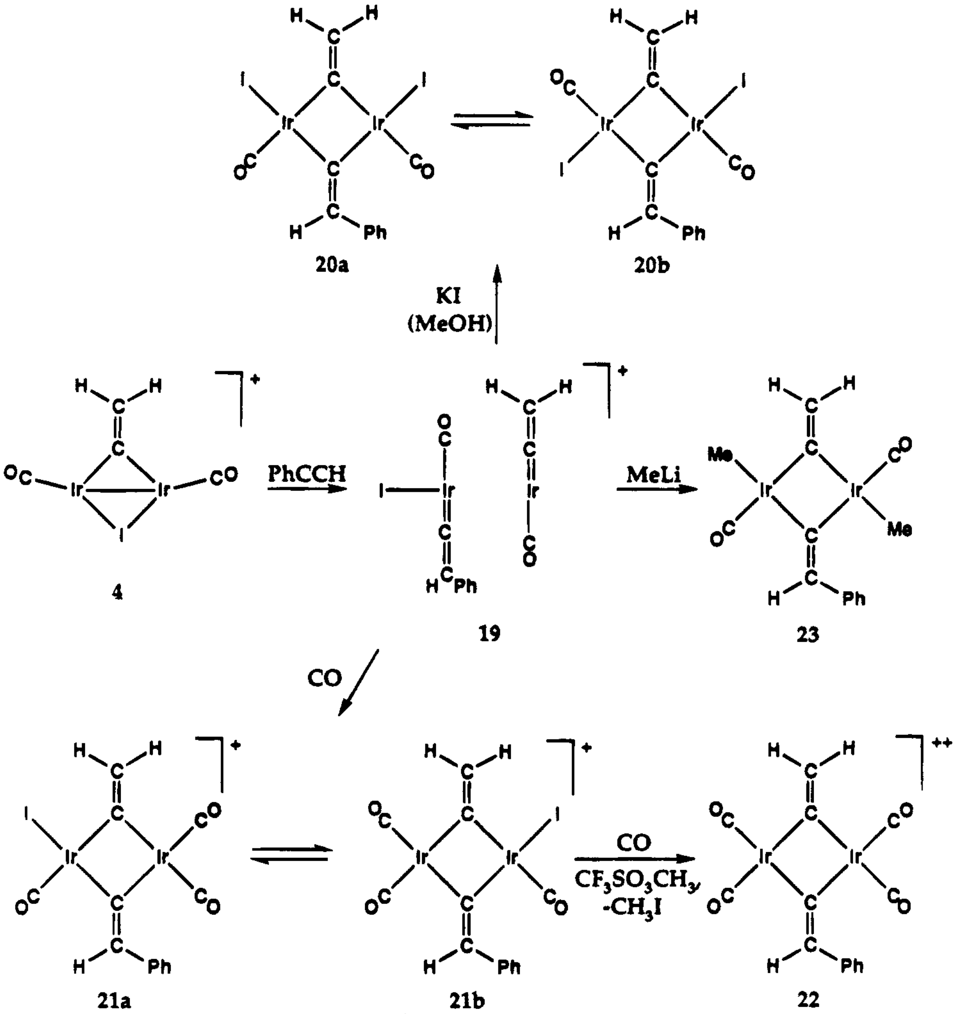
The geometry shown for compound **15** in Figure 1 has the expected octahedral coordinations at both metals. Selected bond lengths and angles are given in Table 5. Around each metal the angles are close to the idealized values, with the major distortions appearing to result from the very long Ir–Ir separation of 3.6011(6) Å, which has resulted from formal insertion of acetylene into the Ir–Ir bond of the precursor. By comparison the metal–metal-bonded, vinylidene-bridged species **8** and **9** have Ir–Ir separations of 2.828(1) and 2.783(1) Å, respectively.[23] All angles at the acetylene carbons and at the α-carbon (C(5)) of the phenylvinylidene group are close to the idealized sp^2 values. The slight distortion at C(6), resulting in a C(91)–C(6)–C(5) angle of 131.5(7)°, appears to be steric in origin, with the phenyl substituent being forced away from the adjacent carbonyl C(1)O(1). This also appears to cause a slight tilting of the vinylidene, resulting in the Ir(1)–C(5)–C(6) angle being slightly larger than Ir(2)–C(5)–C(6) (125.0(5)° *vs* 116.9(5)°). Both C=C bonds of the acetylene (1.316(9) Å) and the phenylvinylidene (1.335(9) Å) groups are close to the value expected for a double bond, in keeping with the 1,2-dimetalated olefin formulation for the acetylene group. All other parameters are essentially as expected.

Compound **14** also reacts with CO to give the cationic tricarbonyl species [$Ir_2I(CO)_3(\mu$-CC(H)Ph)(μ-HCCH)(dppm)$_2$][SO_3CF_3] (**16**), having a structure analogous to **15**. Again the ^{31}P nuclei bound to the metal center having the iodo and carbonyl ligand resonate in the same region as both similar centers in **15** and the similar center in **14** suggesting that they all have similar environments. In the $^{13}C\{^1H\}$ NMR spectrum three resonances for the terminal carbonyls are observed. For both this product and **17** neither the acetylene nor the phenylvinylidene ligand were ^{13}C enriched so ^{13}C resonances for these groups were not observed. The ^{1}H NMR spectrum shows the acetylenic protons as multiplets at typically low field (δ 9.91, 8.57); the phenylvinylidene proton was not observed. Consistent with the two Ir^{3+} centers and an overall positive charge on the complex, the carbonyl stretches are at high frequency.

Reaction of **16** with methyl triflate under carbon monoxide results in loss of CH_3I and formation of the dicationic species [$Ir_2(CO)_4(\mu$-CC(H)Ph)(μ-HCCH)(dppm)$_2$][SO_3CF_3]$_2$ (**17**). Each metal center in **17** has an environment analogous to the dicarbonyl center in **16**, and again the $^{31}P\{^1H\}$ resonances appear in the same region, consistent with the proposal that they have similar environments. Four resonances appear in the $^{13}C\{^1H\}$ NMR spectrum for the four terminal carbonyls, and in the IR spectrum the carbonyl stretches are at even higher frequency than in **15**, consistent with the replacement of I^- by CO. In the ^{1}H NMR spectrum both the acetylenic (δ 9.06, 8.70) and the phenylvinylidene protons (δ 8.31) appear.

Reaction of **6** with phenylacetylene also yields a mixed vinylidene–alkyne-bridged product [$Ir_2I(CO)_2(\mu$-CC(H)Ph)(μ-HCCPh)(dppm)$_2$][SO_3CF_3] (**18**), analogous to **14**. Although no ^{13}C NMR parameters were obtained for the vinylidene and alkyne groups, since the phenylacetylene used was not enriched, the other spectroscopic parameters are closely comparable to those of **14**, so an analogous structure is assigned. Although we have no supporting data, we propose that the phenyl group on

Scheme 5



the bridging phenyl acetylene ligand is directed toward the unsaturated Ir in order to avoid unfavorable contacts with the iodo ligand at the opposite end.

(c) Bis(vinylidene) Complexes. As noted earlier, the reaction of **4** with acetylene was complex yielding a number of unidentified species. However one product was identified as an acetylene–vinylidene-bridged species analogous to that observed in the reaction of **6** with acetylene, for which an acetylene–phenylvinylidene species, $[Ir_2I(CO)_2(\mu\text{-}CC(H)Ph)(\mu\text{-}HCCH)(dppm)_2][SO_3CF_3]$ (**14**), was obtained. It was assumed that the reaction of **4**, having a bridging CCH_2 group, and phenylacetylene would yield an analogous species containing the opposite isomer combination, i.e., vinylidene and phenylacetylene. Surprisingly this is not the case, and instead a bis(vinylidene) complex, $[Ir_2I(CO)_2(CCH_2)(CC(H)Ph)(dppm)_2][SO_3CF_3]$ (**19**), results as outlined in Scheme 5. Compound **19** presents a rare example of a binuclear species in which the vinylidene ligands are not bridging but are terminal. Terminal vinylidene groups in binuclear complexes and clusters have been observed;[48] however in the previous cases the substituents on the β-carbon were bulky so the terminal coordination appeared to be sterically driven. In contrast, there appears to be no steric reason that demands terminal vinylidene coordination in **19**. The present compound also appears to be the only bis(vinylidene) system reported on a binuclear framework. Higher clusters containing two vinylidene groups have been reported, however.[49] In a sample of **19** (triflate salt) that was ^{13}C enriched at the vinylidene ($^{13}C{=}^{13}CH_2$) and at the carbonyls, the $^{13}C\{^1H\}$ NMR spectrum shows the C_α resonance at δ 174.6 with coupling to C_β of 64 Hz, to one of the carbonyls of 35 Hz, and to two phosphorus nuclei on one metal of 10 Hz. The C_β resonance is observed at δ 133.6, with coupling only to C_α. This C_α–C_β coupling is typical for vinylidenes, and coupling of C_α to only two phosphorus nuclei identifies this group as terminal. The high coupling between C_α and the adjacent carbonyl (35 Hz) indicates that the two groups are mutually trans. Overnight data acquisition on the sample containing natural-abundance phenylvinylidene allows the C_α of this group to be identified as a broad multiplet at δ 174.3, close to that for the unsubstituted vinylidene, and C_β to be observed at δ 143.9. Appropriate decoupling experiments could not be carried out to simplify the C_α resonance. The carbonyl resonances, at δ 179.9 and 163.8, each display coupling to two different sets of ^{31}P nuclei establishing that they are terminally bound to different metals, and the high-field resonance also shows the aforementioned coupling to C_α. In the

---

[48] (a) Umland, H.; Behrens, U. *J. Organomet. Chem.* **1984**, *273*, C39. (b) Ewing, P.; Farrugia, L. J. *J. Organomet. Chem.* **1989**, *373*, 259.

[49] (a) Kolobova, N. E.; Ivanov, L. L.; Zhvanko, O. S. *Izvest. Akad. Nauk. SSSR, Ser. Khim.* **1983**, 956. (b) Kolobova, N. E.; Ivanov, L. L.; Zhvanko, O. S.; Batsanov, A. S.; Struchkov, Yu. T. *J. Organomet. Chem.* **1985**, *279*, 419.

^{1}H NMR spectrum the phenylvinylidene proton resonates at δ 8.20 and displays weak coupling to the low-field carbonyl resonance, further supporting our proposal that these two groups are bound to one metal and in a trans orientation. The protons on the unsubstituted vinylidene group appear at δ 6.54 and 6.04, displaying a mutual coupling of 10 Hz and coupling to C_β of *ca.* 157 Hz (^{13}C-enriched vinylidene). These chemical shifts for the vinylidene and phenylvinylidene protons of **19** are not abnormal for such groups of binuclear complexes in which they are usually bridging but are far downfield of those reported for terminally bound groups as observed in mononuclear vinylidene complexes of iridium.[17,41] In particular the ^{1}H resonances for the closely related complexes $[IrI(CC(H)R)(PPr^i_3)_2]$ (R = H, Ph) appear at δ −5.25 and −3.58, respectively.[41] The geometry proposed, in which the iodo group is bound adjacent to the phenylvinylidene rather than the unsubstituted vinylidene group, is based on analogies with the chemistry described of **4** with CO and ^{t}BuNC, in which ligand attack occurred at one Ir center on the face opposite the bridging vinylidene. Assuming an analogous attack by phenylacetylene and subsequent rearrangement to a phenylvinylidene moiety, the most likely geometry which minimizes ligand rearrangements, would have the unsubstituted vinylidene moving to a terminal position on the opposite face of the metal vacated by the iodo ligand. The orientation of the phenyl substituent on the phenylvinylidene group is uncertain. Although we could not find a mononuclear analogue of the saturated Ir^+ site having a carbonyl and a vinylidene unit together, a very analogous species $[IrI(CCH_2)(PPr^i_3)_2]$ was reported to react with CO, but in this case transformation to an Ir^{3+} hydride−acetylide product resulted.[41]

Although the spectroscopic data for **19** do not unequivocally rule out the presence of a phenylacetylene instead of a phenylvinylidene group, two important observations strongly support the phenylvinylidene formulation. First, in the slow transformation of **4** to **19** a hydride intermediate is observed in the ^{1}H NMR spectra. Such a species is consistent with the involvement of a hydride−acetylide intermediate, of the type previously shown to be involved in alkyne-to-vinylidene rearrangements in related binuclear systems.[23] Unfortunately this species is never present in high enough concentrations to obtain additional spectroscopic data, so could not be characterized. Furthermore, the transformation of **19** to **20**, which has been unambiguously characterized as a bis(vinylidene) species (*vide infra*), is essentially instantaneous—so is clearly inconsistent with an alkyne-to-vinylidene rearrangement occurring during this step. All such rearrangements previously noted in related systems have been slow (24−72 h).[23] If **19** had been a mixed alkyne−vinylidene species like **14**, the transformation of **19** to **20** should also have been slow.

The spectroscopic parameters for the triflate and tetrafluoroborate salts of **19** are virtually identical, in spite of the differing anions, suggesting that the anions are noncoordinating. In addition, the conductivity of the BF_4^- salt in CH_3NO_2 indicates a 1:1 electrolyte (73 Ω cm^2 mol^{-1}), which also indicates that the iodo ligand remains coordinated. The IR spectrum of **19**·SO_3CF_3 shows a band at 1580 cm^{-1}, separating into two bands, at 1575 and 1525 cm^{-1} when ^{13}C-labeled vinylidene is used. It appears that in the latter spectrum the higher frequency band corresponds to phenylvinylidene whereas the lower frequency stretch is due to $^{13}C{=}^{13}CH_2$; when natural abundance vinylidene is used both bands overlap.

The addition of either an anionic (I^-) or a neutral (CO) ligand to **19** results in the unusual transformation of the terminal vinylidene ligands to bridging—a transformation that appears to be unprecedented, although it has previously been suggested.[8,50] In addition, the preparation of heterobimetallic, vinylidene complexes from the reaction of a mononuclear vinylidene complex with an unsaturated species is another example of terminal-to-bridging vinylidene rearrangement,[6] and the transfer of a vinylidene from one mononuclear complex to another also presumably occurs via a bridged intermediate.[40] Reaction of **19** with potassium iodide results in iodide coordination to give two isomers of $[Ir_2I_2(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}CC(H)Ph)(dppm)_2]$ (**20**), as shown in Scheme 5. Although other isomers, having an iodo ligand adjacent to the phenyl substituent of the phenylvinylidene group, are possible, they appear not to be favored owing to destabilizing steric repulsions involving these larger groups. At ambient temperature in CH_2Cl_2 only isomer **20a** is observed. Its $^{31}P\{^1H\}$ NMR spectrum shows two resonances indicating two phosphorus environments, and the $^{13}C\{^1H\}$ NMR also shows two terminal-carbonyl resonances at δ 171.9 and 170.4. Each carbonyl shows coupling to two adjacent phosphorus nuclei, and in the $^{13}C{=}^{13}CH_2$ sample each shows coupling (27 Hz) to C_α of this vinylidene group, indicating that both are trans to it. The vinylidene carbon nuclei resonate at δ 102.2 (C_α) and 143.3 (C_β) with a mutual coupling of 61 Hz. Coupling of C_α to the ^{31}P nuclei is not resolved. The chemical shift for C_α is at exceptionally high field and can be compared with previous determinations for bridged vinylidenes which are usually downfield of δ 230;[1] the value observed for **20a** is at even higher field than those noted earlier in the paper, which are already unusual in their chemical shift (vide supra). In the ^{1}H NMR spectrum the vinylidene protons appear at δ 9.19 and 9.16 with coupling (for $^{13}C{=}^{13}CH_2$) of 153 Hz to C_β. No resonance for the phenylvinylidene proton is observed so it is presumed to lie under the phenyl resonances. The IR spectrum of **20a** shows a carbonyl stretch at 2027 cm^{-1}.

At −80 °C in CH_2Cl_2 both isomers, **20a** and **20b**, appear in the approximate molar ratio of 2:1. The $^{31}P\{^1H\}$ NMR spectrum of **20b** displays four different signals indicating a top−bottom as well as a left−right asymmetry in the complex. Although the iodo, carbonyl, and vinylidene ligands all form a plane perpendicular to the plane of the phosphorus atoms, the top−bottom asymmetry can be broken by a skewing of the phenylvinylidene about the C=C bond, as is shown in the X-ray structure (vide infra). In support of the structure shown only the carbonyl resonance at δ 174.7 displays trans coupling (30 Hz) with the $^{13}C{=}^{13}CH_2$ group; the carbonyl at δ 172.7 is cis to the vinylidene ligand, displaying no coupling to it. The resonance for C_α coincidentally occurs at exactly the chemical shift as for **20a**, whereas C_β resonates at δ 133.0. In the ^{1}H NMR spectrum the

---

(50) Garcia Alonso, F. J.; Riera, V.; Ruiz, M. A.; Tiripicchio, A.; Tiripicchio Camellini, M. *Organometallics* **1992**, *11*, 370.

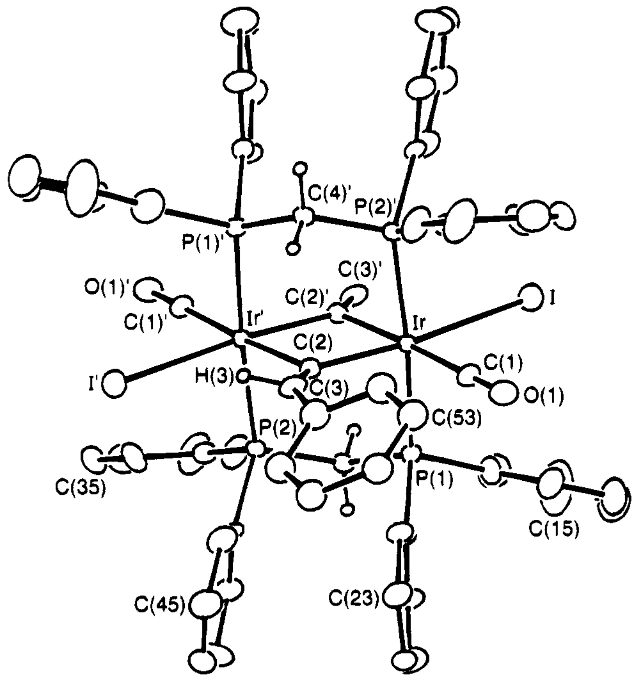


Figure 2. Perspective drawing of $[Ir_2I_2(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}CC(H)Ph)(dppm)_2]$ (**20b**). Numbering and thermal ellipsoids are as described for Figure 1.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for Compound 20b

Bond Lengths			
Ir–I	2.844(1)	Ir–P(1)	2.363(3)
Ir–P(2)′	2.356(3)	Ir–C(1)	1.94(2)
Ir–C(2)	2.08(1)	Ir–C(2)′	2.13(1)
O(1)–C(1)	1.07(2)	C(2)–C(3)	1.28(2)
C(3)–C(51)	1.58(2)		

Bond Angles			
I–Ir–P(1)	92.78(8)	I–Ir–P(2)	89.85(9)
I–Ir–C(1)	84.3(5)	I–Ir–C(2)	173.0(3)
I–Ir–C(2)′	96.6(3)	P(1)–Ir–P(2)′	175.5(1)
P(1)–Ir–C(1)	92.5(5)	P(1)–Ir–C(2)	90.9(3)
P(1)–Ir–C(2)′	85.3(3)	P(2)′–Ir–C(1)	91.6(5)
P(2)′–Ir–C(2)	86.1(3)	P(2)′–Ir–C(2)′	90.8(3)
C(1)–Ir–C(2)	101.5(6)	C(1)–Ir–C(2)′	177.5(5)
C(2)–Ir–C(2)′	77.8(5)	Ir–C(1)–O(1)	177(1)
Ir–C(2)–Ir′	102.2(5)	Ir–C(2)–C(3)	130.3(10)
Ir–C(2)′–C(3)′	127.2(10)	C(2)–C(3)–C(51)	149(1)

vinylidene protons appear at δ 8.81 and 8.14, and again the phenylvinylidene proton is not observed. Although **20a** is the only species observed in solution at ambient temperature, crystallization at this temperature yields only **20b** as a solid, as shown by IR spectroscopy and the X-ray structure. This isomer shows only one carbonyl stretch at 2009 cm^{-1}. The facile interconversion of the two isomers presumably occurs by I^- loss and recoordination.

The structure of **20b** is shown in Figure 2, confirming the geometry assigned in Scheme 5 on the basis of the spectroscopic analysis. Important structural parameters are given in Table 6. Although the phenyl substituent on the phenylvinylidene group is inversion disordered, having half-occupancy on C(3) and half on C(3)′, the rest of the molecule is well behaved and the disorder was satisfactorily resolved. In this disorder the two vinylidene carbons are directly superimposed on those of the phenylvinylidene, masking any subtle differences that there might be in their parameters. Nevertheless the structure unambiguously establishes both the bridging nature of the two vinylidene groups and the mutually trans arrangement of the iodo ligands for this isomer. The metals in **20b** have slightly distorted octahedral geometries that are characteristic of Ir^{3+}, in which case the bridging vinylidene units are considered as dianionic ligands. Structurally this species is closely related to the monovinylidene species **8** and **9** via formal insertion of the second vinylidene (CCH_2 or CC(H)Ph) into the Ir–Ir bond of the respective monobridged species. The major structural differences in the two classes of species is therefore a much longer Ir–Ir separation in **20b** (3.275(1) Å compared to 2.828(1) Å (**8**) and 2.783(1) Å (**9**)) and a wider angle at the bridging vinylidenes (102.2(5)° *vs* 84.6(7)° (**8**) and 86.0(9)° (**9**)). Even so, in **20b**, the idealized 120° angle at C(2) is not attained, presumably because this would generate too acute an angle between the vinylidenes at Ir, with the resulting poor Ir–C_α overlap; this angle is already quite acute (77.8(5)°). By comparison, the structure of **15**, having the acetylene tautomer instead of vinylidene, displays angles involving the bridging groups that are close to ideal. Since the acetylene ligand binds with one end to each metal, rather than to both metals through only one carbon atom, as for the vinylidene group, the metals are able to move apart by over 0.3 Å, compared to **20b**. In this geometry the undistorted angles at the acetylenic and vinylidene carbons and at the metals give rise to optimal metal–ligand overlap. All other parameters within **20b** compare well with those of **8** and **9**, and in particular, the vinylidene C(2)–C(3) separation 1.28(2) Å is typical of a double bond.

Upon reaction of **19** with CO, transformation of the terminal vinylidene ligands to bridging again occurs yielding $[Ir_2I(CO)_3(\mu\text{-}CCH_2)(\mu\text{-}CC(H)Ph)(dppm)_2][SO_3CF_3]$ (**21a,b**) and again two isomers are observed, corresponding to two orientations of the iodo ligand with respect to the phenylvinylidene group (isomers **21a,b** have been arbitrarily assigned since they differ only in the orientations of the substituents on the β-carbon of the phenylvinylidene, which could not be identified). In both of these isomers the iodo ligand remains on the same face of the Ir_2P_4 plane opposite the CC(H)Ph moiety, presumably to minimize steric repulsions. Although it appears that the isomer having the iodo ligand adjacent to the hydrogen substituent on the phenylvinylidene ligand is equivalent to isomers **21a,b**, its absence suggests that the dominant repulsions involve the dppm phenyl groups, the orientations of which will be most affected by the large iodo ligand and the vinylidene phenyl group. Both possible isomers, in which the iodo group is adjacent to CC(H)Ph, can be ruled out by the $^{13}C\{^1H\}$ NMR of a sample containing ^{13}CO and $^{13}C{=}^{13}CH_2$, since both isomers observed display three carbonyl resonances of which two show strong coupling (between 21 and 32 Hz) to C_α of the unsubstituted vinylidene, indicating that both of these CO's are opposite this group. At ambient temperature only isomer **21a** is observed, whereas at −60 °C the **21a:21b** ratio is *ca.* 1:0.75. Although the previously discussed interconversion between isomers **20a** and **20b** can occur via I^- loss and recoordination, since this occurs at the same metal center, the interconversion between **21a** and **21b** appears to be different, since the iodo ligand appears to migrate from metal to metal. If this occurs by I^- dissociation, there must also be an accompanying loss of CO with its subsequent recoordination, since with the bridging vinylidene groups there is no simple way (such as a turnstile motion) that allows ligand exchange between the two metals. Iodide dissociation from **21** also appears less likely than in **20** owing to the positive charge of the former. Another possibility is that exchange between **21a** and **21b** can occur by rotation of the phenylvinylidene group about the C=C axis. Facile rotation of terminal vinylidenes has been previously noted,[2] and examples of rotation about the C=C bond in a bridged group are also known.[51,52] In both isomers of compound **21** the $^{13}C_\alpha$ resonance is again at unusually high field (δ 101.0 (**a**), 99.8 (**b**)), but all other parameters are as expected.

Under an atmosphere of CO compound **21** reacts with methyl triflate resulting in iodide abstraction (as CH_3I) and yielding $[Ir_2(CO)_4(\mu\text{-}CCH_2)(\mu\text{-}CC(H)Ph)(dppm)_2][SO_3CF_3]_2$ (**22**), which is not stable in the absence of CO. This product shows the expected four terminal carbonyl resonances, with two of them displaying strong coupling (26 Hz) to $^{13}C_\alpha$ of the enriched vinylidene, which is again observed at high field. The ^1H NMR spectrum of **22** shows the phenylvinylidene proton resonance at δ 8.19, which appears as an apparent triplet due to coupling to the two ^{13}CO's opposite the phenylvinylidene group, and this signal appears as a singlet when natural abundance CO is used. The protons of the unsubstituted vinylidene appear at δ 7.94 and 7.82 with the usual parameters observed when $^{13}C^{13}CH_2$ is used.

The dialkyl derivative, $[Ir_2(CH_3)_2(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}CC(H)Ph)(dppm)_2]$ (**23**), can be prepared from **19** by reaction with *ca.* 4-fold excess of MeLi. Also obtained in this reaction is compound **20**, resulting from I^- attack on **19** by the LiI produced in the reaction. Compound **23** is unstable and transforms to unidentified products at ambient temperature, so was characterized only by NMR. Two carbonyl resonances, at δ 177.9 and 177.5, are observed in the $^{13}C\{^1H\}$ NMR spectrum, and in the $^{13}C{=}^{13}CH_2$-containing sample the lower field carbonyl signal displays trans coupling (26 Hz) to $^{13}C_\alpha$. The vinylidene carbons resonate at δ 106.0 (C_α) and 133.4 (C_β) and display the normal couplings. Although signals were observed in the ^1H NMR in the regions expected for vinylidene protons, we were unable to unambiguously assign them owing to many impurities in the sample. However the two methyl resonances are obvious at δ −0.45 and −0.92 and are shown, by selective ^{31}P decoupling, to be bound to different metals, by displaying coupling to only the ^{31}P nuclei bound to the respective metal. We had prepared **23** with the intention of studying migratory insertions involving the vinylidene ligands; however the instability of the species has precluded this study. It may be, however, that this instability is induced by migratory insertion which creates unsaturation in the complex. Further studies are underway, investigating other alkyl and aryl derivatives of **23**.

Conclusions

The cationic, vinylidene-bridged complexes $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CC(H)R)(dppm)_2][X]$ (R = H (**4**), Ph (**6**)) were studied with the idea that their incipient coordinative unsaturation could result in the incorporation of alkynes, leading to unusual products, containing the vinylidene group together with a modified or unmodified alkyne. Verification that unsaturation in these species could result from movement of the bridging iodo ligand to a terminal site came from the products in the reactions of **4** with ^{t}BuNC and CO, which showed each of these ligands in the respective products occupying the site vacated by the iodo group. Reaction of **4** or **6** with alkynes appears to proceed in much the same manner yielding two unusual classes of complexes, in which the added alkyne either remains unmodified or undergoes tautomerism to a second vinylidene group.

With the phenylvinylidene-bridged precursor **6**, reaction with either acetylene or phenylacetylene yielded products $[Ir_2I(CO)_2(\mu\text{-}CC(H)Ph)(\mu\text{-}HCCR)(dppm)_2][X]$ (R = H (**14**), Ph (**18**)) bridged by a phenylvinylidene group and the alkyne molecule. In addition to the spectroscopic evidence supporting the presence of two alkyne tautomers in the same complex, an X-ray structure determination of the neutral diiodo species (**15**) confirmed the formulation.

Reaction of the vinylidene-bridged precursor **4** with acetylene gives an analogous vinylidene- and acetylene-bridged product (together with unidentified products); however the reaction of **4** with phenylacetylene yields the unusual bis(vinylidene) species $[Ir_2I(CO)_2(CCH_2)(CC(H)Ph)(dppm)_2][X]$ (**19**), which appears to have each vinylidene group terminally bound to a different metal. Reaction of this species with I^-, CH_3^-, or CO yields the respective adducts in which the vinylidene groups move to the bridging sites. This formulation is confirmed by an X-ray determination of the diiodo species, which is isomeric with **15**, with the two differing in the tautomer of acetylene present. Compound **19** is an unusual example in which a vinylidene ligand is terminally bound in a binuclear system. The previous rare examples involving terminal, instead of bridging vinylidenes, have large vinylidene substituents suggesting that their terminal coordination is sterically driven. This appears not to be the case with **19**, since the addition of ligands leads to a bridged arrangement. The facile reversible interconversion between the terminal and bridging modes is also unusual.

The obvious question that arises from these results relates to the generation of a mixed vinylidene–acetylene complex by one route and a divinylidene complex by another. Why does the unsubstituted vinylidene-bridged compound **4** yield a bis(vinylidene) compound when reacted with phenylacetylene while the other reactions attempted yield the mixed vinylidene–alkyne products? It is noteworthy that only **4** yields the bis(vinylidene) species, and this occurs only with phenylacetylene. We assume that the tendency to yield the bis(vinylidene) species results from the tendency to undergo initial oxidative addition to yield the hydride–acetylide intermediate, which is presumed to precede vinylidene formation.[23,38-41] If our assumption is correct, formation of a bis(vinylidene) complex from the vinylidene-bridged **4**, but *not* from the phenylvinylidene-bridged **6**, can be rationalized on the basis that the stronger π-acidity of the phenylvinylidene group,[53] should leave the metals less electron rich and less prone to oxidative addition. Why this oxidative addition to **4** apparently occurs only with phenylacetylene and

---

(51) Afzol, D.; Lukehart, C. M. *Organometallics* **1987**, *6*, 546.
(52) Wang, L.-S.; Cowie, M. *Organometallics* **1995**, *14*, 2374.

not with acetylene is somewhat more puzzling, since the relative tendencies of these alkynes to oxidatively add has to our knowledge not been reported. However, if these tendencies parallel their acidities,[54] we might expect the phenylacetylene to oxidatively add more readily. It must be noted, however, that the reactivity of **4** with acetylene was not studied in depth owing to the number of resulting products, so we cannot rule out that at least one of the unidentified products may have been a bis(vinylidene) species. These ideas remain to be tested through the use of different substituents on the vinylidene precursor and with different terminal alkynes.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council (NSERC) of Canada and the University of Alberta for financial support. Dr. R. McDonald is thanked for assistance in preparing the tables of data for compound **15**, and Drs. H. Liu, P. N. Swepston, J. M. Troup, and B. R. Vincent at Molecular Structure Corp. are acknowledged for data collection and processing for compound **20b**.

Supplementary Material Available: Tables of positional and thermal parameters for the phenyl carbons, anisotropic thermal parameters, idealized hydrogen parameters, and bond distances and angles involving the phenyl rings for compounds **15** and **20b** (10 pages). Ordering information is given on any current masthead page.

OM940982E

---

(53) This can be seen from the IR spectra of **4** and **6** and of **8** and **9** (ref 23), which show that the carbonyl stretches for the vinylidene-bridged species are at lower frequency than those of the phenylvinylidene species.

(54) Streitwieser, A., Jr.; Hammons, J. H. *Prog. Phys. Org. Chem.* **1965**, *3*, 41.