Synthesis of a DMPM and Hydrido-Bridged Diiridium Complex, $[(Cp^*Ir)_2(\mu\text{-dmpm})(\mu\text{-H})_2][OTf]_2$, and Its Reactivity toward Alkynes and Isocyanides

Ken-ichi Fujita,* Hirohide Nakaguma, Fumihiro Hanasaka, and Ryohei Yamaguchi*

Department of Natural and Environmental Sciences, Faculty of Integrated Human Studies, and Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501, Japan

Received April 4, 2002

Reaction of $[Cp^*IrCl(\mu\text{-H})]_2$ (**2**) (Cp^* = pentamethylcyclopentadienyl) with equimolar amounts of bis(dimethylphosphino)methane (dmpm) in THF followed by 2 equiv of AgOTf gives a new binuclear iridium complex, $[(Cp^*Ir)_2(\mu\text{-dmpm})(\mu\text{-H})_2][OTf]_2$ (**1**). Complex **1** reacts with ethyne to give a μ-vinyl complex, $[(Cp^*Ir)_2(\mu,\eta^1,\eta^2\text{-CH=CH}_2)(\mu\text{-dmpm})(\mu\text{-H})][OTf]_2$ (**4**), via addition of the iridium hydride to the carbon−carbon triple bond. Reactions of **1** with terminal alkynes give mixtures of α-isomers of a μ-vinyl complex, $[(Cp^*Ir)_2(\mu,\eta^1,\eta^2\text{-CR=CH}_2)(\mu\text{-dmpm})(\mu\text{-H})][OTf]_2$ [R = Ph (**5a**), $PhCH_2$ (**5b**), ^{n}Bu (**5c**)], and *β-trans* isomers $[(Cp^*Ir)_2(\mu,\eta^1,\eta^2\text{-CH=CHR})(\mu\text{-dmpm})(\mu\text{-H})][OTf]_2$ [R = Ph (**6a**), $PhCH_2$ (**6b**), ^{n}Bu (**6c**)]. The μ-vinyl ligand in **6a**−**c** undergoes a fluxional process. Heating the α-isomers **5a**−**c** at 120 °C results in isomerization to *β-trans* isomers **6a**−**c**. Complex **1** reacts with *tert*-butylisocyanide to give the simple adduct $[(Cp^*Ir)(CN^tBu)(\mu\text{-dmpm})(\mu\text{-H})(Cp^*Ir)(H)][OTf]_2$ (**7**), while reaction of **1** with phenylisocyanide or cyclohexylisocyanide gives μ-aminocarbyne complexes $[(Cp^*Ir)_2(\mu,\eta^1\text{-CN(H)R})(\mu\text{-dmpm})(\mu\text{-H})][OTf]_2$ [R = Ph (**8a**), Cy (**8b**)]. The structures of **1**, **5c**, **6a**, **7**, and **8a** have been determined by X-ray diffraction methods.

Introduction

There is great interest in the chemistry of transition metal hydrides,[1] owing to their significance as the intermediate in industrial organometallic reactions such as olefin hydrogenation, olefin carbonylation, or the Wacker-Höchst process. Recently, much attention has focused on multinuclear transition metal complexes containing multiple bridging hydrido ligands, because they readily provide a vacant site for the incoming substrates and exhibit attractive reactivities in many cases.[2] Among such complexes, hydrido-bridged multimetallic complexes with pentamethylcyclopentadienyl (Cp^*) ligands are the most interesting, and their fascinating properties have been revealed.[3] For example, Suzuki and co-workers have reported cleavage of carbon−hydrogen and carbon−carbon bonds in hydrocarbon molecules on the triruthenium polyhydrido cluster $(Cp^*Ru)_3(\mu\text{-H})_3(\mu_3\text{-H})_2$.[3c,e,i] Wakatsuki and co-workers have studied the catalytic activity of the binuclear iridium hydrido complex $[Cp^*Ir(\mu\text{-H})]_2$ for carbon−carbon bond cleavage.[3b]

We previously reported the synthesis and structures of binuclear iridium hydrido complexes, $[(Cp^*Ir)_2(\mu\text{-dppm})(\mu\text{-H})(\mu\text{-X})]^{2+}$ (dppm = bis(diphenylphosphino)methane, X = Cl, OMe, OH) and $[(Cp^*Ir)_2(\mu\text{-dppm})(\mu\text{-H})_2]^{2+}$,[4] in which two metals are bridged by dppm as well as hydrides in order to prevent dissociation to a mononuclear species. However, those complexes exhibited rather poor reactivity, probably because the metals are surrounded by bulky diphenylphosphino groups and

(1) (a) Venanzi, L. M. *Coord. Chem. Rev.* **1982**, *43*, 251. (b) Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231.

(2) (a) Lin, J. T.; Huang, P. H. *Organometallics* **1998**, *17*, 3619. (b) Gao, Y.; Kuncheria, J.; Yap, G. P. A.; Puddephatt, R. J. *Chem. Commun.* **1998**, 2365. (c) Jahncke, M.; Neels, A.; Stoeckli-Evans, H.; Süss-Fink G. *J. Organomet. Chem.* **1998**, *561*, 227. (d) Alonso, F. J. G.; Sanz, M. G.; Liu, X. Y.; Oliveira, A.; Ruiz, M. A.; Riera, V.; Bois, C. *J. Organomet. Chem.* **1996**, *511*, 93. (e) Alonso, F. J. G.; Sanz, M. G.; Riera, V.; Abril, A. A.; Tiripicchio, A.; Ugozzoli, F. *Organometallics* **1992**, *11*, 801. (f) Alonso, F. J. G.; Riera, V.; Ruiz, M. A.; Tiripicchio, A.; Camellini, M. T. *Organometallics* **1992**, *11*, 370. (g) McDonald, R.; Sutherland, B. R.; Cowie, M. *Inorg. Chem.* **1987**, *26*, 3333. (h) Legzdins, P.; Martin, J. T.; Einstein, F. W. B.; Willis, A. C. *J. Am. Chem. Soc.* **1986**, *108*, 7971. (i) Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Molinari, H.; Sironi, A. *Inorg. Chem.* **1985**, *24*, 2666. (j) Lee, K.-W.; Brown, T. L. *Organometallics* **1985**, *4*, 1025. (k) Alt, H. G.; Frister, T. *J. Organomet. Chem.* **1985**, *293*, C7. (l) Burgess, K. *Polyhedron* **1984**, *3*, 1175. (m) Burch, R. R.; Shusterman, A. J.; Muetterties, E. L.; Teller, R. G.; Williams, J. M. *J. Am. Chem. Soc.* **1983**, *105*, 3546. (n) Aspinall, H. C.; Deeming, A. J. *Chem. Commun.* **1983**, 838. (o) Adams, R. D. *Acc. Chem. Res.* **1983**, *16*, 67. (p) Mays, M. J.; Prest, D. W.; Raithby, P. R. *Chem. Commun.* **1980**, 171. (q) Churchill, M. R.; Chang, S. W.-Y. N. *Chem. Commun.* **1973**, 691.

(3) (a) Ogo, S.; Nakai, H.; Watanabe, Y. *J. Am. Chem. Soc.* **2002**, *124*, 597. (b) Hou, Z.; Koizumi, T.; Fujita, A.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **2001**, *123*, 5812. (c) Takemori, T.; Inagaki, A.; Suzuki, H. *J. Am. Chem. Soc.* **2001**, *123*, 1762. (d) Faure, M.; Onidi, A.; Neels, A.; Stoeckli-Evans, H.; Süss-Fink, G. *J. Organomet. Chem.* **2001**, *634*, 12. (e) Inagaki, A.; Takemori, T.; Tanaka, M.; Suzuki, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 404. (f) Vicic, D. A.; Jones, W. D. *Organometallics* **1999**, *18*, 134. (g) Nishio, M.; Mizobe, Y.; Matsuzaka, H.; Hidai, M. *Inorg. Chim. Acta* **1997**, *265*, 59. (h) Heinekey, D. M.; Fine, D. A.; Barnhart, D. *Organometallics* **1997**, *16*, 2530. (i) Suzuki, H.; Takaya, Y.; Takemori, T. *J. Am. Chem. Soc.* **1994**, *116*, 10779. (j) Oro, L. A.; Carmona, D.; Puebla, M. P.; Lamata, M. P.; Foces-Foces, C.; Cano, F. H. *Inorg. Chim. Acta* **1986**, *112*, L11. (k) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3722. (l) Gill, D. S.; Maitlis, P. M. *J. Organomet. Chem.* **1975**, *87*, 359. (m) White, C.; Oliver, A. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1973**, 1901.

(4) Fujita, K.; Hamada, T.; Yamaguchi, R. *J. Chem. Soc., Dalton Trans.* **2000**, 1931.

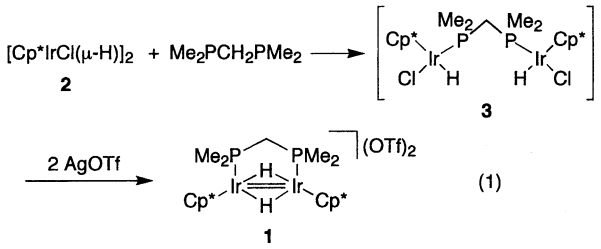
10.1021/om020266+ CCC: $22.00
Publication on Web 08/01/2002

Cp* ligands. Thus, it is anticipated that a less sterically demanding ligand might be indispensable for another organic molecule to access the coordination sphere of the iridium centers.

In this paper we report the synthesis and structure of a new binuclear Cp*Ir complex bridged by less bulky bis(dimethylphosphino)methane (dmpm) and hydrides, $[(Cp^*Ir)_2(\mu\text{-dmpm})(\mu\text{-H})_2]^{2+}$ (**1**), as well as its reactivity toward alkynes and isocyanides.

Results and Discussion

Synthesis of $[(Cp^*Ir)_2(\mu\text{-dmpm})(\mu\text{-H})_2]^{2+}$ (1). Successive treatment of $[Cp^*IrCl(\mu\text{-H})]_2$ (**2**) with equimolar amounts of dmpm in THF and then 2 equiv of AgOTf gave $[(Cp^*Ir)_2(\mu\text{-dmpm})(\mu\text{-H})_2]^{2+}$ (**1**) in high yield (eq 1).

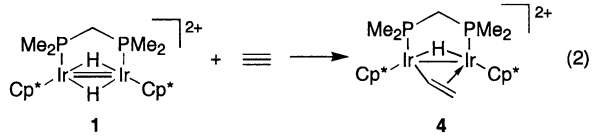


Compared to the synthesis of dppm-bridged complex $[(Cp^*Ir)_2(\mu\text{-dppm})(\mu\text{-H})_2]^{2+}$,[4] the complex **1** could be synthesized by a more simple procedure. Complex **1** was obtained as air-stable dark brown crystals. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR data of **1** are summarized in Table 1. The ^1H NMR spectrum showed a single resonance of Cp* at δ 2.00 together with those due to methylene (δ 2.73) and methyl (δ 2.12) of the dmpm ligand. The signal for the bridging hydrides was found at δ −17.82 as a triplet (J = 10 Hz) coupling to the two phosphorus atoms, indicating that the hydride bridges two iridium centers. All NMR data of **1** are consistent with the proposed structure. Formation of **1** would proceed via neutral intermediate **3**;[5] however, no attempt to isolate **3** was made. The complex **1** is a very rare example of a dicationic complex containing the unsaturated moiety $M_2(\mu\text{-H})_2$ (M═M),[3h,4] although a number of neutral or monocationic complexes are known.[2,3]

Crystal Structure of 1. The structure of **1** was confirmed by X-ray diffraction study. The crystal of the complex **1** contained a solvent molecule (benzene). The molecular geometry and atom-numbering system of **1** are shown in Figure 1, and the results obtained are summarized in Tables 2 and 3. The complex **1** contains a diiridium core bridged by a dmpm and two hydrides. The geometry around each iridium center is described as highly distorted three-legged piano stool, if the iridium−iridium bond is ignored. The complex **1** would be a 32-electron one, so it should possess an Ir═Ir double bond. The iridium−iridium distance is 2.7236(8) Å, which is a little larger than that of the iridium−iridium double bond in $[(Cp^*Ir)_2(\mu\text{-H})_2(\mu_2\text{-}\eta^1,\eta^1\text{-}N_2C_3H_3)]^+$ (2.663(1) Å);[3j] however, it falls between that of the single bond in $[(Cp^*IrCl)_2(\mu\text{-H})(\mu\text{-Cl})]$ (2.903(1) Å)[6] and the triple bond in $[(Cp^*Ir)_2(\mu\text{-H})_3]^+$ (2.455 Å[7] and 2.4677(4) Å[3a]). Compared to the dppm analogue $[(Cp^*Ir)_2(\mu\text{-dppm})(\mu\text{-H})_2]^{2+}$ reported previously,[4] the iridium−iridium distance in **1** is 0.09 Å shorter, suggesting that it is significantly less crowded around the iridium centers.

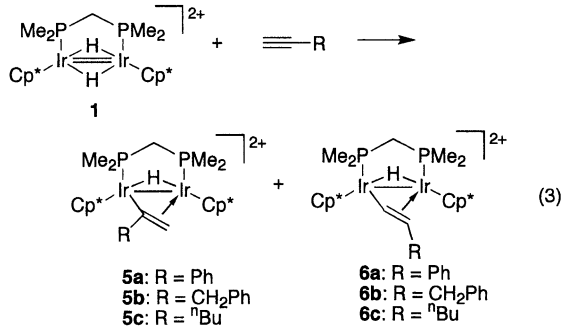
Although a number of multinuclear complexes containing the $M_2(\mu\text{-H})_2$ (M═M) moiety have been known,[2,3] their reactivity has been investigated in detail only for $Os_3(\mu\text{-H})_2(CO)_{10}$[2l] and $Mn_2(\mu\text{-H})_2(CO)_6(\mu\text{-dppm})$.[2d,e,f] We became interested in the reactivity of **1** toward small molecules. Results of the reactions of **1** with alkynes and isocyanides are as follows.

Reactions of 1 with Alkynes. Complex **1** smoothly reacted with atmospheric ethyne in methanol to give a μ-vinyl complex $[(Cp^*Ir)_2(\mu\text{-dmpm})(\mu_2,\eta^1,\eta^2\text{-}CH{=}CH_2)(\mu\text{-H})]^{2+}$ (**4**) via addition of the iridium hydride to the carbon−carbon triple bond (eq 2). The ^1H, $^{13}C\{^1H\}$, and



$^{31}P\{^1H\}$ NMR data of **4** are summarized in Table 1. In the ^1H NMR spectrum, characteristic signals of the μ-vinyl moiety were observed at δ 8.42, 5.15, and 3.09−2.96 in addition to nonequivalent Cp* at δ 2.21 and 2.17. The signal for the iridium hydride was observed at δ −20.36 as a doublet of doublets. In the $^{13}C\{^1H\}$ spectrum, signals for the μ-vinyl moiety were found at δ 115.5 and 59.1. All NMR data of **4** are consistent with the proposed structure and comparable to those of the known μ-vinyl complexes, such as $[(CpM)_2(\mu\text{-}CH{=}CH_2)(\mu\text{-CO})(CO)_2]^+$ (Cp = cyclopentadienyl, M = Fe or Ru)[8a] or $[Rh_2(\mu\text{-}CH{=}CH_2)(\mu\text{-CO})(CO)(\eta^5\text{-}C_9H_7)_2]^+$.[8b]

The complex **1** also reacted with phenylethyne, 3-phenyl-1-propyne, or 1-hexyne to give μ-vinyl complexes (eq 3). In these reactions, products were obtained as a



mixture of α-isomer **5** and *β-trans* isomer **6**. No *β-cis* isomer was obtained. The isomers **5** and **6** could be separated by column chromatography on silica gel. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR data of **5a**−**c** and **6a**−**c** are summarized in Table 1. Reaction of **1** with phenylethyne proceeded at room temperature in methanol to give a mixture of **5a** and **6a** (1.2:1.0; determined by

(5) Isolation of diphosphine-bridged dinuclear Cp*Ir complexes has been reported. Keim, W.; Kraneburg, P.; Dahmen, G.; Deckers, G.; Englert, U.; Linn, K.; Spaniol, T. P.; Raabe, G. *Organometallics*, **1994**, *13*, 3085. See also ref 4.

(6) Churchill, M. R.; Julis, S. A. *Inorg. Chem.* **1977**, *16*, 1488.

(7) Bau, R.; Carroll, W. E.; Teller, R. G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 3872.

(8) (a) Dyke, A. F.; Knox, S. A. R.; Morris, M. J.; Naish, P. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1417. (b) Al-Obaidi, Y. N.; Green, M.; White, N. D.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 319.

Table 1. NMR Spectral Data for Complexes 1, 4, 5, 6, 7, and 8[a]

complex	^{1}H NMR	^{13}C{^{1}H} NMR	^{31}P{^{1}H} NMR
1	2.73 (t, J = 13, 2H, PCH_2P), 2.12 (t, J = 6, 12H, PMe), 2.00 (s, 30H, Cp*), −17.82 (t, J = 10, 2H, Ir−H−Ir)	122.3 (q, J = 322, CF_3), 100.3 (s, Cp*), 33.7 (t, J = 37, PCH_2P), 17.3 (t, J = 22, PMe), 11.1 (s, Cp*)	22.5 (s)
4	8.42 (t, J = 10, 1H, CH=CH_2), 5.15 (d, J = 9, 1H, CH=CH_2), 3.09−2.96 (m, 2H, overlapped CH=CH_2 and PCH_2P), 2.52 (m, 1H, PCH_2P), 2.21 (s, 15H, Cp*), 2.17 (d, J = 3, 15H, Cp*), 2.08 (d, J = 11, 6H, PMe), 2.00 (d, J = 11, 3H, PMe), 1.74 (d, J = 11, 3H, PMe), −20.36 (dd, J = 20, 9, 1H, Ir−H−Ir)	122.4 (q, J = 323, CF_3), 115.5 (d, J = 7, Ir-CH=CH_2), 102.3 (d, J = 2, Cp*), 101.2 (d, J = 3, Cp*), 59.1 (d, J = 7, Ir−CH=CH_2), 31.6 (dd, J = 44, 30, PCH_2P), 20.2 (d, J = 42, PMe), 19.0 (d, J = 42, PMe), 17.7 (dd, J = 39, 7, PMe), 13.8 (dd, J = 38, 7, PMe), 10.5 (s, Cp*), 10.1 (s, Cp*)	−10.3 (d, J = 41) −17.5 (d, J = 41)
5a	7.6−7.2 (m, 5H, Ph), 4.80 [s, 1H, C(Ph)=CH_2], 3.00 (m, 1H, PCH_2P), 2.74−2.64 [m, 2H, overlapped C(Ph)=CH_2 and PCH_2P], 2.18 (m, 3H, PMe), 2.05 (m, 6H, PMe), 2.02 (d, J = 2, 15H, Cp*), 1.93 (s, 15H, Cp*), 1.83 (m, 3H, PMe), −19.62 (dd, J = 21 5, 1H, Ir−H−Ir)	154.5 (s, i-Ph), 144.0 [d, J = 9, Ir-C(Ph)=CH_2], 131.0 (s, Ph), 129.0 (s, Ph), 128.6 (s, Ph), 122.2 (q, J = 322, CF_3), 103.7 (s, Cp*), 103.3 (s, Cp*), 51.1 [d, J = 6, Ir−C(Ph)=CH_2], 31.3 (dd, J = 50, 31, PCH_2P), 19.5 (d, J = 41, PMe), 19.4 (d, J = 45, PMe), 13.5 (dd, J = 38, 7, PMe), 10.3 (s, Cp*), 10.2 (s, Cp*)	4.5 (d, J = 37) −14.4 (d, J = 37)
5b	7.6−7.2 (m, 5H, Ph), 4.78 [t, J = 4, 1H, C(CH_2Ph)=CH_2], 4.56 (d, J = 16, 1H, CH_2Ph), 3.80 (d, J = 16, 1H, CH_2Ph), 2.87 [d, J = 4, 1H, C(CH_2Ph)=CH_2], 2.81 (t, J = 10, 2H, PCH_2P), 2.19 (d, J = 2, 15H, Cp*), 2.16−2.10 (m, 6H, PMe), 2.09 (d, J = 2, 15H, Cp*), 2.08−2.02 (m, 3H, PMe), 1.88 (d, J = 11, 3H, PMe), −20.07 (dd, J = 21, 5, 1H, Ir−H−Ir)	142.8 (s, i-Ph), 140.1 [d, J = 8, Ir-C(CH_2Ph)=CH_2], 129.3 (s, Ph), 128.8 (s, Ph), 127.3 (s, Ph), 122.3 (q, J = 322, CF_3), 103.3 (s, Cp*), 103.1 (d, J = 2, Cp*), 59.0 (s, CH$_2$Ph), 55.9 [d, J = 5, Ir−C(CH_2Ph)=CH_2], 31.2 (dd, J = 45, 29, PCH_2P), 20.3 (d, J = 41, PMe), 19.2 (d, J = 44, PMe), 18.2 (dd, J = 44, 5, PMe), 13.5 (dd, J = 37, 8, PMe), 10.8 (s, Cp*), 10.2 (s, Cp*)	−4.1 (d, J = 42) −18.7 (d, J = 42)
5c	4.62 [t, J = 5, 1H, C(^{n}Bu)=CH_2], 3.00 (m, 2H, ^{n}Bu), 2.82 (m, 1H, PCH_2P), 2.68−2.57 [m, 2H, overlapped C(^{n}Bu)=CH_2 and PCH_2P], 2.33 (m, 2H, ^{n}Bu), 2.21 (d, J = 2, 15H, Cp*), 2.12 (d, J = 6, 15H, Cp*), 2.10 (d, J = 12, 3H, PMe), 2.05 (d, J = 10, 3H, PMe), 1.99 (d, J = 11, 3H, PMe), 1.78 (d, J = 10, 3H, PMe), 1.64 (m, 2H, ^{n}Bu), 1.00 (t, J = 6, 3H, ^{n}Bu), −20.00 (dd, J = 22, 5, 1H, Ir−H−Ir)	144.1 [d, J = 9, Ir-C(^{n}Bu)=CH_2], 122.2 (q, J = 322, CF_3), 102.6 (s, Cp*), 102.5 (s, Cp*), 55.1 (s, ^{n}Bu), 53.0 [d, J = 10, Ir−C(^{n}Bu)=CH_2], 37.9 (s, ^{n}Bu), 31.3 (dd, J = 47, 28, PCH_2P), 23.9 (s, ^{n}Bu), 19.7 (dd, J = 35, 5, PMe), 19.3 (d, J = 44, PMe), 14.4 (s, ^{n}Bu), 13.2 (dd, 36, 8, PMe), 10.7 (s, Cp*), 10.0 (s, Cp*)	−4.9 (d, J = 41) −17.9 (d, J = 41)
6a	9.15 (d,J = 12, 1H, CH=CHPh), 7.6−7.2 (m, 5H, Ph), 5.00 (dt, J = 12, 6, 1H, CH=CHPh), 3.04−2.87 (m, 2H, PCH_2P), 2.02 (m, 6H, PMe), 2.01 (s, 30H, Cp*),1.92 (m, 6H, PMe), −19.95 (t, J = 15, 1H, Ir−H−Ir)	138.8 (s, i-Ph), 129.6 (s, Ph), 129.5 (s, Ph), 129.1 (s, Ph), 122.3 (q, J = 321, CF_3), 107.3 (s, Ir-CH=CHPh), 102.1 (s, Cp*), 81.4 (s, Ir−CH=CHPh), 31.7 (t, J = 36, PCH_2P), 20.2 (d, J = 42, PMe), 15.8 (d, J = 46, PMe), 10.2 (s, Cp*)	−14.3 (brs) −8.7[b](d, J = 41) −18.1[b](d, J = 41)
6b	8.57 [d, J = 11, 1H, CH=CH(CH_2Ph)], 7.5−7.2 (m, 5H, Ph), 3.55 [m, 1H, CH=CH(CH_2Ph)], 3.19 (m, 2H, CH_2Ph), 2.78 (m, 1H, PCH_2P), 2.61 (m, 1H, PCH_2P), 2.25 (s, 30H, Cp*), 2.25 (m, 3H, PMe), 2.06 (m, 6H, PMe), 1.74 (m, 3H, PMe), −19.88 (t, J = 12, 1H, Ir−H−Ir)	141.5 (s, i-Ph), 129.5 (s, Ph), 129.3 (s, Ph), 127.5 (s, Ph), 121.9 (q, J = 322, CF_3), 116.2 [d, J = 8, Ir-CH=CH(CH_2Ph)], 102.0 (s, Cp*), 78.8 [s, Ir−CH=CH(CH_2Ph)], 44.6 (s, CH_2Ph), 32.2 (t, J = 37, PCH_2P), 19.9 (d, J = 41, PMe), 15.7 (br, PMe), 10.6 (s, Cp*)	−12.2[c] (brs) −5.7[d](d, J = 37) −16.2[d](d, J = 37)
6c	8.26 (d,J = 11, 1H, CH=CH^{n}Bu), 3.52 (m, 1H, CH=CH^{n}Bu), 2.81 (t, J = 11, 2H, PCH_2P), 2.21 (d, J = 2, 30H, Cp*), 2.06 (d, J = 11, 6H, PMe), 1.92−1.85 [m, 8H, overlapped ^{n}Bu (2H) and PMe (6H)], 1.69 (m, 2H, ^{n}Bu), 1.47 (m, 2H, ^{n}Bu), 0.94 (t, J = 8, ^{n}Bu), −19.96 (t, J = 15, 1H, Ir−H−Ir)	122.3 (q,J = 322, CF_3), 115.9 (s, Ir-CH=CH^{n}Bu), 101.7 (s, Cp*), 81.1 (s, Ir−CH=CH^{n}Bu), 38.7 (s, ^{n}Bu), 34.4 (s, ^{n}Bu), 31.8 (t, J = 37, PCH_2P), 22.8 (s, ^{n}Bu), 20.1 (d, J = 41, PMe), 16.0 (br, PMe) 14.2 (^{n}Bu), 10.6 (s, Cp*)	−12.4[c] (s) −5.1[b](d, J = 41) −16.2[b](d, J = 41)
7[e]	5.28 (m, 1H, PCH_2P), 2.49 (m, 1H, PCH_2P), 2.15 (d, J = 2, 15H, Cp*), 2.06 (s, 15H, Cp*), 2.05 (m, 3H, PMe), 1.90 (d, J = 11, 3H, PMe), 1.80 (d, J = 10, 3H, PMe), 1.79 (d, J = 10, 3H, PMe), 1.62 (s, 9H, ^{t}Bu), −15.51 (d, J = 35, 1H, Ir−H), −24.00 (d, J = 13, 1H, Ir−H−Ir)	121.3 (q, J = 321, CF_3), 101.9 (s, Cp*), 96.9 (s, Cp*), 50.4 (dd, J = 39, 30, PCH_2P), 30.8 (s, ^{t}Bu), 24.3 (dd, J = 46, 8, PMe), 20.1 (d, J = 46, PMe), 17.5 (d, J = 37, PMe), 13.2 (dd, J = 39, 7, PMe), 11.2 (s, Cp*), 11.1 (s, Cp*)	−30.4 (d, J = 32) −36.7 (d, J = 32)
8a	11.50 (brs, 1H, NH), 7.7−7.4 (m, 5H, Ph), 2.46 (m, 1H, PCH_2P), 2.30 (s, 15H, Cp*), 2.1−2.0 (m, 12H, PMe), 1.96 (s, 15H, Cp*), 1.34 (q, J = 13, 1H, PCH_2P), −18.42 (t, J = 11, 1H, Ir−H−Ir)	255.0 (br, Ir−C−Ir), 142.6 (d, J = 18, i-Ph), 130.5 (s, Ph), 129.6 (s, Ph), 125.7 (s, Ph), 122.3 (q, J = 322, CF_3), 100.8 (s, Cp*), 100.7 (s, Cp*), 24.2 (t, J = 35, PCH_2P), 19.9 (d, J = 39, PMe), 18.8 (d, J = 39, PMe), 14.8 (dd, J = 42, 7, PMe), 14.1 (dd, J = 42, 9, PMe), 10.64 (s, Cp*), 10.57 (s, Cp*)	−11.9 (d, J = 41) −13.5 (d, J = 41)
8b	9.97 (brs, 1H, NH), 3.76 (m, 1H, Cy), 2.83 (s, 2H, PCH_2P), 2.31 (d, J = 2, 15H, Cp*), 2.20 (d, J = 2, 15H, Cp*), 2.1−1.7 (m, 12H, PMe), 2.4−1.0 (m, 11H, Cy), −18.56 (t, J = 13, 1H, Ir−H−Ir)	247.1 (t, J = 7, Ir−C−Ir), 122.2 (q, J = 322, CF_3), 100.4 (s, Cp*), 100.3 (d, J = 3, Cp*), 66.8 (d, J = 20, Cy), 34.2 (s, Cy), 25.7 (s, Cy), 25.4 (s, Cy), 23.2 (t, J = 36, PCH_2P), 19.3 (d, J = 38, PMe), 16.1 (dd, J = 43, 10, PMe), 14.4 (dd, J = 41, 10, PMe), 11.3 (s, Cp*), 10.5 (s, Cp*)	−12.9 (d, J = 41) −13.5 (d, J = 41)

[a] Measured in acetone-d_6 at room temperature; coupling constants in hertz. [b] Measured at −80 °C. [c] Measured at 50 °C. [d] Measured at −60 °C. [e] Measured in CD_2Cl_2.

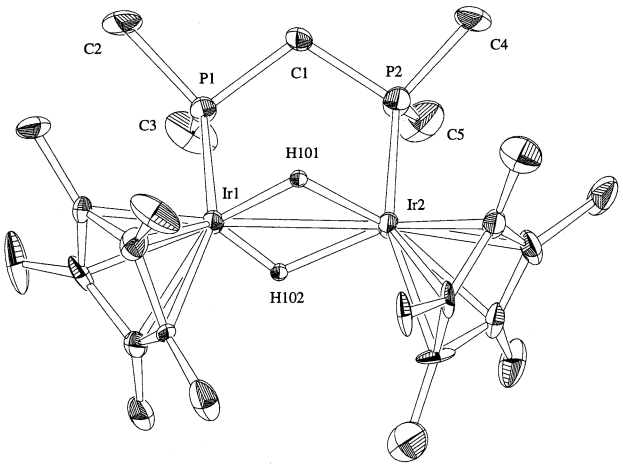
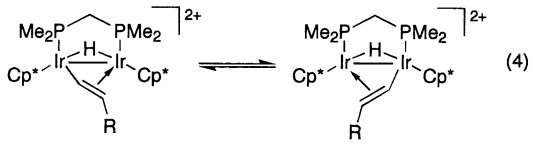


Figure 1. ORTEP view of **1**. Hydrogen atoms except for metal hydrides are omitted for clarity.

NMR analysis of the crude product). It should be noted here that this high reactivity of **1** is in contrast with the previous results that the analogous dppm complex does not react with phenylethyne even at 120 °C. In the ^{1}H NMR spectrum of **5a**, signals of the μ-vinyl moiety were observed at δ 4.80 and 2.74−2.64. In the ^{13}C{^{1}H} spectrum, a signal at δ 51.1 was defined to be that of the terminal methylene by the DEPT spectrum, suggesting that **5a** would be an α-isomer. In the ^{1}H NMR spectrum of **6a**, signals of the μ-vinyl moiety were observed at δ 9.15 and 5.00, which were coupled with J = 12 Hz, indicating they are in *trans* configuration. A signal of Cp* was observed at δ 2.01 as a single resonance. The ^{31}P{^{1}H} spectrum showed one broad single resonance at δ −14.3. These signals were separated in the measurement at lower temperature, indicating fluxional behavior of the μ-vinyl ligand around room temperature (vide infra). Reactions of **1** with 3-phenyl-1-propyne and 1-hexyne proceeded in methanol at reflux temperature to give **5b** and **6b** (1.0:1.2) and **5c** and **6c** (1.1:1.0), respectively. Reactions of **1** with internal alkynes, such as 1,2-diphenylethyne and 1-phenyl-1-propyne, were attempted; however, no reaction occurred.

Formation of the μ-vinyl-μ-hydrido complex by the reaction of the di-μ-hydrido complex with alkyne is the most important step in the stereoselective hydrogenation of alkynes catalyzed by binuclear complexes.[2m] The synthesis of μ-vinyl-μ-hydrido complexes by the reaction of a di-μ-hydrido complex with alkynes has been relatively unexplored.[2f,l,m]

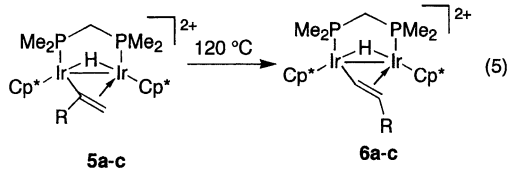
Fluxional Behavior of the μ-Alkenyl Ligand in 6. It has been established that the μ-vinyl ligand in $Os_3(\mu\text{-}C(R)=CHR')(\mu\text{-}H)(CO)_{10}$,[9a] $Re_2(\mu\text{-}CR=CR'R'')(\mu\text{-}H)(CO)_8$,[9b] or other μ-vinyl complexes[2m,8a] undergoes a fluxional process, in which σ- and π-bonds of the μ-vinyl group are rapidly interchanged between two bridged metal atoms. Figure 2 shows the variable-temperature ^{31}P NMR spectra of **6a**. At 50 °C, only one resonance for the phosphorus of dmpm was found. As the temperature was lowered, the peaks coalesced at −15 °C and finally split into two doublet peaks (J = 41 Hz) (∼−80 °C). A similar phenomenon was observed in the variable-temperature ^{1}H NMR spectra. At room temperature, one resonance for the methyl groups of Cp* was found, which split into two nonequivalent peaks at −80 °C. A resonance for the bridging hydride was found as a triplet coupling (J = 15 Hz) to the two phosphorus atoms at room temperature, which changed into a doublet of doublets (J = 19 and 9 Hz) at −80 °C. These results indicate that the μ-vinyl ligand of **6a** undergoes a fluxional process (eq 4). The $\Delta G_c^{\ddagger}$ value estimated from



(4)

the coalescence temperature and peak separation in the ^{31}P NMR is 45.0 kJ/mol.[10] The complexes **6b** and **6c** also showed fluxional behavior with $\Delta G_c^{\ddagger}$ values 52.9 and 51.9 kJ/mol, respectively. These values are comparable to those of the known examples.[8a,9] The complexes **4**, **5a**, **5b**, and **5c** did not show fluxional behavior between −80 °C and room temperature.

α−*β* Alkenyl Isomerization of 5. Heating the methanol solution of the α-isomer of the μ-vinyl complexes **5a**−**c** at 120 °C in a sealed tube resulted in quantitative isomerization to *β-trans*-alkenyl complexes **6a**−**c** (eq 5). While it is known that interconversion of



(5)

β-cis and *β-trans* isomers in binuclear metal μ-vinyl complexes is relatively common,[11] isomerization of the α-isomer to the *β*-isomer is very rare.[12] Although the mechanism for the present α to *β* isomerization is not clear at this stage, we presume that it follows a mechanism similar to that reported for isomerization at diiron centers.[12] Reactions of **1** with phenylethyne, 3-phenyl-1-propyne, or 1-hexyne in methanol at 120 °C in a sealed tube gave **6a**, **6b**, or **6c** in almost quantitative yield.

Crystal Structures of 5c and 6a. The structures of **5c** and **6a** were confirmed by X-ray diffraction study. The molecular geometry and atom-numbering system of **5c** and **6a** are shown in Figures 3 and 4, and the results obtained are summarized in Tables 2 and 3. The crystal of the complex **6a** contained a solvent molecule (acetone).

In complex **5c**, there is a μ_2,η^1,η^2-vinyl ligand with a substituent on α-carbon C(26). The α-carbon atom C(26) is ca. 0.2 Å closer to one iridium atom (Ir(1)−C(26) = 2.043(8) Å) than to the other (Ir(2)−C(26) = 2.264(8)

(9) (a) Shapley, J. R.; Richter, S. I.; Tachikawa, M.; Keister, J. B. *J. Organomet. Chem.* **1975**, *94*, C43. (b) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1984**, *106*, 644.

(10) $\Delta G_c^{\ddagger}$ calculated from the relations $k_c = \pi\Delta\nu/2^{0.5}$ and $k_c = (k_b T_c/h)\exp(-\Delta G_c^{\ddagger}/RT_c)$, where k_b is the Boltzmann constant, h is Plank's constant, $\Delta\nu$ is the stopped-exchange separation of the two resonances, and T_c is the coalescence temperature.

(11) (a) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1984**, *106*, 3474. (b) Hogarth, G.; Lavender, M. H. *J. Chem. Soc., Dalton Trans.* **1994**, 3389.

(12) Anwar, M. K.; Hogarth, G.; Senturk, O. S.; Clegg, W.; Doherty, S.; Elsegood, M. R. J. *J. Chem. Soc., Dalton Trans.* **2001**, 341.

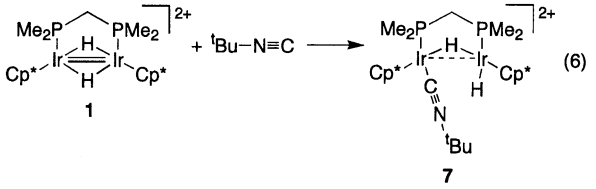
Table 2. Selected Interatomic Distances (Å) and Angles (deg) in the Complexes 1·C_6H_6, 5c, 6a·C_3H_6O, 7, and 8a

	1·C_6H_6	5c	6a·C_3H_6O	7	8a
Ir(1)−Ir(2)	2.7236(8)	2.9329(6)	2.9201(4)	3.168(1)	2.864(2), 2.865(2), 2.855(1)
Ir(1)−P(1)	2.291(2)	2.286(2)	2.275(2)	2.281(4)	2.285(5), 2.285(5), 2.275(6)
Ir(1)−C(26)		2.043(8)	2.020(7)	1.92(1)	1.99(2), 1.98(2), 2.00(2)
Ir(2)−P(2)	2.276(3)	2.303(2)	2.299(2)	2.256(4)	2.272(5), 2.273(5), 2.267(5)
Ir(2)−C(26)		2.264(8)	2.204(7)		1.99(2), 1.96(2), 1.98(2)
Ir(2)−C(27)		2.184(8)	2.324(7)		
P(1)−C(1)	1.84(1)	1.821(9)	1.827(7)	1.82(1)	1.81(2), 1.83(2), 1.81(2)
P(2)−C(1)	1.81(1)	1.821(9)	1.816(7)	1.83(1)	1.80(2), 1.81(2), 1.80(2)
C(26)−C(27)		1.41(1)	1.40(1)		
C(26)−C(28)		1.51(1)			
C(27)−C(28)			1.49(1)		
C(26)−N(1)				1.16(2)	1.31(2), 1.33(2), 1.29(2)
N(1)−C(27)				1.51(2)	1.46(2), 1.42(2), 1.46(2)
Ir(2)−Ir(1)−P(1)	93.10(7)	91.37(6)	92.34(5)		90.0(1), 90.2(1), 91.6(1)
Ir(1)−Ir(2)−P(2)	93.50(8)	86.19(6)	90.52(5)		93.5(1), 94.2(1), 93.4(1)
P(1)−C(1)−P(2)	110.6(6)	112.5(5)	116.8(4)	113.2(7)	113(1), 113.8(9), 116(1)
Ir(1)−C(26)−Ir(2)		85.7(3)	87.4(3)		92.0(8), 93.3(7), 91.7(7)
Ir(1)−C(26)−C(27)		125.9(6)	131.2(5)		
Ir(1)−C(26)−C(28)		119.5(6)			
Ir(1)−C(26)−N(1)				173(1)	138(1), 136(1), 139(1)
Ir(2)−C(26)−N(1)					130(1), 130(1), 129(1)
C(27)−C(26)−C(28)		114.5(7)			
C(26)−C(27)−C(28)			125.2(7)		
C(26)−N(1)−C(27)				175(1)	128(2), 130(2), 129(1)

Å). The β-carbon atom of the vinyl ligand is within bonding distance of Ir(2) (Ir(2)−C(27) = 2.184(8) Å). The iridium−iridium distance (2.9329(6) Å) is lengthened relative to that in **1**, which is probably due to an electronic factor since the μ-vinyl complex has two more electrons than the parent complex **1** and forms a 34-electron complex. The carbon−carbon distance in the vinyl moiety is 1.41(1) Å, which is between the bond distances of a C−C single and C=C double bond.

In complex **6a**, there is a μ_2,η^1,η^2-vinyl ligand with a substituent phenyl group on β-carbon C(27). It is apparent that **6a** has the β-*trans* structure. The bond distances of Ir(1)−C(26), Ir(2)−C(26), and Ir(2)−C(27) are 2.020(7), 2.204(7), and 2.324(7) Å, respectively. The distance of Ir(2)−C(27) was somewhat larger compared to that in **5c** or the reported μ-vinyl diiridium complex,[13] which would be probably because of steric hindrance of the phenyl group. The iridium−iridium distance is 2.9201(4) Å, which is comparable to that in **5c**.

Reaction of 1 with *tert*-Butylisocyanide. The complex **1** smoothly reacted with *tert*-butylisocyanide in methanol at room temperature to give an adduct **7** (eq 6). The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR data of **7** are

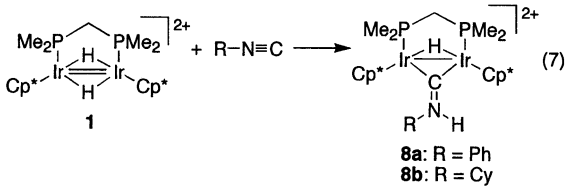


1 7 (6)

summarized in Table 1. In the ^{1}H NMR spectrum, two signals for nonequivalent Cp* were found at δ 2.15 and 2.06. Signals for hydrides were observed at δ −15.51 and −24.00. A signal of the *tert*-butyl group was observed at δ 1.62. In the IR spectrum, absorption corresponding to that of the isocyanide ligand was found at 2175 cm^{-1}. These data indicate that *tert*-butylisocyanide added to one of the iridium centers. The reaction of a dihydride multinuclear species containing the moiety $M_2(\mu\text{-H})_2$ with isocyanides gives μ-formimidoyl μ-HC=NR,[2e,n,o,14,15] μ-aminocarbyne μ,η^1-C−N(H)R,[2k,o,14,16] or μ-isocyanide μ_2,η^1,η^2-CNR[2e] complex in many cases, and the present result demonstrates one of the relatively few examples in which a simple adduct (H)M(μ-H)M-(CNR) is obtained.[2o,14]

Crystal Structure of 7. The structure of **7** was confirmed by X-ray diffraction study. The molecular geometry and atom-numbering system of **7** are shown in Figure 5, and the results obtained are summarized in Tables 2 and 3. In the complex **7**, *tert*-butylisocyanide is evidently coordinated to one of the iridium centers through the terminal carbon atom with a distance of 1.92(1) Å, while the nitrogen atom has no interaction with the iridium centers. Coordination of the isocyanide ligand is linear type with an Ir(1)−C(26)−N(1) angle of 173(1)°. The structure of the isocyanide ligand is also linear with a C(26)−N(1)−C(27) angle of 175(1)°. The iridium−iridium distance (3.168(1) Å) is larger than the other 34-electron complexes **5c**, **6a**, and **8a**, which would be probably because of steric hindrance of the *tert*-butyl group.

Reaction of 1 with Phenylisocyanide or Cyclohexylisocyanide. In contrast to the above result, the complex **1** reacted with phenylisocyanide in methanol at room temperature to give a μ-aminocarbyne complex, **8a** (eq 7). The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR data of



1 **8a**: R = Ph **8b**: R = Cy (7)

8a are summarized in Table 1. In the ^{1}H NMR spec-

(13) Ishii, Y.; Ogio, K.; Nishio, M.; Retbøll, M.; Kuwata, S.; Matsuzaka, H.; Hidai, M. *J. Organomet. Chem.* **2000**, *599*, 221.

(14) Adams, R. D.; Golembeski, N. M. *J. Am. Chem. Soc.* **1979**, *101*, 2579.

Table 3. Crystal Data and Structure Refinement Parameters for 1·C_6H_6, 5c, 6a·C_3H_6O, 7, and 8a

	1·C_6H_6	**5c**	**6a**·C_3H_6O	**7**	**8a**
			Description of Crystal		
color, habit	dark brown, block	yellow, block	yellow, block	red-orange, block	yellow-orange, plate
max cryst dimens (mm)	0.40 × 0.40 × 0.30	0.40 × 0.30 × 0.20	0.40 × 0.40 × 0.30	0.40 × 0.30 × 0.20	0.40 × 0.20 × 0.05
cryst syst	orthorhombic	monoclinic	monoclinic	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1/n$	$P2_1/c$	$Pbca$	$P2_1/c$
a (Å)	17.116(5)	13.704(2)	12.002(2)	22.279(5)	28.16(2)
b (Å)	23.120(6)	17.740(3)	20.585(2)	22.823(3)	11.613(9)
c (Å)	10.485(4)	17.086(2)	18.342	16.402(7)	42.290(9)
α (deg)	90	90	90	90	90
β (deg)	90	92.20(1)	93.70(1)	90	104.96(2)
γ (deg)	90	90	90	90	90
V (Å^3)	4149(2)	4150.6(9)	4522.3(9)	8340(3)	13 360(11)
Z	4	4	4	8	12
formula	$C_{27}H_{46}F_6O_6P_2S_2Ir_2$·$C_6H_6$	$C_{33}H_{56}F_6O_6P_2S_2Ir_2$	$C_{35}H_{52}F_6O_6P_2S_2Ir_2$·$C_3H_6O$	$C_{32}H_{55}F_6NO_6P_2S_2Ir_2$	$C_{34}H_{51}F_6NO_6P_2S_2Ir_2$
fw	1169.27	1173.30	1251.37	1174.29	1194.28
D_{calc} (g cm^{-3})	1.872	1.877	1.838	1.870	1.781
			Data Collection		
radiation (λ, Å)	Mo Kα (0.71069)	Mo Kα (0.71069)	Mo Kα (0.71069)	Mo Kα (0.71069)	Mo Kα (0.71069)
temp (K)	203	203	203	203	203
scan technique	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	ω
scan width (deg)	(1.52 + 0.30 tan θ)	(1.10 + 0.30 tan θ)	(1.10 + 0.30 tan θ)	(0.94 + 0.30 tan θ)	(0.63 + 0.30 tan θ)
$2\theta_{max}$ (deg)	55.0	55.0	55.0	55.0	50.0
no. of rflns measd	5317	10 227	11 168	10 404	25 313
			Structure Determination		
no. of rflns used	3908	5562	8294	4812	13 750
no. of params varied	406	455	479	460	1422
data/param ratio	9.63	12.22	17.32	10.46	9.67
transmn factors	0.6030−1.0000	0.7308−1.0000	0.4997−1.0000	0.5695−1.0000	0.4483−1.0000
goodness of fit	1.75	1.47	1.97	1.74	1.32
R^a	0.038	0.035	0.035	0.055	0.065
$R_w{}^a$	0.041	0.038	0.049	0.053	0.061

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

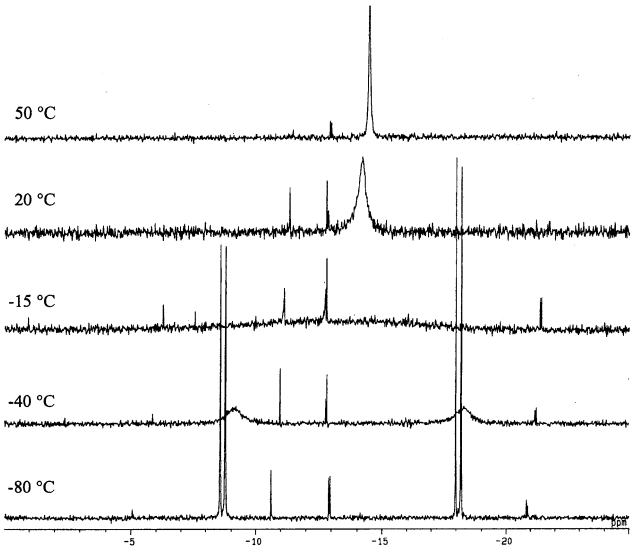


Figure 2. Variable-temperature $^{31}P\{^{1}H\}$ NMR spectra of **6a**.

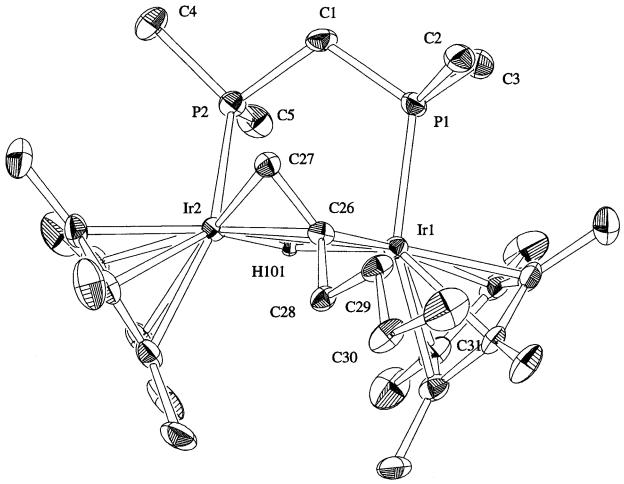


Figure 3. ORTEP view of **5c**. Hydrogen atoms except for metal hydrides are omitted for clarity.

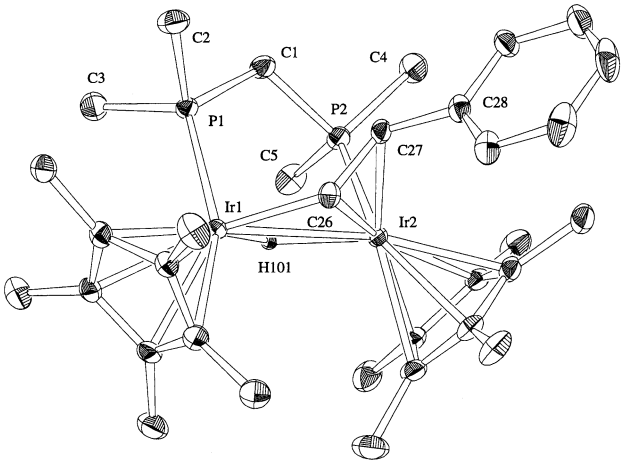


Figure 4. ORTEP view of **6a**. Hydrogen atoms except for metal hydrides are omitted for clarity.

trum, a new signal appeared at δ 11.50, which was assigned to the NH proton because it disappeared upon adding a drop of D_2O. Signals of Cp* were found at δ 2.30 and 1.96, and bridging hydride was found at δ −18.42 as a triplet. In the ^{13}C NMR, a new signal was found at δ 255.0, which was characteristic for a carbyne carbon. In the IR spectrum, absorption of ν(CN) was observed at 1595 cm^{-1}. These data are consistent with the μ-aminocarbyne structure.[2k,o,14,16,17] The complex **1** also reacted with cyclohexylisocyanide to give a μ-aminocarbyne complex **8b** (eq 7). In the NMR spectra of **8b**, all signal patterns except for the cyclohexyl group were similar to those of **8a**, and ν(CN) was observed at 1540 cm^{-1} in the IR spectrum. The formation of the complex **8** would proceed via initial addition of isocyanide to one of the iridium centers (as in the formation of **7**), followed by migration of hydride to the nitrogen atom. Considering the reaction of **1** with *tert*-butylisocyanide gave a simple adduct **7**, the size of the substituent on nitrogen would be important to induce the hydride migration.

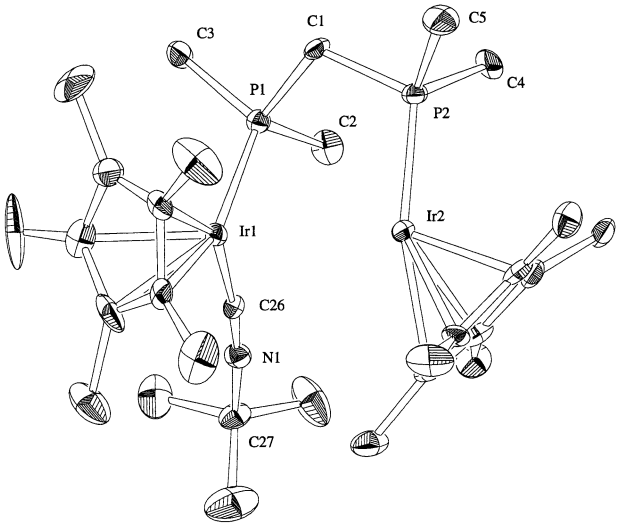


Figure 5. ORTEP view of **7**. Hydrogen atoms are omitted for clarity.

Crystal Structure of 8a. The structure of **8a** was confirmed by X-ray diffraction study. The molecular geometry and atom-numbering system of **8a** are shown in Figure 6, and the results obtained are summarized in Tables 2 and 3. In the unit cell there are three independent molecules, a, b, and c, which are very similar to each other. The μ-carbyne carbon almost symmetrically bridges the iridium−iridium bond with Ir(1)−C(26) 1.99(2), 1.98(2), 2.00(2) Å and Ir(2)−C(26) 1.99(2), 1.96(2), 1.98(2) Å. The distance of the iridium−iridium bond is 2.864(2), 2.865(2), 2.855(1) Å, which is slightly larger than that found in **1**, but comparable to those found in the 34-electron complexes **5b** and **6a**. The five atoms Ir(1), Ir(2), C(26), N(1), and C(27) lie on a plane. The distance of C(26)−N(1), 1.31(2), 1.33(2), 1.29(2) Å, indicates its double-bond character, suggesting a larger contribution of the μ-iminium structure B (Chart 1).

Summary

We have demonstrated the synthesis and reactivity of a new dmpm and hydrido-bridged diiridium complex **1**. Complex **1** is one of the few examples of dicationic

(15) (a) Mays, M. J.; Prest, D. W.; Raithby P. R. *Chem. Commun.* **1980**, 171. (b) Beringhelli, T.; D'Alfonso, G.; Freni, M.; Ciani, G.; Moret, M.; Sironi, A. *J. Organomet. Chem.* **1990**, *399*, 291.
(16) Howell, J. A. S.; Mathur, P. *J. Chem. Soc., Dalton Trans.* **1982**, 43.

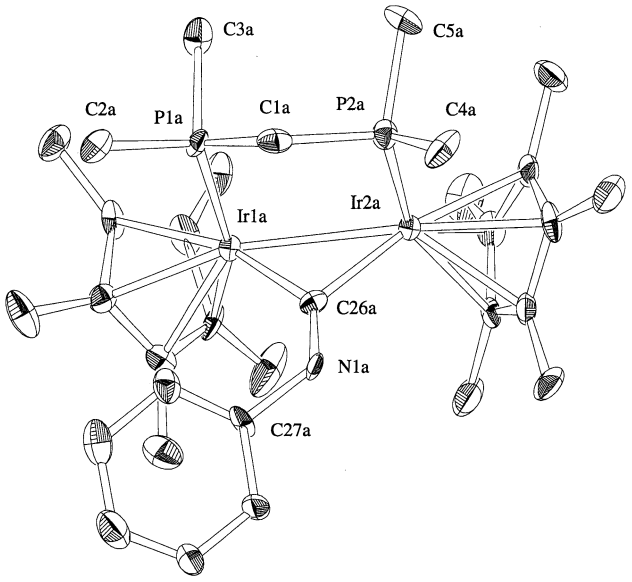
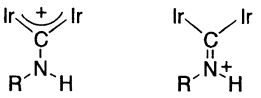


Figure 6. ORTEP view of **8a** (molecule a). Hydrogen atoms are omitted for clarity.

Chart 1



complexes containing the unsaturated moiety $M_2(\mu\text{-}H)_2$ (M═M). Reactivity of **1** toward alkynes and isocyanides was also examined, and derivation into μ-vinyl complexes and μ-aminocarbyne complexes was revealed. These results provide significant information about the properties of dihydrido-bridged binuclear transition metal complexes. Further investigation on the reactivity of these complexes is in progress.

Experimental Section

All manipulations were performed under a dry argon atmosphere with standard Schlenk techniques. Melting points were determined on a Yanagimoto micro melting point apparatus. Elemental analyses were carried out at the Microanalysis Center of Kyoto University. Infrared spectra were taken on a HORIBA FT-300 spectrometer. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} spectra were measured with JEOL EX-270 and JEOL A-500 spectrometers. Solvents were dried by using standard procedures and distilled prior to use. The complex $[Cp^*IrCl(\mu\text{-}H)]_2$ (**2**)[31] and phenylisocyanide[18] were prepared by literature methods. Other reagents were used as obtained from commercial sources.

Synthesis of $[(Cp^*Ir)_2(\mu\text{-dmpm})(\mu\text{-}H)_2][OTf]_2$ (1). To a solution of $[Cp^*IrCl(\mu\text{-}H)]_2$ (**2**) (0.636 g, 0.874 mmol) in THF (16 mL) was added bis(dimethylphosphino)methane (0.120 g, 0.883 mmol) at room temperature, and the mixture was stirred for 3.5 h. Then silver trifluoromethanesulfonate (0.450 g, 1.75 mmol) was added, and the mixture was stirred for 0.7 h. After evaporation of the solvent, the residue was extracted with dichloromethane. Recrystallization from acetone−diethyl ether gave **1** as dark brown crystals (0.858 g, 0.786 mmol, 90%). Crystals of **1** suitable for an X-ray study were obtained by the slow diffusion of benzene into an acetone solution of the complex. Mp: 217.1−218.8 °C. Anal. Calcd for $C_{27}H_{46}F_6O_6P_2S_2Ir_2$: C, 29.72; H, 4.25. Found: C, 29.66; H, 4.37.

Synthesis of $[(Cp^*Ir)_2(\mu_2,\eta^1,\eta^2\text{-}CH{=}CH_2)(\mu\text{-dmpm})(\mu\text{-}H)][OTf]_2$ (4). Complex **1** (0.107 g, 0.0976 mmol) was placed in a 50 mL flask. After evacuation, the system was filled with ethyne (1 atm). Methanol (20 mL) was added, and the solution was stirred at room temperature for 2.5 h. The color of the solution changed to red-orange. Evaporation of the solvent gave **4** as a yellow-orange powder (0.0936 g, 0.0838 mmol, 86%). Mp: 158.1 °C (dec). Anal. Calcd for $C_{29}H_{48}F_6O_6P_2S_2Ir_2$: C, 31.17; H, 4.34. Found: C, 30.91; H, 4.32.

Reaction of 1 with Terminal Alkynes: Formation of α-Isomers of μ-Vinyl Complexes $[(Cp^*Ir)_2(\mu,\eta^1,\eta^2\text{-}CR{=}CH_2)(\mu\text{-dmpm})(\mu\text{-}H)][OTf]_2$ [R = Ph (5a), $PhCH_2$ (5b), ^{n}Bu (5c)] and *β-trans* Isomers $[(Cp^*Ir)_2(\mu,\eta^1,\eta^2\text{-}CH{=}CHR)(\mu\text{-dmpm})(\mu\text{-}H)][OTf]_2$ [R = Ph (6a), $PhCH_2$ (6b), ^{n}Bu (6c)]. To a solution of **1** (0.104 g, 0.0950 mmol) in methanol (5 mL) was added phenylethyne (1.0 mL) at room temperature, and the solution was stirred for 2 h. The color of the solution changed to red-orange. After evaporation of the solvent, the residue was chromatographed on silica gel. Elution with dichloromethane and methanol (10:1) followed by evaporation of the solvent gave **5a** as a yellow oil (0.0475 g, 0.0398 mmol, 42%) and **6a** as a yellow oil (0.0168 g, 0.0141 mmol, 15%). An analytically pure sample of **6a** was obtained by recrystallization from acetone−benzene. Crystals of **6a** suitable for an X-ray study were obtained by the slow diffusion of benzene into an acetone solution of the complex. Mp: 215.1−218.6 °C. Anal. Calcd for $C_{35}H_{52}F_6O_6P_2S_2Ir_2{\cdot}C_3H_6O$: C, 36.47; H, 4.67. Found: C, 36.52; H, 4.60. Elemental analysis for **5a** was unsatisfactory because of a small amount of contaminant.

Similar reaction of **1** (0.109 g, 0.0995 mmol) with 3-phenyl-1-propyne (37.2 μL, 0.299 mmol) in methanol (20 mL) at reflux temperature gave **5b** as a yellow oil (0.0398 g, 0.0330 mmol, 33%) and **6b** as a yellow oil (0.0330 g, 0.0273 mmol, 28%). Elemental analysis for **5b** and **6b** was unsatisfactory because of their hygroscopicity and a small amount of contaminant.

Similar reaction of **1** (0.0990 g, 0.0907 mmol) with 1-hexyne (105 μL, 0.914 mmol) in methanol at reflux temperature gave **5c** as a yellow powder (0.0436 g, 0.0372 mmol, 41%) and **6c** as a yellow powder (0.0286 g, 0.0244 mmol, 27%). Crystals of **5c** suitable for an X-ray study were obtained by the slow diffusion of diethyl ether into a dichloromethane solution of the complex.

5c. Mp: 177.9−179.2 °C. Anal. Calcd for $C_{33}H_{56}F_6O_6P_2S_2Ir_2$: C, 33.78; H, 4.81. Found: C, 33.59; H, 4.58.

6c. Mp: 152.0−156.0 °C. Anal. Calcd for $C_{33}H_{56}F_6O_6P_2S_2Ir_2$: C, 33.78; H, 4.81. Found: C, 34.06; H, 4.75.

Reaction of 1 with Terminal Alkynes at Higher Temperature: Selective Formation of *β-trans* Isomers of μ-Vinyl Complexes $[(Cp^*Ir)_2(\mu,\eta^1,\eta^2\text{-}CH{=}CHR)(\mu\text{-dmpm})(\mu\text{-}H)][OTf]_2$ [R = Ph (6a), $PhCH_2$ (6b), ^{n}Bu (6c)]. Reaction of **1** (0.0504 g, 0.0462 mmol) with phenylethyne (10.1 μL, 0.0919 mmol) in benzene (1.5 mL) at 120 °C for 20 h in a sealed tube resulted in selective formation of **6a** (0.0528 g, 0.042 mmol, 96%).

Similar reaction of **1** (0.102 g, 0.0933 mmol) with 3-phenyl-1-propyne (34.8 μL, 0.280 mmol) in methanol (4 mL) at 120 °C for 22 h in a sealed tube resulted in quantitative formation of **6b**.

Similar reaction of **1** (0.104 g, 0.0954 mmol) with 1-hexyne (33.0 μL, 0.287 mmol) in methanol (4 mL) at 120 °C for 22 h in a sealed tube resulted in quantitative formation of **6c**.

Isomerization of 5 to 6. A solution of **5b** (0.0042 g, 0.0039 mmol) in methanol (2 mL) was heated at 120 °C in a sealed

(17) For example: (a) DeLaet, D. L.; Fanwick, P. E.; Kubiak, C. P. *Organometallics* **1986**, *5*, 1807. (b) Cox, G.; Dowling, C.; Manning, A. R. *J. Organomet. Chem*. **1992**, *438*, 143. (c) Knorr, M.; Faure, T.; Braunstein, P. *J. Organomet. Chem*. **1993**, *447*, C4. (d) Knorr, M.; Strohmann, C. *Organometallics* **1999**, *18*, 248.

(18) Gokel, G. W.; Widera, R. P.; Weber, W. P. *Organic Syntheses*; Wiley: New York, 1988; Collect. Vol. VI, p 232.

tube for 18 h. After evaporation of the solvent, the residue was analyzed by NMR. Quantitative formation of **6b** was observed.

Similar reaction of **5c** (0.0080 g, 0.0068 mmol) in methanol (2 mL) at 120 °C for 18 h gave **6c** quantitatively.

A mixture of **5a** and **6a** (1.2:1.0) (0.110 g, 0.0921 mmol) in methanol (10 mL) was heated at 120 °C in a sealed tube for 13 h. After evaporation of the solvent, the residue was analyzed by NMR. Quantitative formation of **6a** was observed.

Reaction of 1 with *tert*-Butyl Isocyanide: Formation of [(Cp*Ir)(CN^{t}Bu)(μ-dmpm)(μ-H)(Cp*Ir)(H)][OTf]$_2$ (7). To a solution of **1** (0.0551 g, 0.0505 mmol) in methanol (5 mL) was added *tert*-butylisocyanide (6.8 μL, 0.0601 mmol) at room temperature, and the solution was stirred for 30 min. The color of the solution changed to red. Evaporation of the solvent followed by washing with diethyl ether (17 mL) gave **7** as a red-orange powder (0.0417 g, 0.0355 mmol, 70%). Crystals of **7** suitable for an X-ray study were obtained by the slow diffusion of hexane into an acetone solution of the complex. Mp: 148.3 °C (dec). IR (Nujol): ν(CN) 2175 cm^{-1}. Anal. Calcd for $C_{32}H_{55}F_6NO_6P_2S_2Ir_2$: C, 32.73; H, 4.73; N, 1.19. Found: C, 32.32; H, 4.55; N, 1.17.

Reaction of 1 with Phenylisocyanide or Cyclohexylisocyanide: Formation of μ-Aminocarbyne Complexes [(Cp*Ir)$_2$(μ,η^1-CN(H)R)(μ-dmpm)(μ-H)][OTf]$_2$ [R = Ph (8a), Cy (8b)]. To a solution of **1** (0.116 g, 0.106 mmol) in methanol (10 mL) was added phenylisocyanide (13.8 mg, 0.134 mmol) at room temperature, and the solution was stirred for 1 h. The color of the solution changed to yellow. Evaporation of the solvent followed by washing with diethyl ether gave **8a** as a yellow-orange powder (0.0903 g, 0.0756 mmol, 71%). Crystals of **8a** suitable for an X-ray study were obtained by the slow diffusion of hexane into an acetone solution of the complex. Mp: 145.5 °C (dec). IR (Nujol): ν(CN) 1595 cm^{-1}. Anal. Calcd for $C_{34}H_{51}F_6NO_6P_2S_2Ir_2$: C, 34.19; H, 4.31; N, 1.17. Found: C, 34.59; H, 4.38; N, 1.20.

Similar reaction of **1** (0.109 g, 0.100 mmol) with cyclohexylisocyanide (13.1 μL, 0.107 mmol) in methanol at room temperature for 1.5 h gave **8b** as a yellow-orange powder (0.119 g, 0.0992 mmol, 99%). Mp: 138.6 °C (dec). IR (Nujol): ν(CN) 1540 cm^{-1}. Anal. Calcd for $C_{34}H_{57}F_6NO_6P_2S_2Ir_2$: C, 34.02; H, 4.80; N, 1.17. Found: C, 33.66; H, 4.71; N, 1.24.

X-ray Structure Analysis of 1·C$_6$H$_6$, 5c, 6a·C$_3$H$_6$O, 7, and 8a. The crystal data and experimental details for **1**·C_6H_6, **5c**, **6a**·C_3H_6O, **7**, and **8a** are summarized in Table 3. Diffraction data were obtained with a Rigaku AFC-5S. The reflection intensities were monitored by three standard reflections every 150 measurements. Reflection data were corrected for Lorentz and polarization effects. Absorption corrections were empirically applied. Decay correction was applied for **1**·C_6H_6. The structures of **1**·C_6H_6, **5c**, **6a**·C_3H_6O, and **7** were solved by heavy-atom Patterson methods[19,20] and refined anisotropically for non-hydrogen atoms by full-matrix least squares calculations, except for solvent molecules in **1**·C_6H_6 and **6a**·C_3H_6O, which were not refined. The structure of **8a** was solved by heavy-atom Patterson methods[19,20] and refined anisotropically for non-hydrogen atoms by full-matrix least squares calculations, except for two carbyne carbons (in the molecules b and c), which were refined isotropically. Atomic scattering factors and anomalous dispersion terms were taken from literature.[21] The hydrogen atoms were located on idealized positions except for metal hydrides in **1**·C_6H_6, **5c**, and **6a**·C_3H_6O, which were defined on Fourier difference maps. Metal hydrides in **7** and **8a** were not located. In **1**·C_6H_6 the crystal chirality was tested by inverting all the coordinates and refining to convergence once again. The resulting *R* values indicated the original choice should be the correct one. The calculations were performed using the program system teXsan.[22]

Supporting Information Available: X-ray crystal data for **1**, **5c**, **6a**, **7**, and **8a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020266+

(19) PATTY: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. Technical Report of the Crystallography Laboratory; University of Nijmegen, 1992.

(20) DIRDIF94, Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. Technical Report of the Crystallography Laboratory; University of Nijmegen, 1994.

(21) (a) Cromer, D. T.; Waber, G. T. *International Tables for X-ray Crystallography*; Kynoch, Birmingham, U.K., 1974; Vol. IV. (b) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781. (c) Creagh, D. C.; McAuley, W. J. In *International Tables for X-ray Crystallography*; Wilson A. J. C., Ed.; Kluwer Academic Publishers: Boston, MA, 1992; Vol. C. (d) Creagh, D. C.; Hubbell, J. H. In *International Tables for X-ray Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Boston, MA, 1992; Vol. C.

(22) *teXsan for Windows*, Crystal Structure Analysis Package; Molecular Structure Corporation, 1997.