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Articles

Competitive Reaction Pathways in the Addition of Phenylacetylene to Diamidonaphthalene-Bridged Diiridium Complexes[†]

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The oxidative addition of phenylacetylene to the monohydrido diiridium complex $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)H(CO)_2(PiPr_3)_2](CF_3SO_3)$ (**2**) and the diiridium(II) species $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2\text{-}naphth)(CF_3SO_3)_2(CO)_2(PiPr_3)_2]$ (**3**) has been studied. The kinetic product of the addition to **2** is the dihydridoalkynyl complex $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(\mu\text{-}C{\equiv}CPh)H_2(CO)_2(PiPr_3)_2](CF_3SO_3)$ (**4**), in which the alkynyl ligand bridges the iridium atoms in a $\mu,\eta^1:\eta^2$-coordination mode. Compound **4** isomerizes in acetone solution to give the hydride-bridged complex $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(\mu\text{-}H)H(C{\equiv}CPh)(CO)_2(PiPr_3)_2](CF_3SO_3)$ (**5**), in which both the alkynyl and the terminal hydride ligands are in a trans position with respect to the bridging hydride. The reaction of phenylacetylene with **3** gives different kinetic products depending on the solvent used. In CH_2Cl_2, the diiridium(III) derivative $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)H(C{\equiv}CPh)(CO)_2(PiPr_3)_2](CF_3SO_3)_2$ (**6**) is obtained. On heating these CH_2Cl_2 solutions, **6** isomerizes into the vinylidene-bridged complex $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(\mu\text{-}C{=}CHPh)(CF_3SO_3)_2(CO)_2(PiPr_3)_2]$ (**7**), which has been characterized by X-ray diffraction. The triflate ligands of **7** can be substituted by acetonitrile ligands to give the dicationic compound $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(\mu\text{-}C{=}CHPh)(NCCH_3)_2(CO)_2(PiPr_3)_2](CF_3SO_3)_2$ (**8**). With acetone as the reaction solvent, the addition of phenylacetylene to **3** affords deprotonated compounds of formula $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2\text{-}naphth)(C{\equiv}CPh)(CO)_2(PiPr_3)_2](CF_3SO_3)$ (**9** and **10**). The thermally stable isomer **10** can be protonated to give **7** but can also react with an excess of phenylacetylene to give the neutral diiridium(II) species $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(C{\equiv}CPh)_2(CO)_2(PiPr_3)_2]$ (**11**), which is the isolable product of the reaction of **3** with an excess of phenylacetylene in acetone. When this latter reaction is carried out in acetone/H_2O as solvent, the acylalkynyl diiridium(II) complex $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(C{\equiv}CPh)(C(O)CH_2Ph)(CO)_2(PiPr_3)_2]$ (**12**) is the major reaction product. The molecular structure of **12** was determined by X-ray diffraction.

Introduction

The reactivity of a metal atom located in close proximity of another metal can differ greatly from that found in a mononuclear complex, as has been extensively shown by the many studies on the chemistry of dinuclear complexes.[1] As a result of this peculiar behavior, dinuclear complexes may show an enhanced reactivity for some transformations, but can also be inert in processes readily performed by mononuclear species. The latter is the case for reactions such as the oxidative addition of H_2, which readily takes place in mononuclear basic iridium(I) complexes but which has scarcely been reported for analogous dinuclear compounds.[1a,2] This fact can readily be illustrated by the compound $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CO)_2(PiPr_3)_2]$ (**1**), which, despite its apparent high basicity, does not react with H_2 under normal reaction conditions.

Despite the inertness of **1** in these additions, we have recently found that its oxidized derivatives $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)H(CO)_2(PiPr_3)_2](CF_3SO_3)$ (**2**) and $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CF_3SO_3)_2(CO)_2(PiPr_3)_2]$ (**3**) (Scheme 1)

[†] Dedicated to Professor Helmut Werner on the occasion of his 65th birthday.

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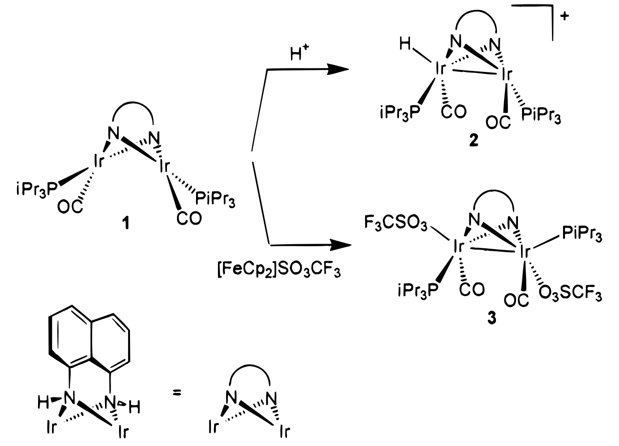
(1) For leading references in the chemistry of dinuclear complexes see: (a) Antwi-Nsiah, F. H.; Oke, O.; Cowie, M. *Organometallics* **1996**, *15*, 1042, and refs therein. (b) Oro, L. A.; Ciriano, M. A.; Tejel, C. *Pure Appl. Chem* **1998**, *70*, 779. (c) Arthurs, M. A.; Bickerton, J.; Stobart, S. R.; Wang, J. *Organometallics* **1998**, *17*, 2743. (d) Stanley, G. G. *Catalysis by Di- and Polynuclear Metal Cluster Complexes*; Adams, R. D., Cotton, F. A., Eds.; Wiley-VCH: Weinheim, 1998.

(2) The occurrence of H_2 activations has been reported for some dinuclear complexes: (a) Heinekey, D. M.; Fine, D. A.; Barnhart, D. *Organometallics* **1997**, *16*, 2530. (b) Schnabel, R. C.; Roddick, D. M. *Organometallics* **1996**, *15*, 3550. (c) Poilblanc, R. *Inorg. Chim. Acta* **1982**, *62*, 75. (d) Guilmet, E.; Maisonnat, A.; Poilblanc, R. *Organometallics* **1983**, *2*, 1123. (e) Beveridge, K. A.; Bushnell, G. W.; Dixon, K. R.; Eadie, D. T.; Stobart, S. R. *J. Am. Chem. Soc.* **1982**, *104*, 920.

10.1021/om9808559 CCC: $18.00

Scheme 1



readily activate hydrogen.[3] Again, this is in contrast with the behavior of mononuclear complexes, where the ability to undergo oxidative addition is enhanced by increasing the electron density at the metal center.[4]

Interestingly, the dihydride complexes obtained in the addition of H_2 to **3** are Brønsted acids in polar solvents such as acetone, where the lifetime of the deprotonated species is long enough for them to undergo a further oxidative addition reaction. In the case of H_2 this reaction sequence leads to the heterolytic activation of hydrogen,[3] whereas, in the case of phenylacetylene—the subject of this work—it can give rise to new alkynyl, hydridoalkynyl, bisalkynyl, vinylidene, or acyl dinuclear complexes. All these complexes, which are key species in many organometallic transformations, are products of a single process—the treatment of complex **3** with phenylacetylene—under different reaction conditions. This observation clearly shows the rich chemistry of these dinuclear species, which is the result of various competitive reaction pathways. In the following pages we will try to provide a comprehensive picture of the versatile reactivity of these dinuclear iridium complexes toward phenylacetylene.

Before starting the description of the results, it may be helpful to remark on the characteristics of the bridging ligand selected for this study: 1,8-diamidonaphthalene, which binds the two metal atoms in both bridging and chelating modes simultaneously.[5] This coordination mode allows the accommodation of the metal atoms in a wide range of intermetallic distances and, more importantly, minimizes the possibility of fragmentation. In fact, the breaking of the dinuclear framework has never been observed in previous synthetic works with this ligand, even in the presence of strong acids, or strong donor or multidentate ligands.[3,5–7] This is important because it seems to rule out the formation of mononuclear reaction intermediates under mild conditions, allowing us to consider the obtained reaction products as the result of true dimetallic reactivity.

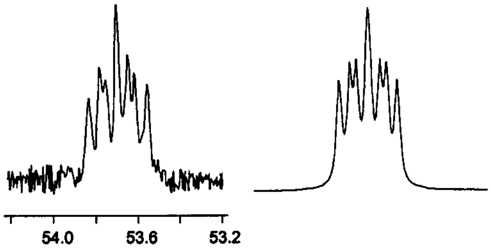
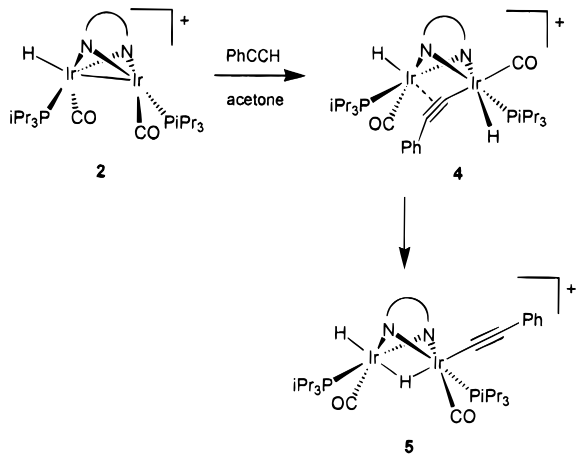


Figure 1. ^{13}C NMR signal of the alkynyl α-carbon of complex **4** (left: experimental; right: calculated).

Scheme 2



Results

1. Oxidative Addition of Phenylacetylene to Complex $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)H(CO)_2(PiPr_3)_2](CF_3SO_3)$ (2). The treatment of complex **2** with 1 equiv of phenylacetylene in acetone readily leads to the formation of a compound of formula $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2\text{-}naphth)(\mu\text{-}C{\equiv}CPh)H_2(CO)_2(PiPr_3)_2](CF_3SO_3)$ (**4**) (Scheme 2).

The ^1H NMR spectrum of **4** in acetone-d_6 shows two high-field doublets at δ −20.55 (J_{HP} = 16.2 Hz) and −18.16 (J_{HP} = 18.0 Hz), respectively, in agreement with two nonequivalent terminal hydride ligands. The $^{31}P\{^1H\}$ spectrum contains two singlets at δ 23.90 and 23.76, which split into two doublets due to the coupling of the hydride under *off-resonance* conditions, indicating that each iridium center coordinates one hydride ligand. The signals in the $^{13}C\{^1H\}$ spectrum corresponding to the C_1 and C_8 carbons of the diamidonaphthalene bridge are both doublets, at δ 154.56 (J_{CP} = 3.6 Hz) and 157.05 (J_{CP} = 2.8 Hz), indicating a transoid arrangement of the phosphine ligands in the dinuclear framework.[3] The α-carbon of the alkynyl ligand appears as a doublet at δ 53.71 with a C−P coupling constant of 10.0 Hz, whereas the β-carbon appears as a singlet at δ 128.63. Under *off-resonance* conditions these two signals split by hydride coupling: the α-carbon gives rise to a multiplet (Figure 1) containing two hydrido−carbon couplings of 6.1 and 3.7 Hz, whereas the β-carbon shows

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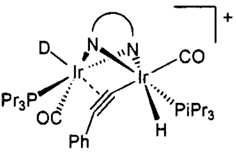
[7] (a) Fernández, M. J.; Modrego, J.; Oro, L. A.; Apreda, M. C.; Cano, F. H.; Foces-Foces, C. *Inorg. Chim. Acta* **1989**, *157*, 61. (b) Fernández, M. J.; Modrego, J.; Oro, L. A.; Apreda, M. C.; Cano, F. H.; Foces-Foces, C. *J. Chem. Soc., Dalton Trans.* **1989**, 1249. (c) Connelly, N. G., Loyns, A.; Fernández, M. J.; Modrego, J.; Oro, L. A. *J. Chem. Soc., Dalton Trans.* **1989**, 683. (d) Matsuzaka, H.; Ariga, K.; Kase, H.; Kamura, T.; Kondo, M.; Kitawaka, S.; Yamasaki, M. *Organometallics* **1997**, *16*, 4514.



4-*d*

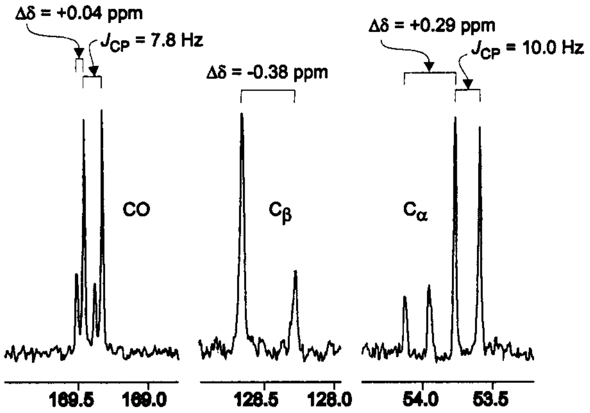


Figure 2. $^{13}C\{^1H\}$ NMR spectrum of a mixture of complexes **4** (75%) and **4-*d*** (25%) in acetone-d_6 (only the signals affected by the isotopic substitution are shown).

a J_{CH} of 3.4 Hz. Both the unusual chemical shifts of the alkynyl carbons[8] and their coupling constants suggest an asymmetric $\mu,\eta^1{:}\eta^2$-coordination of this ligand.[9] This is also suggested by the IR spectrum that shows a sharp band at 1913 cm^{-1} attributable to the ν(C≡C) stretching in the $\mu,\eta^1{:}\eta^2$-coordination mode.[8] In addition, the IR spectrum of **4** shows two carbonyl stretching frequencies at 2029 and 2048 cm^{-1}, in agreement with two Ir(III) centers, and a weak ν(Ir−H) band at 2143 cm^{-1}.

The reaction of phenylacetylene with complex **2-*d***, deuterated at the hydride position, gives a single isotopomer **4-*d*** (Figure 2), which does not undergo appreciable H/D exchange in solution.

The ^1H NMR spectrum of **4-*d*** shows the disappearance of the hydride doublet at highest field. The isotopic substitution also results in the expected downfield isotopic shifts for the signal in the $^{31}P\{^1H\}$ NMR at δ 23.76 ($\Delta\delta = 0.036$ ppm) and for the carbonyl doublet in the $^{13}C\{^1H\}$ NMR spectrum at δ 169.39 ($\Delta\delta = 0.043$ ppm), which correspond to the atoms located cis to the deuteride.[10] On the other hand, larger isotopic shifts of $\Delta\delta + 0.293$ and -0.384 ppm are found for the α- and β-carbons of the alkynyl ligand, respectively (Figure 2). These large isotopic shifts give additional support to the proposed $\mu,\eta^1{:}\eta^2$-coordination mode of the alkynyl ligand, as only coordination of the alkynyl moiety trans to the deuteride ligand can explain the large change in the vibrational energy of the alkynyl carbons.[11] In this respect, it should be mentioned that upon H/D isotopic substitution of terminal alkynes, the shift of the β-carbon is larger in magnitude than that of the α-carbon, although in this case both carbons shift toward higher field.[12] Nevertheless, it has been shown that both high-field and downfield isotopic perturbations can be observed for the bridging ligands of analogous complexes after H/D substitutions of terminal hydrides.[10]

In acetone solution, complex **4** slowly transforms into a new species **5**. The reaction takes several days at room temperature, but can be completed in 1 h on addition of catalytic amounts of NEt_3. The analytical and spectroscopic data indicate that **5** is an isomer of **4** of formula $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(\mu\text{-}H)H(C{\equiv}CPh)(CO)_2(PiPr_3)_2](CF_3SO_3)$ with the structure shown in Scheme 2.

The ^1H NMR spectrum of **5** in acetone-d_6 shows two hydride resonances, a doublet of doublets at δ −14.67 ($J_{HH} = 8.7$, $J_{HP} = 18.3$ Hz) and a signal with a ddd pattern at δ −11.77 ($J_{HH} = 8.7$, $J_{HP} = 6.3$ and 3.0 Hz). The H−P coupling of the former signal is typical of a terminal hydride cis to a phosphine. The second signal, which is coupled to both phosphorus atoms with rather small coupling constants, can be assigned to a bridging hydride. The magnitude of the coupling constant between the bridging and the terminal hydrides ($J_{HH} =$ 8.7 Hz) suggests a trans arrangement of these two ligands.[3,10] In the $^{13}C\{^1H\}$ NMR spectrum, the alkynyl ligand of **5** gives rise to a doublet at δ 68.36 ($J_{CP} = 10.6$ Hz) and a singlet at δ 103.90. Under *off-resonance* conditions, the doublet corresponding to the α-carbon splits into a doublet of doublets, showing a large J_{CH} coupling of 19.9 Hz, in agreement with a trans disposition of the terminal alkynyl and the bridging hydride. Finally, the two doublets found in the $^{13}C\{^1H\}$ NMR spectrum for the C_1 and C_8 carbons of the diamidonaphthalene ligand at δ 147.51 and 148.02 (both $J_{CP} = 3.2$ Hz) indicate a transoid disposition of the triisopropylphophine ligands.

The above-mentioned effect of NEt_3 in the evolution of **4** into the stable isomer **5** suggest that this isomerization most probably involves deprotonated intermediates. In agreement with this observation, when the isomerization is carried out in acetone-d_6, deuterium incorporation into the terminal hydride position is observed. This isotopic substitution produces a shift of $\Delta\delta = +0.045$ ppm in the ^1H NMR signal of the bridging hydride. Similar H/D scrambling processes with acetone have been previously observed[3,13,14] and attributed to the acidity of the hydride complexes.[15]

2. Oxidative Addition of Phenylacetylene to the Diiridium(II) Complex $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CF_3SO_3)_2(CO)_2(PiPr_3)_2]$ (3) in CH_2Cl_2. The addition of 1 equiv of phenylacetylene to CH_2Cl_2 solutions of complex **3** leads to the formation of a dinuclear species **6**, which can be formulated as $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)H(C{\equiv}CPh)(CO)_2(PiPr_3)_2](CF_3SO_3)_2$ (Scheme 3).

The high-field region of the ^1H NMR spectrum of **6** in $CDCl_3$ contains a doublet at δ −17.39 with a H−P coupling constant of 18.6 Hz, in agreement with a terminal hydride. The $^{13}C\{^1H\}$ NMR spectrum displays two signals attributable to the alkynyl moiety, a doublet

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[8] Ara, I.; Berenguer, J.; Forniés, J.; Lalinde, E. *Organometallics* **1997**, *16*, 3921, and references therein.

[9] Precedents for such a coordination mode can be found in platinum and palladium chemistry (ref 8) and in related dirhodium compounds. See ref 1a and: (a) Cowie, M.; Loeb, S. *Organometallics* **1985**, *4*, 852. (b) Esteruelas, M. A.; Lahuerta, O.; Modrego, J.; Nürnberg, O.; Oro, L. A.; Rodriguez, L.; Sola, E.; Werner, H. *Organometallics* **1993**, *12*, 266, and references therein.

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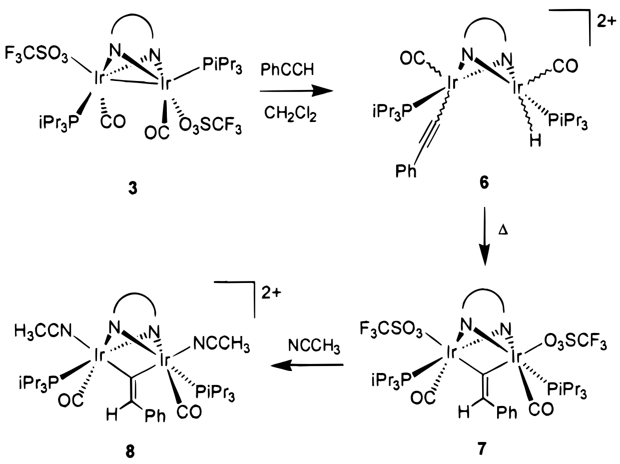
Scheme 3



at δ 64.41 (J_{CP} = 10.5 Hz) and a singlet at δ 96.20. None of these signals is modified under *off-resonance* conditions. The absence of a C−H coupling between the α-carbon and the hydride indicates that this ligand and the alkynyl are bonded to different metal atoms.[16] In addition, the chemical shifts of the acetylenic carbons are very close to those found for the terminal alkynyl of complex **5** and remarkably different from those found for **4**, which contains a $\mu,\eta^1:\eta^2$-alkynyl bridge, suggesting that in complex **6** the alkynyl ligand is terminal.[8] Further evidence for this is provided by the IR spectrum, which shows a sharp band at 2145 cm^{-1}, attributable to the ν(C≡C) mode of a terminal alkynyl. The IR spectrum of **7** also displays two ν(CO) modes at 2062 and 2023 cm^{-1}, in agreement with two terminal carbonyl ligands and Ir(III) metal centers.[3]

Unfortunately, the structure of **6** cannot be unambiguously assigned on the basis of the collected spectroscopic data. Thus, although the signals in the $^{13}C\{^1H\}$ NMR of the C_1 and C_8 carbons of the diamidonaphthalene ligand (two doublets at δ 148.32 and 149.71 with J_{CP} = 3.7 Hz) indicate transoid phosphines, the relative positions of the carbonyl ligands within the dinuclear framework cannot be determined. The proposed structure for **6** (Scheme 3), which takes into account all the above considerations, shows two unsaturated Ir(III) centers. Despite this, the spectroscopic evidence suggests that, in solution, this complex does not coordinate the triflate anions or solvent molecules. Thus, the ^{1}H NMR spectrum of **6** in $CDCl_3$ does not change in the presence of small amounts of coordinating solvents such as acetone or acetonitrile, whereas the ^{19}F NMR spectrum in $CDCl_3$ shows a singlet at δ −79.17, in agreement with the value for a nonbonded triflate ligand.[3,13,17] Also, acetone solutions of **6** show molar conductivities characteristic of 1:2 electrolytes.[18]

Complex **6** is moderately stable in $CDCl_3$ or acetone-d_6 solutions, but after several hours at room temperature, significant quantities of a new species are formed. Following this observation, a complex of formula $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(\mu\text{-}C{=}CHPh)(CF_3SO_3)_2(CO)_2(PiPr_3)_2]$ (**7**) (Scheme 3) was prepared in good yields by refluxing CH_2Cl_2 solutions of **6** during 72 h.

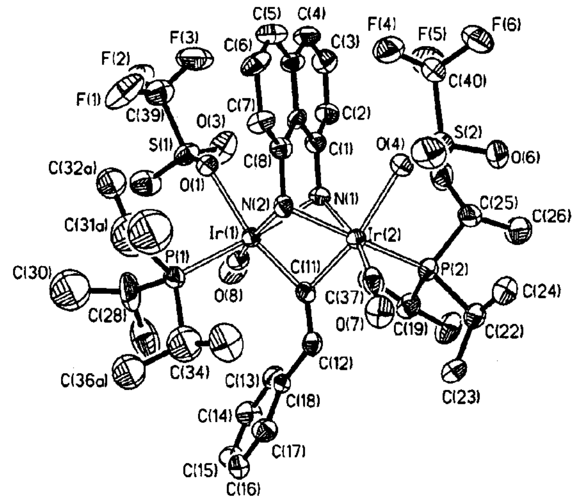


Figure 3. Molecular structure of complex **7**.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 7

Ir(1)···Ir(2)	2.9277(7)		
Ir(1)−P(1)	2.383(3)	Ir(2)−P(2)	2.379(3)
Ir(1)−O(1)	2.255(6)	Ir(2)−O(4)	2.234(6)
Ir(1)−N(1)	2.174(7)	Ir(2)−N(1)	2.148(7)
Ir(1)−N(2)	2.140(7)	Ir(2)−N(2)	2.154(7)
Ir(1)−C(38)	1.863(10)	Ir(2)−C(37)	1.854(12)
Ir(1)−C(11)	2.040(9)	Ir(2)−C(11)	2.014(8)
O(1)−S(1)	1.471(7)	O(4)−S(2)	1.471(7)
N(1)−C(1)	1.423(11)	N(2)−C(8)	1.444(11)
C(38)−O(8)	1.135(11)	C(37)−O(7)	1.141(12)
C(11)−C(12)	1.325(13)		

P(1)−Ir(1)−O(1)	90.00(17)	P(2)−Ir(2)−O(4)	91.04(18)
P(1)−Ir(1)−N(1)	168.4(2)	P(2)−Ir(2)−N(1)	98.87(19)
P(1)−Ir(1)−N(2)	96.9(2)	P(2)−Ir(2)−N(2)	170.4(2)
P(1)−Ir(1)−C(38)	94.2(3)	P(2)−Ir(2)−C(37)	93.4(3)
P(1)−Ir(1)−C(11)	101.2(3)	P(2)−Ir(2)−C(11)	96.8(3)
O(1)−Ir(1)−N(1)	88.9(2)	O(4)−Ir(2)−N(1)	89.6(3)
O(1)−Ir(1)−N(2)	91.9(3)	O(4)−Ir(2)−N(2)	91.1(3)
O(1)−Ir(1)−C(38)	90.9(3)	O(4)−Ir(2)−C(37)	97.6(3)
O(1)−Ir(1)−C(11)	166.5(3)	O(4)−Ir(2)−C(11)	167.7(3)
N(1)−Ir(1)−N(2)	71.6(3)	N(1)−Ir(2)−N(2)	71.8(3)
N(1)−Ir(1)−C(38)	97.4(4)	N(1)−Ir(2)−C(37)	165.7(3)
N(1)−Ir(1)−C(11)	78.6(3)	N(1)−Ir(2)−C(11)	79.8(3)
N(2)−Ir(1)−C(38)	168.5(3)	N(2)−Ir(2)−C(37)	95.6(4)
N(2)−Ir(1)−C(11)	79.3(3)	N(2)−Ir(2)−C(11)	79.6(3)
C(38)−Ir(1)−C(11)	95.7(4)	C(37)−Ir(2)−C(11)	91.5(4)
Ir(1)−O(1)−S(1)	124.3(4)	Ir(2)−O(4)−S(2)	140.4(4)
Ir(1)−C(38)−O(8)	174.9(9)	Ir(2)−C(37)−O(7)	174.2(8)
Ir(1)−C(11)−C(12)	139.2(7)	Ir(2)−C(11)−C(12)	128.3(7)
Ir(1)−C(11)−Ir(2)	92.5(4)		

Figure 3 shows the molecular structure of **7**, as determined by X-ray diffraction, and Table 1 lists the relevant bond distances and angles. Complex **7** is a neutral isomer of **6** which contains a bridging vinylidene ligand and the two triflate anions coordinated in positions trans to the bridge. Excluding the vinylidene moiety, the molecule has a pseudo C_2 symmetry, which also affects the orientation of the triflate ligands. The intermetallic distance is 2.9277(7) Å: very long compared with that found for metal−metal-bonded compounds with the 1,8-diamidonaphthalene bridge.[3,7d] The structural features of the vinylidene ligand are consistent with those reported for other vinylidene complexes. Thus, the C=C distance of 1.322(13) Å compares well to that found in mononuclear[19] and dinuclear[20] iridium vinylidene complexes. The metal-to-vinylidene α-carbon distances, 2.049(9) and 2.014(8) Å, are similar to those

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(16) In the same ^{13}C *off-resonance* NMR spectrum a J_{CH} coupling of 7.5 Hz can be observed for one carbonyl signal.

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found in the previously reported phenylvinylidene-bridged complex $[Ir_2I_2(CO)_2(\mu\text{-}CC(H)Ph)(dppm)_2]$.[20]

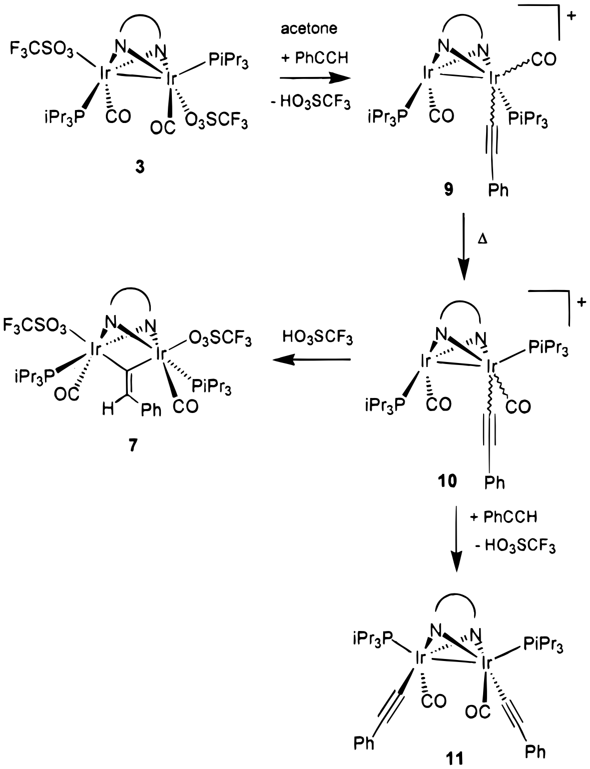
The dimetallic core of complex **7** closely resembles that of the related methylene-bridged complex $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(\mu\text{-}CH_2)I_2(CO)_2(PPh_3)_2]$, showing a similar intermetallic separation and Ir$-$C$_\alpha$ distances.[6] The IR spectrum of **7** shows two strong ν(CO) modes at 2054 and 2034 cm^{-1}, which also compares well to the value of 2030 cm^{-1} obtained for the methylene-bridged derivative which contains iridium(III) centers.[3] In light of these data, **7** seems to contain two nonbonded iridium(III) atoms connected to the vinylidene α-carbon through two localized σ-bonds. Probably related with this bonding mode, the chemical shift of the α-carbon in the ^{13}C{^{1}H} spectrum appears at very high field (δ = 100.09) compared to the normal range for these resonances (δ = 250−380 ppm).[21] However, similar shifts have also been reported for vinylidene-bridged diiridium complexes which also show both long intermetallic distances and carbonyl stretches above 2050 cm^{-1}.[20]

The Ir−O distances found in the structure of **7** (2.255(6) and 2.234(6) Å) are in the range for those found in iridium complexes containing labile triflate ligands.[2b,22] In agreement with this observation, the ^{19}F NMR spectrum in CDCl$_3$ shows a unique broad signal at δ −78.76, which suggests the existence of a fast equilibrium between **7** and cationic species resulting from triflate dissociation. Similar behavior is found for one of the triflate ligands of the starting product **3**.[3] In accordance with these observations, acetone solutions of complex **7** show molar conductivities in the range associated with 1:2 electrolytes. This indicates that under these conditions the triflate ligands are dissociated, most probably being substituted by acetone ligands. Attempts to isolate this dicationic acetone adduct did not give a pure compound. The treatment of **7** with acetonitrile, however, allows the isolation of the dicationic species $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(\mu\text{-}C{=}CHPh)(NCCH_3)_2(CO)_2(PiPr_3)_2](CF_3SO_3)_2$ (**8**) (Scheme 3).

The spectroscopic data obtained for **8** are, in general, quite similar to those of **7**, indicating that both complexes have similar structures. In the ^{1}H NMR spectrum, in CDCl$_3$ at room temperature, the acetonitrile, ligands of **8** give rise to a unique singlet at δ 1.45. On addition of an excess of acetonitrile only one broad, coalesced signal can be observed for the free and coordinated acetonitrile, revealing a fast exchange process at room temperature.

3. Oxidative Addition of Phenylacetylene to Complex 3 in Acetone. When the stoichiometric reaction between phenylacetylene and complex **3** is carried out in acetone as solvent, the reaction products are very different from those described in the previous section. The first observable product in this solvent is a thermally unstable species, **9**, which could not be isolated but which can be maintained in solution for long periods of time at temperatures below 253 K. On the basis of the spectroscopic information collected, **9** can be formulated as an alkynyl complex of formula $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(C{\equiv}CPh)(CO)_2(PiPr_3)_2](CF_3SO_3)$ (Scheme 4).

Scheme 4



In acetone-d_6, the ^{13}C{^{1}H} NMR spectrum of **9** shows two signals for quaternary carbons attributable to an alkynyl moiety: a singlet at δ 93.81 and a broad signal at δ 64.96, the broadening most probably being due to an unresolved C−P coupling. The relative transoid position of the phosphine ligands shown in the proposed structure is deduced from the ^{13}C{^{1}H} NMR signals corresponding to the C$_1$ and C$_8$ carbons, which are both doublets (δ 145.55; J_{CP} = 3.1 and 145.66; J_{CP} = 3.3). Unfortunately, the relative positions of the carbonyl ligands remain unknown. The signals in the proton NMR spectrum are those expected for the proposed structure. In addition, a broad resonance centered at about δ 4.9 is consistent with the formation of triflic acid as a reaction product.

On raising the temperature, the ^{31}P NMR spectrum of the reaction mixture containing **9** shows the disappearance of this complex to give a new species, **10**. This new compound also evolves to give mainly complex **7** (or its acetone-d_6 adduct) together with minor amounts of **6**. After a period of a few hours under these reaction conditions, only small amounts of complex **7** remain in the reaction solution, which then contains a mixture of several unidentified products. This sequential reaction prevents the isolation of pure complex **10** from these solutions, although on the basis of its NMR spectra it could be identified as an isomer of **9**, having the structure depicted in Scheme 4. Alternatively, complex **10** can be prepared in good yield by treatment of complex **1** with IC≡CPh followed by iodide abstraction (see Experimental Section).

The ^{31}P{^{1}H} NMR spectrum of **10**, in acetone-d_6,

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(19) (a) Höhn, A.; Otto, H.; Dziallas, M.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1987**, 852. (b) Werner, H.; Schulz, M.; Windmuller, B. *Organometallics* **1995**, *14*, 3659. (c) Fryzuk, M. D.; Huang, L.; McManus, N. T.; Paglia, P.; Rettig, S. J.; White, G. S *Organometallics* **1992**, *11*, 2979.

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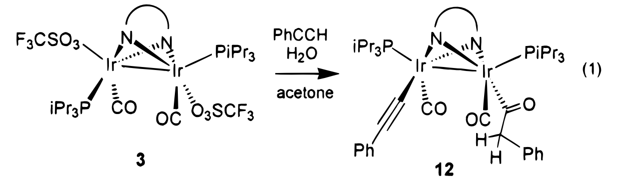
consists of two doublets at δ 33.14 and −2.30, both with a J_{PP} coupling constant of 5.8 Hz. The presence of this small coupling is characteristic of metal−metal-bonded diiridium complexes which, as with complex **3**, have one phosphine in the axial position and another trans to the diamidonaphthalene bridge.[3] In agreement with this observation, the signals in the $^{13}C\{^1H\}$ NMR spectrum of the C_1 and C_8 carbons of the bridge appear as a singlet at δ 144.92 and a doublet at δ 148.32, respectively, both with a C−P coupling constant of 3.2 Hz. The acetylenic carbons appear as a doublet at δ 77.82 ($J_{CP} = 12.1$) and a singlet at δ 105.47, in agreement with a terminal alkynyl ligand ($\nu(C{\equiv}C) = 2122$ cm^{-1}). Again the cisoid or transoid position of the carbonyl ligands is undetermined.

As shown in Scheme 4, complex **10** reacts with triflic acid in chloroform to give complex **7**. In this case, the reaction is complete in $CHCl_3$ within minutes. Also, compound **10** readily reacts with phenylacetylene. The isolable product of this reaction, either in acetone or chloroform, is the neutral bisalkynyl complex $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(C{\equiv}CPh)_2(CO)_2(PiPr_3)_2]$ (**11**), which precipitates as a yellow solid from the reaction media. In agreement with this observation, **11** can be obtained in low yields (ca. 30%) by treatment of complex **3** with an excess of phenylacetylene in acetone. Spectroscopic analysis of these reaction mixtures shows the presence of other metallic species and also organic products resulting from the coupling of acetylenic fragments, which can be detected by mass spectrometry.[23] All these observations suggest a complex reaction scheme in which **11**, which can be isolated due to its insolubility, is just one of the participating species.

Alternatively, complex **11** can be obtained in quantitative yields by treatment of complex **3** with 2 equiv of lithiumphenylacetylide. The $^{31}P\{^1H\}$ NMR spectrum of complex **11** in C_6D_6 consists of a singlet at δ 6.20, whereas in the proton spectrum a single broad N−H signal is observed at δ 4.70, indicating that **11** has C_2 symmetry. The ^1H NMR signals corresponding to the $PiPr_3$ methyl groups consist of two doublets of virtual triplets at δ 0.58 and 1.09. In agreement with this, the $^{13}C\{^1H\}$ NMR spectrum shows a virtual triplet corresponding to the phosphine CH carbons with $N = J_{CP} + J_{CP'} = 20.0$ Hz. The existence of coupling between the phosphine CH carbons and both magnetically nonequivalent phosphorus atoms is typical of mononuclear complexes with two equivalent $PiPr_3$ ligands trans to each other. This suggests that in **11** the phosphine ligands occupy both axial positions. In agreement with the proposed structure, both terminal alkynyl ligands are equivalent, showing two virtual triplets in the $^{13}C\{^1H\}$ NMR spectrum at δ 78.61 ($N = 4.7$, C_α) and at δ 105.15 ($N = 2.7$, C_β). Related dinuclear bisalkynyl complexes have been reported for ruthenium.[24]

When the reaction of complex **3** with an excess of phenylacetylene is carried out in acetone/H_2O as solvent, the insoluble residue obtained contains a mixture of complex **11** (ca. 30%) and a major component **12**. On the basis of the spectroscopic analysis of this mixture, complex **12** can be formulated as $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(C{\equiv}CPh)(C(O)CH_2Ph)(CO)_2(PiPr_3)_2]$ (eq 1). Attempts to separate both components of the mixture by recrystallization in various solvents failed, but despite this fact, single crystals suitable for an X-ray experiment were obtained. The crystal examined contained two independent molecules of **12** in the asymmetric unit, one of them partially disordered due to the simultaneous crystallization of complex **11** (see Experimental Section).



(1)

Figure 4 shows the molecular structure of complex **12**, as determined by X-ray diffraction, and Table 2 lists the relevant bond distances and angles. Complex **12** is an asymmetric species where one of the iridium atoms binds to an alkynyl ligand and the other to a phenylacetyl group. Both metallic centers are in a distorted square pyramidal ligand environment and complete their coordination spheres by means of a metal−metal bond. The intermetallic distance is 2.5575(4) Å, close to the shortest Ir−Ir bond length hitherto reported (2.518 Å)[25] and 0.42 Å shorter than that found in the vinylidene-bridged complex **7**. The distances and angles involved in the alkynyl and acyl ligands are normal with regard to previously reported iridium complexes.[25] Three of the four Ir−N distances are equal and shorter than that corresponding to the position trans to the acyl ligand, reflecting the larger structural trans influence of the acyl group compared to those of the alkynyl and carbonyl ligands.

In accordance with the presence of a metal−metal bond and with the axial positions of the phosphines, the $^{31}P\{^1H\}$ NMR spectrum of **12** in C_6D_6 consists of an AB system showing a large P−P coupling of 117.5 Hz. In the $^{13}C\{^1H\}$ NMR, the terminal alkynyl ligand gives rise to a doublet at δ 77.50 ($J_{CP} = 10.0$, C_α) and an apparent triplet at δ 104.40 ($J_{CP} = 2.0$, C_β), respectively. The ketonic carbon appears at δ 215.22 as an apparent triplet ($J_{CP} = 1.9$), and the benzylic CH_2 carbon gives rise to a doublet at δ 71.22 with a J_{CP} of 4.7 Hz. The presence of an acyl ligand in **12** is also shown by the IR spectrum, which exhibits a strong absorption at 1615 cm^{-1} corresponding to the $\nu(C{=}O)$ mode.

Complex **11** does not react with water under the conditions of formation of **12**; therefore the alkyne hydration that leads to the acyl ligand of **12** must take place on a reaction intermediate. The hydration of terminal alkynes promoted by a transition metal complex has been reported for some ruthenium[26,27] and

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(23) Peaks corresponding to fragments $C_{16}H_{12}$, $C_{15}H_{10}$, and $C_{14}H_{10}$ are observed by electron impact MS analysis of the reaction mixtures.

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Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 12[a]

Ir(1)−Ir(2)	2.5599(5)	2.5550(5)			
Ir(1)−P(1)	2.379(3)	2.387(3)	Ir(2)−P(2)	2.385(2)	2.388(3)
Ir(1)−N(1)	2.124(6)	2.125(7)	Ir(2)−N(1)	2.125(6)	2.103(6)
Ir(1)−N(2)	2.124(5)	2.132(7)	Ir(2)−N(2)	2.192(7)	2.164(7)
Ir(1)−C(11)	1.868(9)	1.836(9)	Ir(2)−C(29)	1.839(9)	1.829(9)
Ir(1)−C(21)	2.008(8)	2.011(8)	Ir(2)−C(39)	2.000(9)	1.997(9)
N(1)−C(1)	1.428(11)	1.441(9)	N(2)−C(9)	1.409(9)	1.438(10)
C(11)−O(1)	1.117(11)	1.166(11)	C(29)−O(2)	1.145(11)	1.168(10)
C(21)−C(22)	1.199(12)	1.167(12)	C(39)−O(3)	1.234(10)	1.266(17)[b]
C(22)−C(23)	1.427(12)	1.457(11)	C(39)−C(40)	1.530(10)	1.52(2)[b]
Ir(2)−Ir(1)−P(1)	154.90(7)	155.90(6)	Ir(1)−Ir(2)−P(2)	153.49(6)	153.58(8)
Ir(2)−Ir(1)−N(1)	52.98(17)	52.42(17)	Ir(1)−Ir(2)−N(1)	52.93(17)	53.2(2)
Ir(2)−Ir(1)−N(2)	54.86(19)	54.1(2)	Ir(1)−Ir(2)−N(2)	52.39(15)	52.92(19)
Ir(2)−Ir(1)−C(11)	104.7(3)	107.0(3)	Ir(1)−Ir(2)−C(29)	105.4(4)	103.9(4)
Ir(2)−Ir(1)−C(21)	102.7(2)	100.4(3)	Ir(1)−Ir(2)−C(39)	97.4(2)	99.8(3)
P(1)−Ir(1)−N(1)	111.14(19)	113.91(19)	P(2)−Ir(2)−N(1)	105.40(18)	103.8(2)
P(1)−Ir(1)−N(2)	104.6(2)	105.2(2)	P(2)−Ir(2)−N(2)	110.44(17)	112.3(2)
P(1)−Ir(1)−C(11)	95.0(3)	93.5(3)	P(2)−Ir(2)−C(29)	95.9(3)	99.2(4)
P(1)−Ir(1)−C(21)	91.7(3)	91.0(3)	P(2)−Ir(2)−C(39)	97.3(3)	92.6(3)
N(1)−Ir(1)−N(2)	73.8(3)	73.4(3)	N(1)−Ir(2)−N(2)	72.4(2)	73.2(3)
N(1)−Ir(1)−C(11)	94.0(3)	96.4(3)	N(1)−Ir(2)−C(29)	158.2(4)	156.9(4)
N(1)−Ir(1)−C(21)	155.7(3)	152.8(3)	N(1)−Ir(2)−C(39)	89.4(3)	90.7(3)
N(2)−Ir(1)−C(11)	159.6(4)	161.0(4)	N(2)−Ir(2)−C(29)	96.5(4)	96.2(4)
N(2)−Ir(1)−C(21)	92.9(3)	90.1(3)	N(2)−Ir(2)−C(39)	149.8(3)	152.8(3)
C(11)−Ir(1)−C(21)	92.2(4)	92.6(3)	C(29)−Ir(2)−C(39)	92.0(4)	90.3(4)
Ir(1)−N(1)−Ir(2)	74.09(19)	74.4(2)	Ir(1)−N(2)−Ir(2)	72.7(2)	73.0(2)
Ir(1)−N(1)−C(1)	121.3(6)	121.4(6)	Ir(1)−N(2)−C(9)	124.3(5)	122.0(5)
Ir(2)−N(1)−C(1)	120.3(5)	122.2(5)	Ir(2)−N(2)−C(9)	120.9(6)	119.3(6)
Ir(2)−C(11)−O(1)	178.0(9)	173.6(9)	Ir(2)−C(29)−O(2)	173.7(11)	178.7(8)
Ir(1)−C(21)−C(22)	172.9(8)	178.2(9)	Ir(2)−C(39)−O(3)	120.9(6)	119.9(9)[b]
C(21)−C(22)−C(23)	174.8(10)	178.7(8)	Ir(2)−C(39)−C(40)	120.0(6)	124.0(11)[b]
C(39)−C(40)−C(41)	114.6(8)	115.2(18)	O(3)−C(39)−C(40)	118.4(8)	116.0(14)[b]

[a] Data shown in the two columns correspond to the two independent molecules. [b] Bond parameters affected by ligand disorder; values for the acetylenic ligand are C(89)−C(90) 1.208(16), C(90)−C(91) 1.42(2), Ir−C(89)−C(90) 169.2(10), C(89)−C(90)−C(91) 176.4(14) (see Experimental Section).

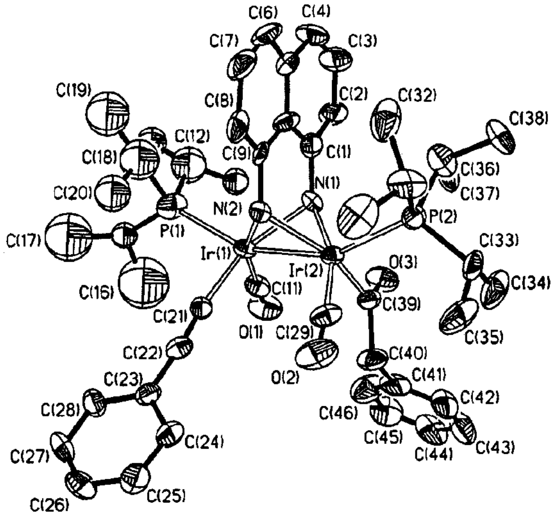

Figure 4. Molecular structure of complex **12** (the non-disordered independent molecule has been represented).

osmium[27e,28] derivatives. This reaction typically affords acyl or alkylcarbonyl complexes and has been found to involve terminal vinylidene intermediates.[26] In our iridium system, this reaction most probably involves the addition of water to the bridging vinylidene species **7**, which is formed under the reaction conditions. The resulting acyl complex could then undergo a new oxidative addition−deprotonation process similar to that leading to **11**. To the best of our knowledge, the reaction leading to complex **12** is the first reported example of alkyne hydration promoted by an iridium compound.[29]

Discussion

Oxidative Addition of Phenylacetylene to Complexes 2 and 3. The reactions depicted in Scheme 2 show that the addition of phenylacetylene to complex **2** results in a kinetic isomer **4**, which slowly isomerizes into the thermodynamically stable isomer **5**. As discussed above, this isomerization may involve the formation of deprotonated intermediates. The structure deduced for the kinetic product **4**, in which the hydride and alkynyl ligands occupy mutual cis positions, points to a concerted oxidative addition occurring at the *pocket* of the dinuclear framework of **2**.

To obtain further evidence for the concerted nature of this addition, a heterolytic process was emulated by the stepwise addition of lithiumphenylacetylide and a proton. Thus, treatment of **2** with lithiumphenylacetylide quantitatively gives the deprotonated complex **1**. On the other hand, treatment of **2** with triflic acid results in a second protonation, to give the already reported dihydride $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(\mu\text{-}H)H(OC(CH_3)_2)(CO)_2(PiPr_3)_2](CF_3SO_3)_2$.[3] On treatment with lithiumphenylacetylide, this dihydride readily gives a mixture of **5** (ca. 60%) and **4** (ca. 20%), together with some minor unidentified species. This lack of selectivity observed for the heterolytic addition contrasts strongly with the quantitative formation of **4**, under the same conditions, by using phenylacetylene.

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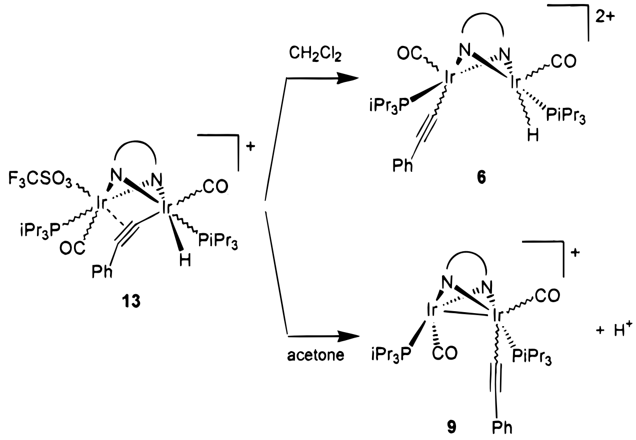
(28) (a) Buil, M.; Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **1997**, *16*, 3169. (b) Knaup, W.; Werner, H. *J. Organomet. Chem.* **1991**, *411*, 471. (c) Harman, W. D.; Dobson, J. C. Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 3061.

(29) In a related process, an iridium allenylidene complex has been found to react with water to give a vinyl-carbonyl complex: O'Connor, J. M.; Hiibner, K. *J. Chem. Soc., Chem. Commun.* **1995**, 1209.

Scheme 5



In light of the above-mentioned reactions of **2** and the previous results of the H_2 oxidative additions,[3] the formation of a kinetic intermediate **13**, similar to **4,** could be a likely initial step for the reaction of **3** with phenylacetylene. Such an unobserved intermediate may also allow us to rationalize the formation of different products (**6** and **9**) depending on the solvent properties (Scheme 5). As observed for **4**, a ligand redistribution process can be expected for **13**, in view of the different coordination spheres of the two metal centers (one iridium coordinates six σ-ligands whereas the other is π-bonded to the alkynyl triple bond and to a weakly donating triflate ligand). Deprotonation of **13** seems to be a plausible initial step for this rearrangement in polar solvents, giving rise to the observed complex **9**. In nonpolar solvents, where deprotonation is not favored, the transfer of the bridging ligand may occur, generating complex **6**.

Formation of the Vinylidene Complex 7. As expected, the two observed kinetic products of phenylacetylene addition to **3**, species **6** and **9**, transform into the same thermodynamically stable compound, the vinylidene-bridged complex **7**. In this respect, compounds **6**, **9**, and **10** could be regarded as intermediate species in the alkyne-to-vinylidene tautomerization[30] assisted by complex **3**. From the reactions depicted in Schemes 3 and 4, it seems to be clear that for our diiridium d^7-d^7 complex the tautomerization follows the hydridoalkynyl oxidative addition mechanism, which also operates for other electron-rich d^6 complexes[30a] and d^8 compounds.[20,30b,31]

Previous studies concerning the hydridoalkynyl-to-vinylidene transformations show that this isomerization can occur with the participation of deprotonated intermediates.[30a,31] This is the case for the formation of **7** in acetone (Scheme 4), via the deprotonated intermediates **9** and **10**, which are stable enough to be characterized in solution. However, our experimental observations suggest that such a mechanism does not operate for the isomerization of **6** into **7** (Scheme 3). In contrast to that found for the related complexes **2** and [Ir_2(μ-1,8-$(NH)_2$-naphth)(μ-H)H($OC(CH_3)_2$)$(CO)_2$$(PiPr_3)_2$]$(CF_3SO_3)_2$,[3] the hydride ligand of **6** does not undergo H/D exchange in acetone-d_6 solutions, which indicates its poor Brønsted acidity. In fact, deprotonation of **6** is not observed even in the presence of an excess of NEt_3. Furthermore, the rate of isomerization seems to be unaffected by changing the solvent polarity or by addition of catalytic amounts of NEt_3. All the above observations suggest that deprotonation of **6** is a very disfavored process, which may preclude a dissociative mechanism for the isomerization of **6** into **7**.

Alternatively, an intramolecular hydrogen shift mechanism may be considered. In this context it should be mentioned that recent theoretical work by Wakatsuki et al. has proved that, even for bulky mononuclear complexes, a bimolecular hydrogen shift mechanism is energetically favored.[30b] In such a mechanism, the metal centers have to approximate each other to distances shorter than 5 Å. In light of the features of this mechanism and the proposed structure of complex **6**, it can be envisaged that direct transfer of the metal-bound hydrogen to the β-carbon of the alkynyl constitutes a very suitable mechanistic proposal for our **6**-to-**7** isomerization, provided that these two ligands can reach positions mutually cisoid in the dinuclear framework. In this respect, we have recently shown that intramolecular rearrangements in these diamidonaphthalene-bridged complexes are energetically accessible and do not require previous ligand dissociation.[3]

Competitive Reactions on the Observed Intermediates. The kinetic complexes characterized in acetone solution, complex **9** and its thermally stable isomer **10**, are isoelectronic with the hydrido complex **2**. These complexes, and also some other reported isoelectronic derivatives with pyrazolate bridges,[32,33] represent electronic situations where the assignment of charges and formal oxidation states to the metal centers is not obvious. In fact, these complexes can be regarded as either d^7-d^7 or d^6-d^8 species. Recent structural and theoretical work on the isoelectronic complex [Ir_2(μ-Pz)(CH_3)$(CO)_2$$(PiPr_3)_2$]($ClO_4$) indicates that it could be better described as an $Ir^{III}-Ir^{I}$ species, where the weak metal−metal bond connecting the metals partially equilibrates their electronic differences.[33] This description leads to a complex having a weakly acidic and a weakly basic metal center which can be characterized by the presence of two very different ν(CO) modes. Complex **2** has been found to fit well in this description, showing an unusual reactivity. Thus, despite its cationic character, **2** can be further protonated at the bridging position,[3] where most of the available electronic density accumulates, and the compound is basic enough to undergo H−H[3] or phenylacetylene-C−H bond activations (Scheme 2).

Complex **10** shows two infrared ν(CO) modes at 2053 and 1973 cm^{-1}, which suggests that the above-mentioned electronic description could also be appropriate in this case. In fact, **10** can be protonated by triflic acid to give **7** and can undergo a new oxidative addition leading to **11**. Due to the fact that the formation of **10**

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(30) For a review on vinylidene chemistry see ref 21. For recent work in this area with leading references see: (a) De los Rios, I.; Jiménez Tenorio, M.; Puerta, C.; Valerga, P. *J. Am. Chem. Soc.* **1997**, *119*, 6529. (b) Wakatsuki, Y.; Koga, N.; Werner, H.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 360.

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is accompanied by the formation of triflic acid (Scheme 4), both of the above-mentioned transformations may take place in acetone solutions, accounting for the complexity of the reactions in excess of phenylacetylene. Furthermore, the formation of complex **12** strongly suggest that the vinylidene compound **7** can undergo further reaction in the presence of water (eq 1). In light of previous results[26−29] and the structure of complex **12**, this reaction may involve the formation of an acyl complex, again isoelectronic with **2** and **10**, which can participate in the dual reactivity features of this class of complexes. Also, the poor yields obtained for complex **11** suggest that this species can also undergo further reaction under the given reaction conditions, thus accounting for the formation of C−C coupling products.

Concluding Remarks

The variety of products obtained by reaction of the diiridium(II) complex **3** with phenylacetylene can be considered as the result of competitive reactions affecting intermediates **13** and **10**. Thus, the proposed intermediate **13** can give different products depending on the solvent polarity, and compound **10** can undergo either protonation or oxidative addition depending on the reaction conditions employed. Our observations on the system also indicate that compounds **7**, **11**, and **12** are still reactive species, which can undergo further reactions. This implies that the reactions depicted in Schemes 3 and 4 are just a fragment of a more complex reaction scheme, which shows a promising potential for C−C coupling reactions. In any case, we believe that the conclusions provided by this study could constitute a helpful tool for the future work in this system and may also be of use to understand the unusual reactivity of other dinuclear systems. Further work in this area is in progress.

Experimental Section

Physical Measurements. Infrared spectra were recorded as Nujol mulls on polyethylene sheets using a Nicolet 550 spectrometer. C, H, N, and S analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. NMR spectra were recorded on a Varian UNITY, a Varian Gemini 2000, or a Bruker ARX, 300 MHz spectrometer. ^{1}H and ^{13}C NMR chemical shifts were measured relative to partially deuterated solvent peaks but are reported in ppm relative to tetramethylsilane. ^{31}P and ^{19}F NMR chemical shifts were measured relative to H_3PO_4 (85%) and $CFCl_3$ respectively. Coupling constants, J and N, are given in hertz. Generally, spectral assignments were achieved by ^{1}H COSY and ^{13}C DEPT experiments. MS data were recorded on a VG Autospec double-focusing mass spectrometer operating in the positive mode; ions were produced with the Cs^+ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used as the matrix. Conductivities were measured in ca. 3×10^{-4} M solutions using a Philips PW 9501/01 conductimeter.

Synthesis. All reactions were carried out with exclusion of air by using standard Schlenk techniques. Solvents were dried by known procedures and distilled under argon prior to use. The complexes [$Ir_2(\mu$-1,8-$(NH)_2$naphth)$(CO)_2(PiPr_3)_2$] (**1**), [$Ir_2(\mu$-1,8-$(NH)_2$naphth)H$(CO)_2(PiPr_3)_2$](CF_3SO_3) (**2**), and [$Ir_2(\mu$-1,8-$(NH)_2$naphth)$(CF_3SO_3)_2(CO)_2(PiPr_3)_2$] (**3**) were prepared following the procedure described in ref 3.

Preparation of [$Ir_2(\mu$-1,8-$(NH)_2$naphth)(μ-C≡CPh)$H_2(CO)_2(PiPr_3)_2$](CF_3SO_3) (4). A solution of **2** (100 mg, 0.099 mmol) in acetone (5 mL) was treated with phenylacetylene (11 μL, 0.099 mmol). After stirring for 30 min at room temperature, the resulting orange solution was concentrated to ca. 0.5 mL and treated with diethyl ether to give an orange-yellow precipitate. The solvent was then decanted and the solid washed several times with diethyl ether and dried in vacuo: yield 80 mg (73%); IR (Nujol mull, cm^{-1}) 3317 (br, ν(N−H)), 2143 (w, ν(Ir−H)), 2048, 2029 (vs, ν(CO)), 1913 (vs, ν(C≡C)); ^{1}H NMR (acetone-d_6, 293 K) δ −20.55 (d, J_{HP} = 16.2, 1H, Ir−H), −18.16 (d, J_{HP} = 18.0, 1H, Ir−H), 1.05 (dd, J_{HP} = 14.7, J_{HH} = 6.9, 9H, PCHCH_3), 1.06 (dd, J_{HP} = 15.0, J_{HH} = 6.9, 9H, PCHCH_3), 1.29 (dd, J_{HP} = 14.7, J_{HH} = 6.9, 9H, PCHCH_3), 1.31 (dd, J_{HP} = 14.4, J_{HH} = 7.2, 9H, PCHCH_3), 2.56 (m, 6H, PCHCH$_3$), 5.12, 5.69 (both br, 1H, NH), 7.25 (t, J_{HH} = 8.1, 1H, CH), 7.29 (t, J_{HH} = 7.5, 1H, CH), 7.55−7.71 (m, 9H, all CH); ^{31}P{^{1}H} NMR (acetone-d_6, 293 K) δ 23.90 (s), 23.76 (s); ^{13}C{^{1}H} NMR (acetone-d_6, 293 K) δ 18.98, 19.03, 19.32 (s, all PCHCH$_3$), 24.65 (d, J_{CP} = 29.2, PCHCH$_3$), 27.04 (d, J_{CP} = 32.2, PCHCH$_3$), 53.71 (d, J_{CP} = 10.0, Ir−C≡C), 110.07 (d, J_{CP} = 2.9, CH), 110.63 (d, J_{CP} = 2.6, CH), 122.43 (s, CH), 122.56 (s, C), 123.89 (s, CH), 124.19 (s, C), 126.16, 126.94 (s, both CH), 128.63 (s, Ir−C≡C), 130.26, 132.02, 134.66 (s, all CH), 137.01 (s, C), 154.56 (d, J_{CP} = 3.6, C), 157.05 (d, J_{CP} = 2.8, C), 167.90 (dd, J_{CP} = 6.5, 1.5, CO), 169.39 (d, J_{CP} = 7.8, CO); ^{19}F NMR (acetone-d_6, 293 K) δ −78.32 (s); Λ_M (5×10^{-4} M, acetone) = 131.4 Ω^{-1} cm^2 mol^{-1} (1:1). Anal. Calcd for $C_{39}H_{57}N_2SF_3Ir_2O_5P_2$: C, 40.06; H, 4.91; N, 2.39; S, 2.74. Found: C, 40.51; H, 4.20; N, 2.48; S, 2.44.

Preparation of [$Ir_2(\mu$-1,8-$(NH)_2$naphth)(μ-H)H(C≡CPh)$(CO)_2(PiPr_3)_2$](CF_3SO_3) (5). A solution of **4** (100 mg, 0.085 mmol) in acetone (3 mL) was treated with NEt_3 (0.5 μL, 0.035 mmol). After 1 h, the solution was evaporated to dryness and the residue treated with diethyl ether to give a pale yellow microcrystalline solid. This solid was isolated by filtration, washed with diethyl ether, and dried in vacuo: yield 80 mg (80%); IR (Nujol mull, cm^{-1}) 3358 (br, ν(N−H)), 2115 (vs, ν(C≡C)), 2062, 2033 (vs, ν(CO)); ^{1}H NMR (acetone-d_6, 293 K) δ −14.67 (dd, J_{HP} = 18.3, J_{HH} = 8.7, 1H, Ir−H), −11.77 (ddd, J_{HP} = 6.3, 3.0, J_{HH} = 8.7, 1H, Ir−H−Ir), 1.39 (dd, J_{HP} = 15.0, J_{HH} = 6.9, 9H, PCHCH_3), 1.40 (dd, J_{HP}= 14.7, J_{HH} = 6.9, 9H, PCHCH_3), 1.49 (dd, J_{HP} = 15.9, J_{HH} = 7.2, 9H, PCHCH_3), 1.50 (dd, J_{HP}= 14.1, J_{HH} = 7.2, 9H, PCHCH_3), 2.75, 2.94 (both m, 3H, PCHCH$_3$), 6.21, 6.25 (both br, 1H, NH), 6.30 (m, 2H, CH), 6.96 (m, 3H, all CH), 7.25 (m, 2H, CH), 7.62 (d, J_{HH} = 7.5, 1H, CH), 7.66 (d, J_{HH} = 7.8, 1H, CH), 7.77 (d, J_{HH} = 7.8, 1H, CH), 7.78 (d, J_{HH} = 8.1, 1H, CH); ^{31}P{^{1}H} NMR (acetone-d_6, 293 K) δ 32.37 (s), 23.86 (s); ^{13}C{^{1}H} NMR (acetone-d_6, 293 K) δ 18.89, 18.90, 19.69, 20.55 (s, all PCHCH$_3$), 25.83 (d, J_{CP} = 30.7, PCHCH$_3$), 68.36 (d, J_{CP} = 10.6, Ir−C≡C), 103.90 (s, Ir−C≡C), 113.18 (d, J_{CP} = 2.3, CH), 113.67 (d, J_{CP} = 4.4, CH), 123.35 (s, CH), 123.42, 123.59 (s, both C), 126.65, 127.40 (s, both CH), 127.81 (s, C), 128.35, 131.80, 131.84 (s, all CH), 136.23 (s, C), 147.51 (d, J_{CP} = 3.2, C), 148.02 (d, J_{CP} = 3.2, C), 165.72 (d, J_{CP} = 8.2, CO), 167.86 (d, J_{CP} = 7.7, CO).^{19}F NMR (acetone-d_6, 293 K) δ −78.32 (s). Anal. Calcd for $C_{39}H_{57}N_2SF_3Ir_2O_5P_2$: C, 40.06; H, 4.91; N, 2.39; S, 2.74. Found: C, 40.32; H, 4.80; N, 2.11; S, 2.49.

Preparation of [$Ir_2(\mu$-1,8-$(NH)_2$naphth)H(C≡CPh)$(CO)_2(PiPr_3)_2$]$(CF_3SO_3)_2$ (6). A solution of **3** (200 mg, 0.16 mmol) in CH_2Cl_2 (5 mL) at 273 K was treated with phenylacetylene (18 μL, 0.17 mmol). After 90 min, the resulting yellow solution was concentrated to ca. 0.5 mL and diethyl ether added to give a pale yellow precipitate. The solvent was then decanted and the solid washed with diethyl ether and dried in vacuo: yield 175 mg (81%); IR (Nujol mull, cm^{-1}) 3421, 3275 (br, ν(N−H)), 2145 (s, ν(C≡C)), 2062, 2023 (vs, ν(CO)); ^{1}H NMR ($CDCl_3$, 293 K) δ −17.39 (d, J_{HP} = 18.6, 1H, Ir−H), 1.27 (dd, J_{HP} = 14.7, J_{HH} = 6.9, 9H, PCHCH_3), 1.30 (dd, J_{HP} = 14.7, J_{HH} = 6.0, 9H, PCHCH_3), 1.41 (dd, J_{HP} = 14.4, J_{HH} = 7.2, 9H, PCHCH_3), 1.43 (dd, J_{HP} = 15.3, J_{HH} = 7.5, 9H, PCHCH_3), 2.54, 2.93 (both m, 3H, PCHCH$_3$), 4.78, 5.37 (both br, 1H, NH), 6.21 (m, 2H, CH), 6.92 (m, 3H, all CH), 7.17−7.27 (m, 4H, all CH), 7.57 (d, J_{HH}

= 7.8, 1H, CH), 7.61 (m, 2H, CH); ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K) δ 29.02 (s), 11.61 (s); ^{13}C{^{1}H} NMR (CDCl$_3$, 293 K) δ 18.77, 18.80 (s, both PCH*C*H$_3$), 18.88 (d, J_{CP} = 2.7, PCH*C*H$_3$), 19.15 (d, J_{CP} = 1.9, PCH*C*H$_3$), 25.08 (d, J_{CP} = 31.1, P*C*HCH$_3$), 25.84 (d, J_{CP} = 28.8, P*C*HCH$_3$), 64.41 (d, J_{CP} = 10.5, Ir-*C*≡C), 96.2 (s, Ir−C≡*C*), 110.87 (d, J_{CP} = 3.2, CH), 111.14 (brd, CH), 121.81, 122.90 (s, both CH), 123.98 (s, C), 125.52, 125.74, 126.38 (s, all CH), 126.63 (s, C), 127.25, 131.14 (s, both CH), 135.46 (s, C), 148.32 (d, J_{CP} = 3.7, C), 149.71 (d, J_{CP} = 3.7, C), 160.97 (d, J_{CP} = 9.6, CO), 161.23 (d, J_{CP} = 6.4, CO); ^{19}F NMR (CDCl$_3$, 293 K) δ −79.17 (s); Λ_M (5×10^{-4} M, acetone) = 163.2 Ω^{-1} cm^2 mol^{-1} (1:2). Anal. Calcd for $C_{40}H_{56}N_2S_2F_6Ir_2O_8P_2$: C, 36.47; H, 4.28; N, 2.12; S, 4.87. Found: C, 36.22; H, 4.22; N, 2.63; S, 4.48.

Preparation of [Ir$_2$(μ-1,8-(NH)$_2$naphth)(μ-C=CHPh)(CF$_3$SO$_3$)$_2$(CO)$_2$(PiPr$_3$)$_2$] (7). A solution of **6** (200 mg, 0.15 mmol) and phenylacetylene (2 μL, 0.02 mmol) in CH$_2$Cl$_2$ (5 mL) was refluxed during 48 h and then reduced to ca. 1 mL. Addition of diethyl ether to this residue produced the precipitation of a pale yellow microcrystalline solid, which was separated by decantation, washed with diethyl ether, and dried in vacuo: yield 174 mg (87%); IR (Nujol mull, cm^{-1}) 3330, 3281 (br, ν(N−H)), 2054, 2034 (vs, ν(CO)); ^{1}H NMR (CDCl$_3$, 293 K) δ 1.07 (dd, J_{HP} = 15.0, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 1.19 (dd, J_{HP} = 14.6, J_{HH} = 6.6, 9H, PCHC*H*$_3$), 1.33 (dd, J_{HP} = 14.4, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 1.42 (dd, J_{HP} = 14.3, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 2.23, 2.79 (both m, 3H, PC*H*CH$_3$), 4.65, 4.81 (both br, 1H, NH), 7.11 (s, 1H, =CHPh), 7.26−7.43 (m, 9H, all CH), 7.72 (d, J_{HH} = 7.8, 2H, CH); ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K) δ 4.43 (s), 0.70 (s); ^{13}C{^{1}H} NMR (CDCl$_3$, 293 K) δ 18.68, 18.84, 19.05, 20.43 (s, all PCH*C*H$_3$), 26.39 (d, J_{CP} = 27.0, P*C*HCH$_3$), 27.41 (d, J_{CP} = 26.6, P*C*HCH$_3$), 100.09 (t, J_{CP} = 3.0, Ir−*C*=CHPh), 116.64 (d, J_{CP} = 3.1, CH), 117.98 (d, J_{CP} = 4.3, CH), 121.12 (s, C), 124.91, 122.90, 126.22, 126.36, 127.28, 128.17, 129.08 (s, all CH), 134.57, 139.55 (s, both C), 139.80 (d, J_{CP} = 3.0, C), 139.95 (d, J_{CP} = 4.6, C), 140.59 (s, Ir−C=*C*HPh), 164.87 (d, J_{CP} = 9.0, CO), 165.01 (d, J_{CP} = 7.6, CO); ^{19}F NMR (CDCl$_3$, 293 K) δ −79.01 (br); Λ_M (5×10^{-4} M, acetone) = 162.6 Ω^{-1} cm^2 mol^{-1} (1:2). Anal. Calcd for $C_{40}H_{56}N_2S_2F_6Ir_2O_8P_2$: C, 36.47; H, 4.28; N, 2.12; S, 4.87. Found: C, 37.01; H, 3.90; N, 2.02; S, 4.53.

Preparation of [Ir$_2$(μ-1,8-(NH)$_2$naphth)(μ-C=CHPh)(NCCH$_3$)$_2$(CO)$_2$(PiPr$_3$)$_2$](CF$_3$SO$_3$)$_2$ (8). A solution of **7** (200 mg, 0.15 mmol) in CH$_2$Cl$_2$ (5 mL) was treated with acetonitrile (500 μL). After 60 min, the resulting colorless solution was concentrated to ca. 0.5 mL and diethyl ether added to give a white microcrystalline solid, which was separated by decantation, washed with diethyl ether, and dried in vacuo: yield 197 mg (93%); IR (Nujol mull, cm^{-1}) 3358, 3327 (br, ν(N−H)), 2050, 2035 (vs, ν(CO)); ^{1}H NMR (CDCl$_3$, 293 K) δ 0.90 (dd, J_{HP} = 14.1, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 1.10 (dd, J_{HP} = 15.3, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 1.30 (dd, J_{HP} = 13.8, J_{HH} = 6.0, 9H, PCHC*H*$_3$), 1.33 (dd, J_{HP} = 14.4, J_{HH} = 6.9, 9H, PCHC*H*$_3$), 1.45 (s, 6H, NCCH$_3$), 2.27, 2.64 (both m, 3H, PC*H*CH$_3$), 5.17, 5.21 (both br, 1H, NH), 7.29 (m, 3H, all CH), 7.34 (s, 1H, =CH), 7.36−7.44 (m, 4H, all CH), 7.72 (d, J_{HH} = 8.7, 2H, CH), 8.02 (brd, 2H, CH); ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K) δ 8.21 (s), 4.41 (s); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 293 K) δ 1.84 (s, NC*C*H$_3$), 18.45 (d, J_{CP} = 3.1, PCH*C*H$_3$), 18.61 (d, J_{CP} = 3.9, PCH*C*H$_3$), 19.36 (d, J_{CP} = 1.8, PCH*C*H$_3$), 20.09 (d, J_{CP} = 1.8, PCH*C*H$_3$), 26.52 (d, J_{CP} = 27.4, P*C*HCH$_3$), 107.30 (t, J_{CP} = 2.6, Ir−*C*=CHPh), 117.58 (d, J_{CP} = 4.1, CH), 117.87 (d, J_{CP} = 3.0, CH), 121.33 (br, N*C*CH$_3$), 121.38 (q, J_{CF} = 319.7, O$_3$SCF$_3$), 123.33 (s, C), 124.55 (s, CH), 127.28 (s, CH), 127.92 (s, CH), 128.42 (s, CH), 129.46 (s, CH), 134.20 (s, C), 141.11 (s, C), 141.95 (s, Ir−*C*=CHPh), 144.12 (d, J_{CP} = 4.1, C), 144.32 (d, J_{CP} = 3.1, C), 162.70 (d, J_{CP} = 7.8, CO), 162.97 (d, J_{CP} = 7.5, CO). ^{19}F NMR (CDCl$_3$, 293 K) δ −79.17 (s); Λ_M (5×10^{-4} M, acetone) = 181.7 Ω^{-1} cm^2 mol^{-1} (1:2). Anal. Calcd for $C_{44}H_{62}N_4S_2F_6Ir_2O_8P_2$: C, 37.76; H, 4.46; N, 4.00; S, 4.58. Found: C, 37.40; H, 4.20; N, 3.85; S, 4.33.

[Ir$_2$(μ-1,8-(NH)$_2$naphth)(C≡CPh)(CO)$_2$(PiPr$_3$)$_2$](CF$_3$SO$_3$) (9). In an NMR tube, a solution of **3** (64 mg, 0.05 mmol) in acetone-*d*$_6$ (0.5 mL) at 273 K was treated with phenylacetylene (6 μL, 0.05 mmol). The NMR spectra of the sample at 253 K show the formation of complex **9** in a yield greater than 90%; ^{1}H NMR (acetone-*d*$_6$, 253 K) δ 1.34 (dd, J_{HP} = 15.0, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 1.41 (dd, J_{HP} = 14.6, J_{HH} = 6.9, 9H, PCHC*H*$_3$), 1.43 (dd, J_{HP} = 14.4, J_{HH} = 6.9, 9H, PCHC*H*$_3$), 1.48 (dd, J_{HP} = 14.0, J_{HH} = 6.9, 9H, PCHC*H*$_3$), 2.82, 2.91 (both m, 3H, PC*H*CH$_3$), 6.21 (m, 2H, CH), 6.93 (m, 3H, all CH), 7.22 (br, 1H, NH), 7.29 (t, J_{HH} = 7.8, 1H, CH), 7.30 (t, J_{HH} = 7.8, 1H, CH), 7.43 (br, 1H, NH), 7.70 (d, J_{HH} = 7.8, 1H, CH), 7.79 (d, J_{HH} = 7.8, 2H, CH), 7.82 (d, J_{HH} = 7.8, 1H, CH); ^{31}P{^{1}H} NMR (acetone-*d*$_6$, 253 K) δ 31.56 (s), 24.00 (s); ^{13}C{^{1}H} NMR (acetone-*d*$_6$, 253 K) δ 18.01 (d, J_{CP} = 2.7, PCH*C*H$_3$), 18.49 (d, J_{CP} = 2.0, PCH*C*H$_3$), 18.66, 19.16 (s, both PCH*C*H$_3$), 23.33 (d, J_{CP} = 30.1, P*C*HCH$_3$), 23.86 (d, J_{CP} = 30.1, P*C*HCH$_3$), 64.96 (br, Ir−*C*≡C), 93.81 (s, Ir−C≡*C*), 112.97 (d, J_{CP} = 4.3, CH), 113.06 (d, J_{CP} = 3.3, CH), 120.87, 121.61 (s, both CH), 122.00 (s, C), 125.36 (s, CH), 126.09 (s, C), 126.82, 127.11, 130.78 (s, all CH), 134.89 (s, C), 145.55 (d, J_{CP} = 3.1, C), 145.66 (d, J_{CP} = 3.3, C), 171.48 (d, J_{CP} = 9.0, CO), 176.02 (d, J_{CP} = 10.5, CO); ^{19}F NMR (acetone-*d*$_6$, 293 K) δ −78.32 (s).

Preparation of [Ir$_2$(μ-1,8-(NH)$_2$naphth)(C≡CPh)(CO)$_2$(PiPr$_3$)$_2$](CF$_3$SO$_3$)$_2$ (10). A solution of **1** (150 mg, 0.16 mmol) in CH$_2$Cl$_2$ (5 mL) was treated with iodophenylacetylene (23 μL, 0.16 mmol). After 90 min, the resulting red solution was evaporated to dryness, redissolved in 5 mL of acetone, and treated with AgCF$_3$SO$_3$ (41 mg, 0.16 mmol). After 30 min at 313 K in the dark, the resulting deep red solution was filtered through Celite and dried in vacuo. Treatment of the resulting residue with diethyl ether gave a brown solid, which was filtered off, washed with diethyl ether, and dried in vacuo: yield 144 mg (77%); IR (Nujol mull, cm^{-1}) 3238 (br, ν(N−H)), 2122 (s, ν(C≡C)), 2053, 1973 (vs, ν(CO)); ^{1}H NMR (acetone-*d*$_6$, 293 K) δ 0.83 (dd, J_{HP} = 14.1, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 1.30 (dd, J_{HP} = 15.6, J_{HH} = 6.6, 9H, PCHC*H*$_3$), 1.36 (dd, J_{HP} = 14.7, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 1.38 (dd, J_{HP} = 13.8, J_{HH} = 6.6, 9H, PCHC*H*$_3$), 1.97, 2.88 (both m, 3H, PC*H*CH$_3$), 6.23 (br, 1H, NH), 7.20−7.39 (m, 7H, all CH), 7.58 (br, 1H, NH), 7.64 (d, J_{HH} = 7.2, 1H, CH), 7.71 (d, J_{HH} = 6.9, 1H, CH), 7.76 (d, J_{HH} = 8.7, 1H, CH), 7.80 (d, J_{HH} = 8.7, 1H, CH); ^{31}P{^{1}H} NMR (acetone-*d*$_6$, 293 K) δ 33.14 (d, J_{PP} = 5.8 Hz), −2.30 (d, J_{PP} = 5.8 Hz); ^{13}C{^{1}H} NMR (acetone-*d*$_6$, 293 K) δ 19.86, 20.10, 20.24, 20.29 (s, all PCH*C*H$_3$), 25.06 (d, J_{CP} = 32.5, P*C*HCH$_3$), 26.17 (d, J_{CP} = 28.4, P*C*HCH$_3$), 77.82 (d, J_{CP} = 12.1, Ir−*C*≡C), 105.47 (s, Ir−C≡*C*), 113.67 (s, CH), 113.94 (d, J_{CP} = 3.7, CH), 121.54 (s, C), 122.41, 123.04, 127.01 (s, all CH), 128.23 (s, C), 128.56, 129.20, 131.92 (s, all CH), 136.57, 144.92 (both s, C), 148.32 (d, J_{CP} = 3.2, C), 170.83 (d, J_{CP} = 7.8, CO), 175.00 (dd, J_{CP} = 11.5, 2.3, CO); ^{19}F NMR (acetone-*d*$_6$, 293 K) δ −78.32 (s). Anal. Calcd for $C_{39}H_{55}N_2S_2F_3Ir_2O_5P_2$: C, 40.13; H, 4,75; N, 2.34; S, 2.75. Found: C, 39.54; H, 4.57; N, 2.29; S, 2.99.

Preparation of [Ir$_2$(μ-1,8-(NH)$_2$naphth)(C≡CPh)$_2$(CO)$_2$(PiPr$_3$)$_2$] (11). A solution of **3** (100 mg, 0.08 mmol) in toluene (5 mL) was treated with lithiumphenylacetylide (17.8 mg, 0.16 mmol), and the mixture stirred for 2 h at room temperature. The suspension obtained was filtered through Celite and the resulting yellow solution evaporated to dryness. Treatment of the residue with pentane gave a yellow microcrystalline solid, which was filtered off, washed with pentane, and dried in vacuo: yield 66 mg (72%); IR (Nujol, cm^{-1}) 3335, 3312 ν(N−H), 2123, 2112 ν(C≡C), 1992, 1977 ν(CO); ^{1}H NMR (C$_6$D$_6$, 293 K) δ 0.58 (dvt, *N* = 13.9, J_{HH} = 6.9, 18H, PCHC*H*$_3$), 1.09 (dvt, *N* = 14.3, J_{HH} = 7.0, 18H, PCHC*H*$_3$), 1.70 (m, 6H, PC*H*CH$_3$), 4.70 (br, 2H, NH), 6.32 (d, J_{HH} = 7.3, 2H, CH), 6.69 (dd, J_{HH} = 8.0, 7.3, 2H, CH), 6.95 (t, J_{HH} = 7.0, 2H, CH), 7.15 (t, J_{HH} = 7.0, 4H, CH), 7.23 (d, J_{HH} = 8.0, 2H, CH), 7.72 (d, J_{HH} = 7.0, 4H, CH); ^{31}P{^{1}H} NMR (C$_6$D$_6$, 293 K) δ 6.20 (s); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 293 K) δ 18.61 (s, PCH*C*H$_3$), 20.18 (s, PCH*C*H$_3$), 24.79 (vt, *N* = 20.0, P*C*HCH$_3$), 78.61 (vt, *N* = 4.7,

Table 3. Crystallographic Data and Structure Refinement for 7 and 12

	7	**12**
formula	$C_{40}H_{56}F_6Ir_2N_2O_8P_2S_2$	$C_{46}H_{61.5}Ir_2N_2O_{2.75}P_2$
M	1317.33	1132.81
cryst size	0.06 × 0.16 × 0.23	0.03 × 0.10 × 0.30
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$	$Pca2_1$
a, Å	11.954(2)	22.7162(9)
b, Å	13.423(2)	16.3072(6)
c, Å	16.775(3)	24.2865(10)
α, deg	81.917(10)	90.0
β, deg	69.931(8)	90.0
γ, deg	65.829(8)	90.0
V, Å^3	2306.6(7))	8996.6(6)
Z	2	8
ρ_{calc} (g cm^{-3})	1.897	1.673
T (K)	173(2)	160(2)
μ, mm^{-1}	6.000	6.021
2θ range data collec (deg)	3−50	3−54
index ranges	$-14 \leq h \leq 1$, $-15 \leq k \leq 14$, $-19 \leq l \leq 18$	$-28 \leq h \leq 28$, $-21 \leq k \leq 12$, $-27 \leq l \leq 31$
no. of measd refls	8802	40 304
no. of unique refls	8099 ($R_{int} = 0.0334$)	18112 ($R_{int} = 0.0358$)
abs corr method	ψ-scan	empirical
min., max. trans. factors	0.538, 0.738	0.265, 0.840
no. of data/restraints/params	8099/39/563	18112/33/918
$R(F)$ [$F^2 > 2\sigma(F^2)$][a]	0.0440 (6199 refls)	0.0354 (16548 refls)
$wR(F^2)$ [all data][b]	0.1003	0.0865[c]
S [all data][d]	1.055	0.948

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR(F^2) = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2])^{1/2}$. [c] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$with $P = (F_o^2 + 2F_c^2)/3$; $a = 0.0473$ and $b = 20.4777$ for **12**, and $a = 0.0290$ and $b = 20.1243$ for **7**. [d] $S = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$; n = number of reflections, p = number of parameters.

Ir−*C*≡C), 105.15 (vt, $N = 2.7$, Ir−C≡*C*), 110.87, 119.77 (both s, CH), 121.33 (s, C), 125.29, 126.69, 127.89 (all s, CH), 129.83 (s, C), 132.36 (s, CH), 136.25 (s, C), 151.06 (vt, $N = 3.0$, C), 175.44 (s, CO). MS (FAB+, *m/z* (%)) 1123 (75) [M$^+$], 1092 (100) [M$^+$ − CO]. Anal. Calcd for $C_{46}H_{60}N_2Ir_2O_2P_2$: C, 49.36; H, 5.40; N, 2.50. Found: C, 48.98; H, 5.03; N, 2.39.

Preparation of [Ir$_2$(*μ*-1,8-(NH)$_2$naphth)(C≡CPh)(C(O)-CH$_2$Ph)(CO)$_2$(PiPr$_3$)$_2$] (12). A solution of **3** (200 mg, 0.16 mmol) in acetone (5 mL) was treated with water (1 mL) and phenylacetylene (40 *μ*L, 0.39 mmol). Stirring of the solution during 48 h produced the precipitation of a yellow solid, which was decanted, washed with methanol, and dried in vacuo: yield 67 mg. The spectroscopic analysis of the solid revealed a mixture of complexes **11** and **12** in a 0.22:0.78 molar ratio. Data for complex **12**: IR (Nujol, cm^{-1}) 3315 ν(N−H), 2116 ν(C≡C), 1985, 1971, 1615 ν(CO); ^{1}H NMR (C_6D_6, 293 K) δ 0.53 (dd, $J_{HP} = 13.2$, $J_{HH} = 6.9$, 9H, PCHC*H*$_3$), 0.60 (dd, $J_{HP} = 12.9$, $J_{HH} = 7.2$, 9H, PCHC*H*$_3$), 0.90 (dd, $J_{HP} = 13.8$, $J_{HH} = 7.2$, 9H, PCHC*H*$_3$), 1.12 (dd, $J_{HP} = 14.4$, $J_{HH} = 7.2$, 9H, PCHC*H*$_3$), 1.36 (m, 3H, PC*H*CH$_3$), 1.71 (m, 3H, PC*H*CH$_3$), 4.11 (br, 1H, NH), 4.74 (AB system, $\delta_A = 4.62$, $\delta_B = 4.85$, $J_{HH} = 16.5$, 2H, C*H*$_2$-Ph), 5.36 (br, 1H, NH), 6.41 (d, $J_{HH} = 7.2$, 1H, CH), 6.72 (dd, $J_{HH} = 7.8$, 7.2, 1H, CH), 6.76 (dd, $J_{HH} = 8.4$, 6.9, 1H, CH), 6.94 (d, $J_{HH} = 6.9$, 1H, CH), 7.10−7.31 (m, 8H, all CH), 7.57 (dd, $J_{HH} = 7.9$, 1.3, 2H, CH), 7.82 (dd, $J_{HH} = 8.1$, 1.5, 2H, CH); ^{31}P{^{1}H} NMR (C_6D_6, 293 K) δ_A 12.61, δ_B 6.01 ($J_{PP} = 117.5$); ^{13}C{^{1}H} NMR (C_6D_6, 293 K) δ 18.61, 18.77, 19.82, 20.25 (all s, PCH*C*H$_3$), 24.90 (dd, $J_{CP} = 18.3$, 1.0 P*C*HCH$_3$), 26.71 (dd, $J_{CP} = 20.2$, 1.4, P*C*HCH$_3$), 71.22 (d, $J_{CP} = 4.7$, Ir−CO*C*H$_2$Ph), 77.50 (d, $J_{CP} = 10.0$, Ir−*C*≡C), 104.40 (dd, $J_{CP} = 2.0$, Ir−C≡*C*), 110.21, 110.98, 118.06, 119.60 (all s, CH), 122.32 (s, C), 125.26, 126.09, 126.85, 126.89, 128.24 (all s, CH), 129.95 (d, $J_{CP} = 1.4$, C), 130.87, 132.27, 132.29 (all s, CH), 136.56, 138.23 (both s, C), 152.15 (dd, $J_{CP} = 2.0$, 0.7, C), 152.52 (dd, $J_{CP} = 3.0$, 1.0, C), 175.08 (d, $J_{CP} = 3.5$, CO), 180.75 (dd, $J_{CP} = 2.6$, 1.4, CO), 215.22 (dd, $J_{CP} = 1.9$, Ir−*C*(O)CH$_2$Ph).

X-ray Structure Analysis of 7 and 12. Crystals of **7** were obtained by slow diffusion of diethyl ether into a solution of the compound in CH_2Cl_2 at room temperature. Those of **12** were formed by the same procedure at 273 K. Data for **7** were measured on a Siemens-Stoe AED-2 four-circle diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). In the case of **12** the diffraction experiment was carried out with a Bruker AXS SMART CCD diffractometer using synchrotron radiation ($\lambda = 0.688\,90$ Å) at the Daresbury SRS station 9.8. Unit cell dimensions were determined by a least-squares fit on the setting angles of 57 high-angle carefully centered reflections (25° ≤ 2θ ≤ 32°) for **7**, and 33 977 reflections for **12**. Data collection for **8** was carried out at 173 K using the $\omega/2\theta$ scan technique to a 2θ maximum of 50°; three standard reflections were measured every hour as a check on crystal and instrument stability. No decay was observed. For **12**, the Bragg reflections were measured at 160 K through the use of CCD recording of omega rotation frames (0.3° each); the observed intensity decay (25%) was evaluated from the measurement of equivalent reflections at different measuring times and subsequently corrected. For both structures data were corrected for Lorentz and polarization effects. Reflections were also corrected for absorption by semiempirical methods (see Table 3).[34,35] Both structures were solved by standard Patterson and difference Fourier methods.[36] The positions and anisotropic thermal parameters of the nondisordered non-hydrogen atoms were refined satisfactorily by full-matrix least-squares calculations on F^2 (SHELXL-97).[37] For complex **12** the estimation of the absolute structure Flack parameter x after isotropic modeling evidences the presence of a racemic twin; this parameter was included and refined along the convergence process (final value 0.460(8)).

In the analysis of **7** the anomalous high thermal parameters observed for several carbon atoms revealed the existence of static disorder in one of the triisopropylphosphine ligands (atoms bonded to P(1)). A geometrically restrained disorder model was established on the basis of displacement parameters and residual peaks (see Supporting Information). Hydrogen atoms were included at calculated positions only for nondis-

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ordered atoms and were refined with riding positional and displacement parameters. The residual electron density peaks over 1.0 e/Å^3(1.60−1.14 e/Å^3) were situated in close proximity to disordered atoms.

For **12** two independent molecules were found in the asymmetric unit. High thermal parameters in the first stages of refinement identified the presence of static disorder in two phosphine ligands (C(12)−C(20) bonded to P(1); C(80)−C(88) bonded to P(4)) and in the acyl group of one of the independent molecules (O(6) and C(90)−C(96)). Phosphine disorder was modeled with the splitting of several atoms: C(13)−C(15) in one case and C(80)−C(85) in the second. The detailed analysis of the disorder at the ketonic group revealed the alternative presence of a second phenylacetylene ligand bonded to Ir(4); this fact implies the cocrystallization of the bisalkynyl derivative **11**, together with the acyl complex **12**. A 0.5 fixed occupancy factor was used for both ligands bonded to Ir(4), and isotropic displacement parameters were included for disorder atoms (C(90)−C(96)). Geometrical constraints were applied for the phenyl groups of the two disordered ligands (AFIX command); these were liberated in the last cycles of refinement. Hydrogen refinement was as described for **7**.

In both structures the function minimized was $\sum[w(F_o^2 - F_c^2)^2]$. Final agreement parameters are collected in Table 3, together with some crystallographic data and additional experimental details. Scattering factors were used as implemented in the refinement program.[37]

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Supporting Information Available: Full listings of crystallographic data, complete atomic coordinates, isotropic and anisotropic thermal parameters, and bond distances and angles for complexes **7** and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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