Reactions of Diamidonaphthalene-Bridged Diiridium Tetrahydrides with Alkynes: Hydrogenation, Vinylidene Formation, and Catalytic C−C Coupling

M. Victoria Jiménez, Eduardo Sola,* Fernando J. Lahoz, and Luis A. Oro*

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, and Instituto Universitario de Catálisis Homogénea, Universidad de Zaragoza, 50009 Zaragoza, Spain

Received January 21, 2005

The diamidonaphthalene-bridged diiridium tetrahydride $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(\mu\text{-}H)H_3(NCMe)(P\textit{i}Pr_3)_2]$ (**1**) reacts with an excess of internal alkynes such as diphenylacetylene, 2-butyne, or 1-phenyl-1-propyne to give the diiridium(I) alkene compounds $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}\{\eta^2\text{-}\textit{Z}\text{-}CH(R)=CHR'\}_2(P\textit{i}Pr_3)_2]$ (R, R′ = Ph, **4**; R, R′ = Me, **5**; and R = Ph, R′ = Me, **6**), respectively. The bis-*Z*-alkenyl reaction intermediate $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(\mu\text{-}H)H\{\textit{Z}\text{-}C(Ph)=CHPh\}_2(NCMe)(P\textit{i}Pr_3)_2]$ (**3**) has been isolated and characterized in the case of diphenylacetylene as substrate. The reactions of diphenylacetylene and 2-butyne with the carbonyl analogue of **1**, $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(\mu\text{-}H)H_3(CO)(P\textit{i}Pr_3)_2]$ (**2**), afford the alkene-carbonyl compounds $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}\{\eta^2\text{-}\textit{Z}\text{-}CH(R)=CHR\}(CO)(P\textit{i}Pr_3)_2]$ (R = Ph, **7**; R = Me, **8**). Similar reactions using silyl-substituted alkyne substrates seem to involve alkyne to vinylidene rearrangements. Thus, reaction of **1** with excess trimethylsilyl-1-propyne affords the product $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}\{\eta^2\text{-}CH_2=C(Me)SiMe_3\}_2(P\textit{i}Pr_3)_2]$ (**10**) through the bis-gem-alkenyl intermediate $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(\mu\text{-}H)H\{CH=C(Me)SiMe_3\}_2(NCMe)(P\textit{i}Pr_3)_2]$ (**9**). A similar reaction with bis(trimethylsilyl)acetylene forms the bis-vinylidene complex $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}\{C=C(SiMe_3)_2\}_2(P\textit{i}Pr_3)_2]$ (**11**) together with 2 equiv of $H_2C=C(SiMe_3)_2$. The corresponding reactions of these silyl-substituted alkynes with complex **2** give the mixed-valence compound $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}H\{CH=C(Me)SiMe_3\}(CO)(P\textit{i}Pr_3)_2]$ (**12**) and the vinylidene-carbonyl derivative $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}\{C=C(SiMe_3)_2\}(CO)(P\textit{i}Pr_3)_2]$ (**13**) as final products, respectively. The complexes **4**−**6** and **11** are effective catalysts for 1-alkyne couplings to give mixtures of *Z*-butenyne dimers and hexadienyne trimers.

Introduction

The chemistry of di- and polynuclear metal complexes is a subject of current research interest since cooperation among close metal centers constitutes a frequent source of novel chemical transformations and enhanced catalytic activities.[1] Our recent research in this area has mainly comprised the study of dinuclear rhodium and iridium complexes having robust N-donor bridging ligands and has been focused on the identification of mechanistic aspects of cooperation and their impact in elementary reactions relevant to homogeneous catalysis. This has led us to the characterization of singular reactivity patterns due to apparently subtle structural effects or weak interactions,[2−5] and to the recognitionof the more versatile chemistry of these compounds compared to that of mononuclear analogues. Good examples of such versatility can be found in the reactions of diamidonaphthalene-bridged iridium complexes in low oxidation states with terminal alkynes, which are dominated by the formation of vinylidene bridges.[6] As a continuation of this chemistry, we describe here the reactivity toward alkynes of parent diiridium(III) tetrahydrides. Again, the reactions have been found to involve the facile formation of vinylidene compounds and intermediates whenever good migrating groups such as hydrogen or silyl are present at the alkynyl carbons. Vinylidene intermediates are also likely to mediate in the catalytic di- and trimerizations of terminal alkynes observed for these compounds.

* To whom correspondence should be addressed. E-mail: sola@unizar.es (E.S.); oro@unizar.es (L.A.O.).

(1) (a) *Catalysis by Di- and Polynuclear Metal Cluster Complexes*; Adams, R. A., Cotton, F. A., Eds.; Wiley-VCH: New York, 1998. (b) Braunstein, P.; Rosé, J. In *Metal Clusters in Chemistry*; Braunstein, P., Oro, L. A., Raithby, P. R., Eds.; Wiley-VCH: Weinheim, 1999; p 616. (c) Van der Beuken, E. K.; Feringa, B. L. *Tetrahedron* **1998**, *54*, 12985−13011.

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(6) Jiménez, M. V.; Sola, E.; Martínez, A. P.; Lahoz, F. J.; Oro, L. A. *Organometallics* **1999**, *18*, 1125−1136.

10.1021/om050044m CCC: $30.25
Publication on Web 04/20/2005

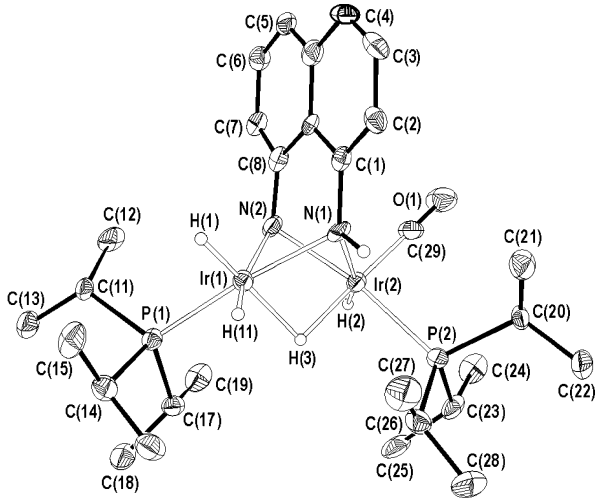


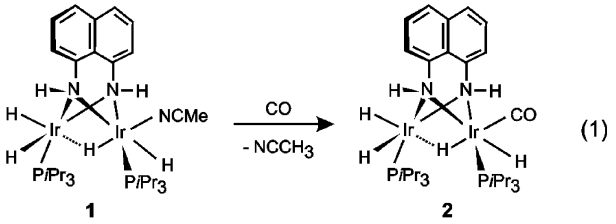
Figure 1. Molecular structure of complex **2**.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 2

Ir(1)···Ir(2)	2.7346(5)		
Ir(1)−P(1)	2.224(3)	Ir(2)−P(2)	2.301(2)
Ir(1)−N(1)	2.141(8)	Ir(2)−N(1)	2.159(8)
Ir(1)−N(2)	2.206(8)	Ir(2)−N(2)	2.118(7)
		Ir(2)−C(29)	1.853(10)
P(1)−Ir(1)−N(1)	174.2(2)	P(2)−Ir(2)−N(1)	103.6 (2)
P(1)−Ir(1)−N(2)	107.5(2)	P(2)−Ir(2)−N(2)	169.2(2)
		P(2)−Ir(2)−C(29)	93.1(3)
N(1)−Ir(1)−N(2)	72.6(3)	N(1)−Ir(2)−N(2)	74.0(3)
		N(1)−Ir(2)−C(29)	105.6(4)
		N(2)−Ir(2)−C(29)	97.7(4)

Results and Discussion

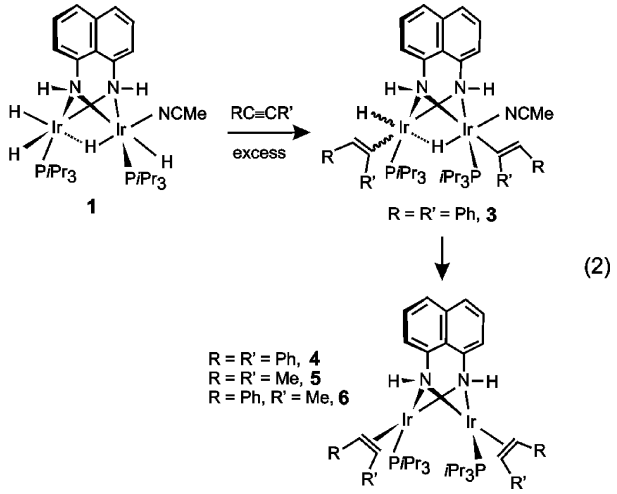
The starting compounds used in this study were the diamidonaphthalene-bridged tetrahydride Ir(III) complexes $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(\mu\text{-}H)H_3(NCMe)(P\textit{i}Pr_3)_2]$ (**1**) and $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(\mu\text{-}H)H_3(CO)(P\textit{i}Pr_3)_2]$ (**2**) (eq 1). Compound **1** was prepared in high yield by reaction of the reported mononuclear tris-acetonitrile complex[7] $[IrH_2(NCMe)_3(P\textit{i}Pr_3)]BF_4$ with a solution of dipotassium diamidonaphthalene in acetone. Complex **2** could be readily obtained from **1** after its treatment with CO. The structure of **2** determined by X-ray diffraction, with the hydride ligands at the positions calculated by the HYDEX program,[8] is shown in Figure 1. Important distances and angles of the molecule are collected in Table 1.



(1)

With regard to the solution NMR data, compounds **1** and **2** are isostructural, having most of their structural features in common with the analogous bis-pyrazolate complex $[Ir_2(\mu\text{-}Pz)_2(\mu\text{-}H)H_3(NCMe)(P\textit{i}Pr_3)_2]$.[2] The peculiar characteristics of these structures have been described in detail elsewhere[2a] and will not be discussed here. Nevertheless, it should be mentioned that, despite their structural similarity, compounds **1** and **2** can display very different reactivity as a result of the different lability of their NCMe and CO ligands. In fact, the stronger coordination of CO has been exploited in this work to obtain from **2** asymmetric versions of the symmetric compounds formed by **1**.

Reactions with Internal Alkynes. The reactions of **1** with an excess of alkynes such as diphenylacetylene, 2-butyne, or 1-phenyl-1-propyne have been found to slowly afford diiridium(I) complexes after the hydrogenation of the alkynes to alkene ligands (eq 2). These transformations have been observed by NMR to involve nonsymmetric bis-alkenyl intermediate complexes. In the case of diphenylacetylene, the relative insolubility in toluene of the corresponding intermediate, $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(\mu\text{-}H)H\{Z\text{-}C(Ph)=CHPh\}_2(NCMe)(P\textit{i}Pr_3)_2]$ (**3**), has favored its separation from the reaction mixture and subsequent characterization.



(2)

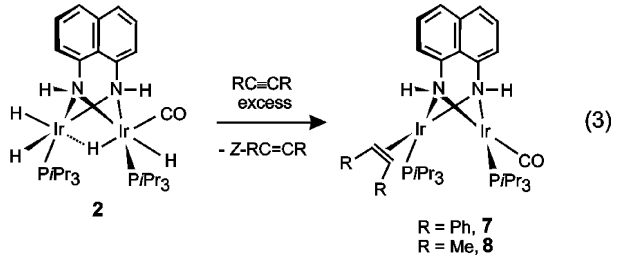
The most likely structure of **3**, depicted in eq 2, has been deduced from a number of NMR parameters. The high-field region of the ^1H NMR spectrum displays two doublets: one at δ −25.75 with a J_{HP} coupling constant of 27.6 Hz, characteristic of a terminal hydride cis to a phosphine, and another at δ −19.66, coupled to the other phosphine ligand with J_{HP} = 12.6 Hz and attributable to a bridging hydride asymmetrically located between the iridium atoms.[2] The $^{13}C\{^1H\}$ NMR signals corresponding to the C_1 and C_8 carbons of the diamidonaphthalene bridge are both doublets with J_{CP} coupling constants around 3 Hz, a characteristic pattern for a transoid arrangement of the phosphine ligands.[2a,4b] In addition, this spectrum shows two doublets corresponding to quaternary carbons at δ 138.06 and 145.60, displaying J_{CP} coupling constants of 6.9 and 6.0 Hz, respectively, and attributable to alkenyl ligand α-carbons coordinated cis relative to a phosphine. From the various possible structures still compatible with the spectroscopic data, those of eq 2, with the acetonitrile ligand trans to the bridging hydride, account better for the observed lability of this ligand, which readily exchanges with acetonitrile-d_3 at room temperature.[2,3]

The structure proposed for **3** has a close precedent in that of complex $[Ir_2(\mu\text{-}Pz)(\mu\text{-}H)H\{Z\text{-}C(Ph)=CHPh\}_2$-

(7) Sola, E.; Navarro, J.; López, J. A.; Lahoz, F. J.; Oro, L. A.; Werner, H. *Organometallics* **1999**, *18*, 3534−3546.
(8) Orpen, A. G. *J. Chem. Soc., Dalton. Trans.* **1980**, 2509−2516.

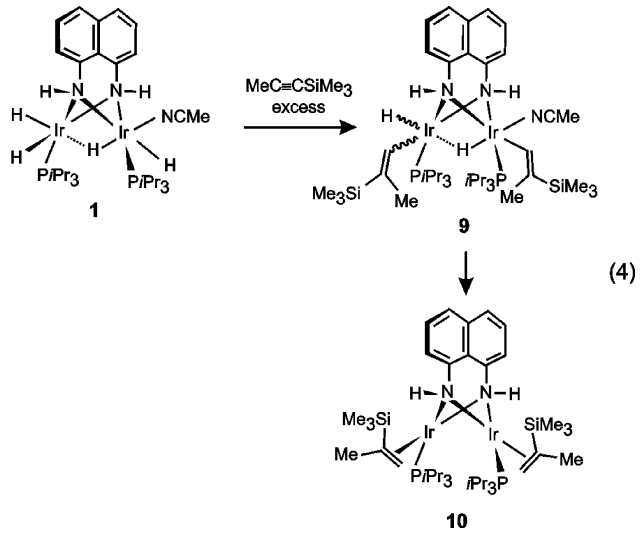
(NCMe)(P*i*Pr$_3$)$_2$], which was obtained from the bis-pyrazolate analogue of **1** after insertion of 2 equiv of diphenylacetylene.[3] Nevertheless, in contrast to the preferred evolution of this latter compound by ortho-metalation of a phenyl group, intermediate **3** has been observed to undergo two C−H reductive eliminations to form the bis-alkene complex **4**. The spectroscopic data obtained for the complexes [Ir$_2$\{μ-1,8-(NH)$_2$C$_{10}$H$_6$\}\{η^2-*Z*-CH(R)=CHR′\}$_2$(P*i*Pr$_3$)$_2$] (R, R′ = Ph, **4**; R, R′ = Me, **5**; and R = Ph, R′ = Me, **6**) are indicative of equivalent N−H protons and phosphines, hence in agreement with the proposed C_2 symmetric structures. The diagnostic J_{HH} coupling constants between the olefinic protons are in the range 6−9 Hz, therefore confirming the *Z*-stereochemistry of the alkene ligands. The structure of **5** determined by X-ray diffraction and the reactivity of this compound in the context of C−H activation has been previously communicated.[4a]

With regard to mechanistic studies on the aforementioned bis-pyrazolate analogue of **1**,[2,3] the most likely sequence of reactions leading to **4**−**6** would be initiated by an acetonitrile dissociation from complex **1** that provides a coordination vacancy for the first incoming alkyne. Under this assumption, it could be expected that replacement of this labile ligand by a stronger one, such as CO, would inhibit the reaction.[2] However, our experimental observations contradict this expectation since complex **2** has been observed to remain reactive toward 2-butyne and diphenylacetylene (eq 3). The reactions have been found to afford the diiridium(I) alkene-carbonyl complexes [Ir$_2$\{μ-1,8-(NH)$_2$C$_{10}$H$_6$\}\{η^2-*Z*-CH(R)=CHR\}(CO)(P*i*Pr$_3$)$_2$] (R = Ph, **7**; R = Me, **8**) together with 1 equiv of the corresponding *Z*-alkenes. Even though these latter hydrogenations require reaction temperatures higher than those using precursor **1**, their feasibility confirms that dissociation of a labile ligand is not the only alternative for the generation of reactive sites at this type of dinuclear tetrahydride compounds.[2]



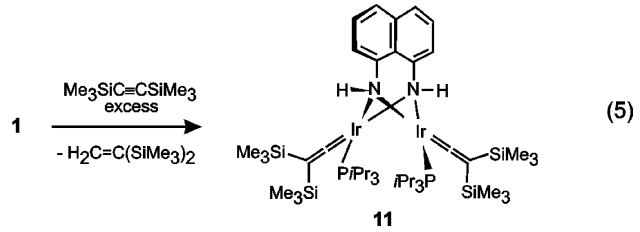
(3)

Reactions with Silyl-Substituted Alkynes. The likely sequence of coordination, insertion, and reductive elimination elementary steps that eventually affords complexes **3**−**8** seems to be altered in the presence of alkynes with silyl substituents. Actually, even though the reaction of **1** with trimethylsilyl-1-propyne has been found to reproduce the sequence in eq 2, the NMR data of the isolated intermediate [Ir$_2$\{μ-1,8-(NH)$_2$C$_{10}$H$_6$\}-(μ-H)H\{CH=C(Me)SiMe$_3$\}$_2$(NCMe)(P*i*Pr$_3$)$_2$] (**9**), and those of the final product [Ir$_2$\{μ-1,8-(NH)$_2$C$_{10}$H$_6$\}\{η^2-CH$_2$=C(Me)SiMe$_3$\}$_2$(P*i*Pr$_3$)$_2$] (**10**), are indicative of a gem arrangement of the methyl and trimethylsilyl substituents in their respective alkenyl and alkene ligands (eq 4). In light of related previous results and mechanistic studies, this would require an alkyne to vinylidene rearrangement preceding the insertion step.[9]



(4)

The occurrence of such a rearrangement is further supported by the reaction of **1** with an excess of bis-(trimethylsilyl)acetylene, which has been found to afford 2 equiv of the gem olefin H$_2$C=C(SiMe$_3$)$_2$ together with the bis-vinylidene complex [Ir$_2$\{μ-1,8-(NH)$_2$C$_{10}$H$_6$\}-\{C=C(SiMe$_3$)$_2$\}$_2$(P*i*Pr$_3$)$_2$] (**11**) (eq 5). In this case, the larger size of the alkene ligands formed after hydrogenation seems to favor their replacement by substrate excess. After this substitution, the incoming alkynes could again undergo rearrangement to vinylidene ligands, thus forming the final reaction product.



(5)

The structure of **11** determined by X-ray diffraction is shown in Figure 2, and its most significant distances and angles are given in Table 2. The two Ir=C and C=C bond lengths of this structure lie well within the range defined by the three iridium vinylidene complexes previously characterized by X-ray diffraction,[10] while deviation from linearity of the Ir=C=C moieties is only slightly larger than in these precedents. The solution NMR data of the complex also agree with a C_2 symmetric structure with terminal vinylidene ligands. A typical ^{13}C\{^{1}H\} NMR low-field signal at δ 256.26, with a J_{CP} coupling constant of 11.1 Hz, can be attributed to the equivalent vinylidene α-carbons cis to phosphine. The two β-carbons give rise to a singlet at δ 88.28.

The reactions of these silyl-substituted alkynes with the carbonyl complex **2** are also indicative of the facile

(9) Li, X.; Vogel, T.; Incarvito, C. D.; Crabtree, R. H. *Organometallics* **2005**, *24*, 62−76, and references therein.

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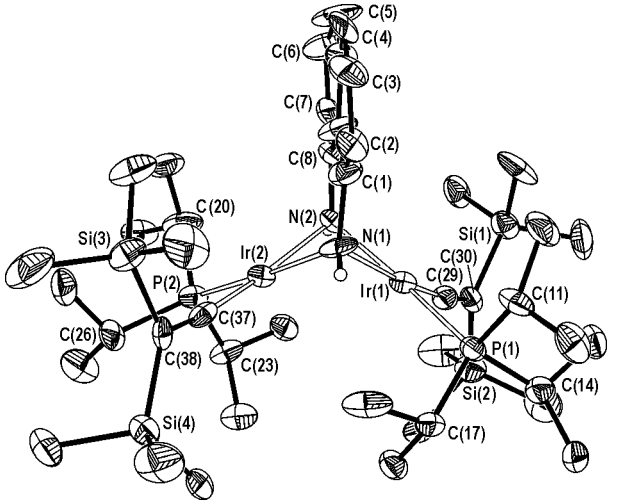
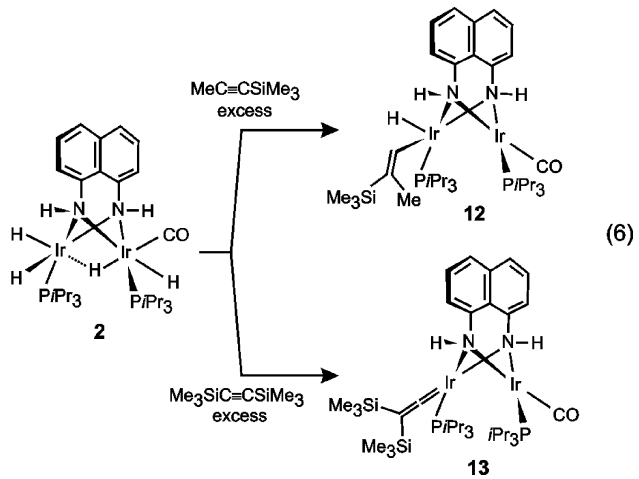


Figure 2. View of the molecular structure of complex **11**.

formation of vinylidene ligands and intermediates (eq 6). Noteworthy, the final product of the reaction between **2** and trimethylsilyl-1-propyne excess has been found to be the Ir(III)−Ir(I) alkenyl-hydride complex $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}H\{CH{=}C(Me)SiMe_3\}(CO)(P\textit{i}Pr_3)_2]$ (**12**) instead of the expected diiridium(I) alkene-carbonyl compound. Actually, **12** has been observed to remain reluctant toward the C−H reductive elimination of alkene even under prolonged heating at 373 K in alkyne excess. Nevertheless, such a reductive elimination could be readily provoked by reaction with CO or H_2, to afford the gem alkene together with either the previously reported dicarbonyl compound $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(CO)_2(P\textit{i}Pr_3)_2]$[4b] or the precursor **2**, respectively. The structural proposal for **12** in eq 6 strongly relies on the ^1H NMR signal corresponding to the hydride ligand, a ddd at very high field, δ −38.08. This signal displays a J_{HP} coupling constant of 26.4 Hz, characteristic of a terminal hydride cis to a phosphine, but shows an additional coupling to the other phosphine ligand (J_{HP} = 2.0 Hz), a common feature for hydrides and other ligands trans to metal−metal bonds or interactions.[2a,4b,5b,11] This hydride is also coupled to the vinylic proton of the cis-located alkenyl ligand with a J_{HH} coupling constant of 2.5 Hz.



(11) Oro, L. A.; Sola, E.; López, J. A.; Torres, F.; Elduque, A.; Lahoz, F. J. *Inorg. Chem. Commun.* **1998**, *1*, 64−67.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 11

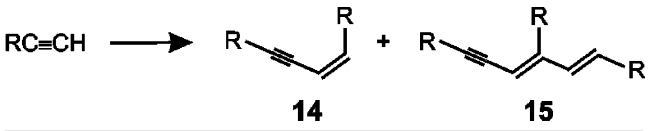
Ir(1)···Ir(2)	2.8621(5)		
Ir(1)−P(1)	2.250(2)	Ir(2)−P(2)	2.242(2)
Ir(1)−N(1)	2.114(6)	Ir(2)−N(1)	2.135(6)
Ir(1)−N(2)	2.123(6)	Ir(2)−N(2)	2.138(6)
Ir(1)−C(29)	1.805(9)	Ir(2)−C(37)	1.794(8)
C(29)−C(30)	1.334(10)	C(37)−C(38)	1.339(10)
C(30)−Si(1)	1.881(7)	C(38)−Si(3)	1.863(8)
C(30)−Si(2)	1.846(8)	C(38)−Si(4)	1.879(8)
P(1)−Ir(1)−N(1)	96.5(2)	P(2)−Ir(2)−N(1)	171.25 (17)
P(1)−Ir(1)−N(2)	169.88(17)	P(2)−Ir(2)−N(2)	98.48(18)
P(1)−Ir(1)−C(29)	95.2(2)	P(2)−Ir(2)−C(37)	93.7(2)
N(1)−Ir(1)−N(2)	73.5(2)	N(1)−Ir(2)−N(2)	72.8(2)
N(1)−Ir(1)−C(29)	168.1(3)	N(1)−Ir(2)−C(37)	95.0(3)
N(2)−Ir(1)−C(29)	94.9(3)	N(2)−Ir(2)−C(37)	166.3(3)
Ir(1)−C(29)−C(30)	172.2(6)	Ir(2)−C(37)−C(38)	170.5(7)

In contrast to the behavior of the trimethylsilyl-1-propyne, the bis(trimethylsilyl)acetylene takes the hydrogenation reaction to completion by affording 2 equiv of the gem alkene and the asymmetric vinylidene-carbonyl compound $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}\{C{=}C(SiMe_3)_2\}(CO)(P\textit{i}Pr_3)_2]$ (**13**) (eq 6). The presence of a terminal vinylidene in **13** could again be inferred from the $^{13}C\{^1H\}$ NMR spectrum, which displays a doublet at δ 255.08 (J_{CP} = 11.0 Hz) and a singlet at δ 88.82 corresponding to the α- and β-carbons of this ligand, respectively.

Reactions with Terminal Alkynes. Taking into account the precedent reactions and the often similar migrating capabilities of SiR_3 and H groups,[12] the reactions of terminal alkynes with complexes **1** and **2** are also expected to involve facile alkyne to vinylidene rearrangements. Unfortunately, these reactions have been found to be rather unselective, affording mixtures of various metallic species and several organic compounds. During the analysis of these product mixtures, we observed the systematic appearance of products of alkyne di- and trimerization, which suggested these diiridium complexes to be potential catalysts for alkyne couplings. In fact, compounds **1** and **2** have been found to be rather slow and unselective catalysts, although better results have been obtained by using the diiridium(I) alkene complexes **4**−**6** or the bis-vinylidene derivative **11** as catalyst precursors. Illustrative results of these catalytic reactions are given in Table 3. The reactions have proved to be very regio- and stereoselective, giving only the butenyne dimers of head-to-head coupling with *Z*-stereochemistry and a single isomer for the hexadienyne trimers. In contrast, good chemoselectivity toward dimerization products has been obtained only for silyl-substituted terminal alkynes. The NMR observations on the catalytic solutions have shown that precursor complexes remain the only detectable iridium compounds during catalysis. This suggests that these catalytic processes do not require dissociation of the alkene or vinylidene ligands present at the precursors, an observation that also accounts for the precursor-dependent selectivity of the various reactions with phenylacetylene (Table 3).

(12) See for example: (a) Huang, D.; Folting, K.; Caulton, K. G. *J. Am. Chem. Soc.* **1999**, *121*, 10318−10322. (b) Werner, H.; Baum, M.; Schneider, D.; Windmüller, B. *Organometallics* **1994**, *13*, 1089−1097. (c) Edelbach, B. L.; Lachicotte, R. L.; Jones, W. D. *Organometallics* **1999**, *18*, 4660−4668. (d) Braunstein, P.; Knorr, M.; Reinhard, G.; Schubert, U.; Stährfeldt, T. *Chem. Eur. J.* **2000**, *6*, 4265−4278. (e) Brookhart, M.; Grant, B. E. *J. Am. Chem. Soc.* **1993**, *115*, 2151−2156.

Table 3. Catalytic 1-Alkyne Coupling Reactions[a]



14 **15**

catalyst	R	*T* (K)	time (h)	conversion (%)	product distribution **14**	**15**
4	Ph	323	12	96	20	80
5	Ph	323	24	90	45	55
6	Ph	323	20	85	50	50
11	Ph	323	48	65	48	52
5	Ph	363	24	100	27	73
5	*t*Bu	333	12	100	46	54
5	$SiMe_3$	313	12	100	100	
5	$SiEt_3$	313	12	100	100	

[a] Conditions: catalyst (0.02 mmol), alkyne (1 mmol), solvent: toluene (4 mL).

Catalytic C−C couplings such as those in Table 3 are relatively common in the chemistry of rhodium and ruthenium,[13,14] but remain rare with iridium catalysts.[15] Taking into account that, at least for *Z*-enyne coupling products, these reactions are assumed to involve vinylidene intermediates,[14] this fact could correlate with the abundance of rhodium and ruthenium vinylidene compounds and their scarcity in iridium chemistry.[10,16] In this context, the unusual facility with which vinylidenes have been observed to form in our dinuclear systems could be tentatively attributed to the recognized effectiveness of bimetallic mechanisms for alkyne to vinylidene tautomerizations.[17] Hence, the intermetallic cooperation favoring vinylidene formation could be regarded as ultimately responsible for the feasibility of these iridium-catalyzed C−C forming reactions.

Experimental Section

Equipment. Infrared spectra were recorded in toluene solution in KBr cells or as Nujol mulls on polyethylene sheets using a Nicolet 550 spectrometer. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. NMR spectra were recorded on Varian Gemini 2000 and a Bruker Avance 300 MHz spectrometers. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR chemical shifts were measured relative to partially deuterated solvent peaks but are reported in ppm relative to tetramethylsilane. ^{31}P (121 MHz) NMR chemical shifts were measured relative to H_3PO_4 (85%). Coupling constants (*J*) are given in hertz. Generally, spectral assignments were achieved by ^{1}H COSY, NOESY, 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 a Cs^+ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used as the matrix.

Synthesis. All experiments were carried out under argon by using standard Schlenk techniques. Solvents were dried by known procedures and distilled under argon prior to use.[18] The precursor mononuclear complex $[IrH_2(NCMe)_3(PiPr_3)]BF_4$ was prepared by a reported method.[7] The synthesis and characterization data of complexes **4** and **5** have been previously reported.[4a] Alkynes were obtained from common commercial sources and distilled prior to use. Commercial 1,8-diaminonaphthalene was recrystallized from hot hexane before use. All new compounds described below are air sensitive in solution.

Preparation of $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(\mu\text{-}H)H_3(NCMe)(PiPr_3)_2]$ (1). A solution of 1,8-diaminonaphthalene (140 mg, 0.89 mmol) in acetone (5 mL) was treated with 1.78 equiv of a concentrated solution of KOH in methanol and then added to a solution of $[IrH_2(NCMe)_3(PiPr_3)]BF_4$ (1.0 g, 1.77 mmol) in acetone. The mixture was stirred for 30 min, and the solid formed was removed by filtration through Celite. The resulting solution was concentrated to ca. 2 mL and treated with 10 mL of methanol. The pale gray solid formed was decanted, washed with methanol, and dried in vacuo: yield 497 mg (62%). Anal. Calcd for $C_{30}H_{57}N_3Ir_2P_2$: C, 39.76; H, 6.34; N, 4.64. Found: C, 39.64; H, 6.62; N, 4.70. MS (FAB+, *m/z* (%)) 864 (100) [M^+ − NCMe]. IR (cm^{-1}): 3361, 3353 ν(NH), 2173, 2124, 2098 ν(IrH), 1801 ν(IrHIr). ^{1}H NMR (C_6D_6, 293 K): δ −23.15 (dd, J_{HP} = 21.3, J_{HH} = 8.7, 1H, IrH), −22.18 (ddd, J_{HP} = 24.9, 2.1, J_{HH} = 8.7, 1H, IrH), −20.36 (dd, J_{HP} = 20.4, J_{HH} = 3.6, 1H, IrH), −19.93 (ddd, J_{HP} = 12.9, 2.1, J_{HH} = 3.6, 1H, IrH), 0.20 (s, 3H, $NCCH_3$), 1.15 (dd, J_{HP} = 13.5, J_{HH} = 7.5, 18H, $PCHC\mathit{H}_3$), 1.21 (dd, J_{HP} = 12.9, J_{HH} = 7.2, 9H, $PCHC\mathit{H}_3$), 1.23 (dd, J_{HP} = 13.2, J_{HH} = 7.2, 9H, $PCHC\mathit{H}_3$), 2.03, 2.08 (both m, 3H each, $PC\mathit{H}CH_3$), 4.22 (br, 2H, NH), 6.86 (d, J_{HH} = 7.2, 1H, CH), 6.91 (d, J_{HH} = 6.9, 1H, CH), 7.01 (dd, J_{HH} = 8.4, 7.2, 1H, CH), 7.04 (dd, J_{HH} = 8.4, 6.9, 1H, CH), 7.32 (m, 2H, CH). ^{31}P{^{1}H} NMR (C_6D_6, 293 K): δ 39.12, 29.72 (both s). ^{13}C{^{1}H} NMR (C_6D_6, 293 K): δ −0.18 (s, $NC\mathit{C}H_3$), 19.39, 19.68, 19.96, 20.69 (all s, $PCH\mathit{C}H_3$), 26.70 (d, J_{CP} = 29.0, $P\mathit{C}HCH_3$), 27.93 (d, J_{CP} = 29.4, $P\mathit{C}HCH_3$) 108.15 (d, J_{CP} = 4.1, CH), 108.33 (d, J_{CP} = 3.7, CH), 114.36 (br, $N\mathit{C}CH_3$), 116.13, 116.34 (both s, CH), 123.93 (s, C), 127.07, 127.53 (both s, CH), 137.16 (s, C), 156.15 (d, J_{CP} = 2.3, C), 156.49 (d, J_{CP} = 1.4, C).

Preparation of $[Ir_2\{\mu\text{-}1,8\text{-}(NH)_2C_{10}H_6\}(\mu\text{-}H)H_3(CO)(PiPr_3)_2]$ (2). A solution of **1** (300 mg, 0.33 mmol) in toluene (5 mL) was placed under CO atmosphere (1 bar) and allowed to react during 10 min at room temperature. The resulting suspension was concentrated to ca. 0.5 mL and treated with methanol (5 mL). The white solid was separated by decantation, washed with methanol, and dried in vacuo: yield 260 mg (88%). Anal. Calcd for $C_{29}H_{54}Ir_2N_2OP_2$: C, 39.00; H, 6.09; N, 3.14. Found: C, 39.41; H, 6.12; N, 3.35. MS (FAB+, *m/z* (%)): 893 (80) [M^+], 865 (100) [M^+ − CO]. IR (cm^{-1}): 3364, 3350 ν(NH), 2146 ν(IrH), 2000 ν(CO). ^{1}H NMR (C_6D_6, 293 K): δ −23.75 (dd, J_{HP} = 21.6, J_{HH} = 7.9, 1H, IrH), −19.50 (dddd, J_{HP} = 23.4, 3.1, J_{HH} = 7.9, 4.2, 1H, IrH), −17.36 (d, J_{HP} = 16.2, 1H, IrH), −11.36 (ddd, 1H, J_{HP} = 7.2, 4.2, J_{HH} 4.2, 1H, IrHIr), 1.15 (dd, J_{HP} = 13.2, J_{HH} = 7.2, 18H, $PCHC\mathit{H}_3$), 1.28 (dd, J_{HP} = 14.7, J_{HH} = 7.5, 9H, $PCHC\mathit{H}_3$), 1.29 (dd, J_{HP} = 14.4, J_{HH} = 7.5, 9H, $PCHC\mathit{H}_3$), 2.00, 2.36 (both m, 3H each, $PC\mathit{H}CH_3$), 4.07 (br, 2H, NH), 6.89−7.04 (m, 2H, CH), 7.34 (d, J_{HH} = 7.8, 2H, CH), 7.35 (d, J_{HH} = 8.1, 2H, CH). ^{31}P{^{1}H} NMR (C_6D_6, 293 K): δ 38.07, 24.01 (both s). ^{13}C{^{1}H} NMR (C_6D_6, 293 K): δ 19.92 (d, J_{CP} = 5.4, $PCH\mathit{C}H_3$), 19.99, 20.17, 20.97 (all s, $PCH\mathit{C}H_3$), 28.22 (d, J_{CP} = 30.9, $P\mathit{C}HCH_3$), 28.25 (d, J_{CP} = 30.4, $P\mathit{C}HCH_3$), 107.08, 107.32 (both d, J_{CP} = 3.6, CH),

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118.66, 118.93 (both s, CH), 123.32 (s, C), 127.23, 127.48 (both s, CH), 137.41 (s, C), 156.98 (d, J_{CP} = 3.2, C), 157.68 (d, J_{CP} = 1.8, C), 168.23 (d, J_{CP} = 7.4, CO).

Preparation of [Ir$_2$\{μ-1,8-(NH)$_2$C$_{10}$H$_6$\}(μ-H)H\{*Z*-C(Ph)=CHPh\}$_2$(NCMe)(P*i*Pr$_3$)$_2$] (3). A solution of **1** (200 mg, 0.22 mmol) in toluene (8 mL) at 263 K was treated with diphenylacetylene (81 mg, 0.45 mmol). After 12 h of reaction, the yellow solid formed was separated by decantation, washed with small amounts of acetone, and dried in vacuo: yield 110 mg (41%). Anal. Calcd for $C_{58}H_{77}Ir_2N_3P_2$: C, 55.17; H, 6.15; N, 3.33. Found: C, 55.09; H, 5.87; N, 3.12. IR (Nujol, cm^{-1}): 3353 ν(NH), 1828 ν(IrHIr), 1595, 1568 ν(C=C). ^{1}H NMR (CD_2Cl_2, 293 K): δ −25.75 (d, J_{HP} = 27.6, 1H, IrH), −19.66 (d, J_{HP} = 12.6, 1H, IrHIr), 0.79 (s, 3H, NCC*H*$_3$), 1.26 (dd, J_{HP} = 11.1, J_{HH} = 7.2, 18H, PCHC*H*$_3$), 1.29 (dd, J_{HP} = 12.8, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 1.31 (dd, J_{HP} = 12.9, J_{HH} = 6.9, 9H, PCHC*H*$_3$), 2.47, 2.62 (both m, 3H each, PC*H*CH$_3$, 3.09, 3.59 (both br, 1H each, NH), 5.68 (d, J_{HH} = 7.5, 1H, CH), 6.61 (d, J_{HP} = 7.2, 1H, CH), 6.38−7.31 (25H, CH), 7.50 (d, J_{HH} = 8.1, 1H, CH). ^{31}P\{^{1}H\} NMR (CD_2Cl_2, 293 K): δ 7.31, 18.77 (both s). ^{13}C\{^{1}H\} NMR (CD_2Cl_2, 293 K): δ 0.74 (s, NC*C*H$_3$), 19.48, 19.89, 20.00, 20.12 (all s, PCH*C*H$_3$), 24.84 (d, J_{CP} = 27.6, P*C*HCH$_3$), 25.74 (d, J_{CP} = 27.2, P*C*HCH$_3$), 108.94 (d, J_{CP} = 3.7, CH), 109.24 (d, J_{CP} = 3.7 Hz, CH), 115.10 (s, CN), 117.15, 117.59, 122.71, 123.03 (all s, CH), 123.46 (s, C), 123.46−130.00 (CH), 135.66 (s, C), 136.09 (s, CH), 138.06 (d, J_{CP} = 6.9, C), 140.88 (s, CH), 143.21, 142.37 (both s, C), 145.60 (d, J_{CP} = 6.0, C), 152.54 (s, C), 153.45 (d, J_{CP} = 3.2, C), 153.69 (d, J_{CP} = 2.8, C), 154.82 (s, C).

Preparation of [Ir$_2$\{μ-1,8-(NH)$_2$C$_{10}$H$_6$\}\{η^2-*Z*-CH(Me)=CHPh\}$_2$(P*i*Pr$_3$)$_2$] (6). A solution of **1** (100 mg, 0.11 mmol) in toluene (10 mL) was treated with 1-phenyl-1-propyne (27.6 μL, 0.22 mmol) and stirred for 8 h at 293 K. The red solid formed after concentration of the solution to ca. 2 mL was separated by decantation, washed with methanol, and dried in vacuo: yield 171 mg (71%). Anal. Calcd for $C_{46}H_{70}Ir_2N_2P_2$: C, 50.34; H, 6.43; N, 2.55. Found: C, 50.31; H, 5.99; N, 2.58. IR (Nujol, cm^{-1}): 3325 ν(NH), 1568 ν(C=C). ^{1}H NMR (C_6D_6, 293 K): δ 1.02 (d, J_{HH} = 6.6, 6H, CH$_3$), 1.06, 1.18 (both dd, J_{HP} = 12.0, J_{HH} = 7.2, 18H each, PCHC*H*$_3$), 1.38 (m, 6H, PC*H*CH$_3$), 3.13 (d, J_{HH} = 8.1, 2H, =CHPh), 3.22 (dqd, J_{HH} = 8.1, 6.6, J_{HP} = 2.0, 2H, =C*H*(CH$_3$)), 5.01 (br, 2H, NH), 7.15−7.27 (10H, CH), 7.47 (d, J_{HH} = 7.8, 2H, CH), 7.62 (m, 4H, CH). ^{31}P\{^{1}H\} NMR (C_6D_6, 293 K): δ 11.66 (s). ^{13}C\{^{1}H\} NMR (C_6D_6, 293 K): δ 17.07 (s, CH$_3$), 20.02, 20.27 (both s, PCH*C*H$_3$), 22.86 (d, J_{CP} = 26.7, P*C*HCH$_3$), 31.99, 40.43 (both s, =CH), 107.91 (d, J_{CP} = 2.8, CH), 118.87, 122.79 (both s, CH), 125.64 (s, C), 127.30, 128.43, 131.84 (all s, CH), 136.04, 146.76 (both s, C), 153.15 (d, J_{CP} = 4.2, C).

Preparation of [Ir$_2$\{μ-1,8-(NH)$_2$C$_{10}$H$_6$\}\{η^2-*Z*-CH(Ph)=CHPh\}(CO)(P*i*Pr$_3$)$_2$] (7). A suspension of **2** (125 mg, 0.14 mmol) in toluene (5 mL) was treated with diphenylacetylene (50 mg, 0.28 mmol) and stirred for 48 h at 323 K. The resulting red solution was concentrated to ca. 0.5 mL, and methanol (3 mL) was added to give a red solid. The solid was separated by decantation, washed with methanol, and dried in vacuo: yield 93 mg (62%). Anal. Calcd for $C_{43}H_{62}Ir_2N_2OP_2$: C, 48.30; H, 5.84; N, 2.62. Found: C, 48.68; H, 6.29; N, 2.56. IR (toluene, cm^{-1}): 1931 ν(CO). ^{1}H NMR (C_6D_6, 293 K): δ 0.95 (dd, J_{HP} = 13.5, J_{HH} = 7.5, 9H, PCHC*H*$_3$), 1.01 (dd, J_{HP} = 13.8, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 1.25 (dd, J_{HP} = 12.6, J_{HH} = 6.9, 9H, PCHC*H*$_3$), 1.40 (dd, J_{HP} = 12.0, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 1.57, 2.07 (both m, 3H each, PC*H*CH$_3$), 3.56 (d, J_{HH} = 9.0, 1H, =CH), 3.61 (br, 1H, NH), 4.57 (dd, J_{HH} = 9.0, J_{HP} = 9.3, 1H, =CH), 6.34 (br, 1H, NH), 6.59 (d, J_{HH} = 7.2, 1H, CH), 6.80 (d, J_{HH} = 7.5, 1H, CH), 6.84 (d, J_{HH} = 7.2, 1H, CH), 6.93 (dd, J_{HH} = 7.5, 7.2, 1H, CH), 7.02−7.59 (12H, CH). ^{31}P\{^{1}H\} NMR (C_6D_6, 293 K): δ 10.91, 41.71 (both s). ^{13}C\{^{1}H\} NMR (C_6D_6, 293 K): δ 19.42, 19.62, 20.49 (all s, PCH*C*H$_3$), 22.07 (d, J_{CP} = 26.7, P*C*HCH$_3$), 25.98 (d, J_{CP} = 29.5, P*C*HCH$_3$), 31.45 (s, =CH), 40.42 (d, J_{CP} = 3.6, =CH), 108.20 (d, J_{CP} = 2.8, CH), 108.57 (d, J_{CP} = 3.2, CH), 119.22, 119.28 (both s, CH), 122.79 (s, CH), 123.06 (s, C), 124.92, 127.10, 127.37, 127.50, 128.52, 129.42, 130.40 (all s, CH), 135.89, 141.64, 146.11 (all s, C), 150.12, 151.94 (both d, J_{CP} = 3.7, C), 180.81 (d, J_{CP} = 11.9, CO).

Preparation of [Ir$_2$\{μ-1,8-(NH)$_2$C$_{10}$H$_6$\}\{η^2-*Z*-CH(Me)=CHMe\}(CO)(P*i*Pr$_3$)$_2$] (8). A suspension of **2** (125 mg, 0.14 mmol) in toluene (5 mL) was treated with 2-butyne (17.2 μL, 0.28 mmol) and stirred for 24 h at 323 K. The resulting red solution was evaporated to dryness to give a red solid: yield 90 mg (68%). Anal. Calcd for $C_{33}H_{58}Ir_2N_2OP_2$: C, 41.93; H, 6.18; N, 2.96. Found: C, 41.58; H, 6.45; N, 2.66. IR (toluene, cm^{-1}): 1931 ν(CO). ^{1}H NMR (C_6D_6, 293 K): δ 1.03 (dd, J_{HP} = 13.5, J_{HH} = 7.5, 9H, PCHC*H*$_3$), 1.12 (dd, J_{HP} = 12.3, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 1.12 (d, J_{HH} = 6.9, 3H, CH$_3$), 1.21 (dd, J_{HP} = 13.5, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 1.22 (d, J_{HH} = 6.3, 3H, CH$_3$), 1.42 (dd, J_{HP} = 12.3, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 1.92, 2.15 (both m, 3H each, PC*H*CH$_3$), 2.34 (dq, J_{HH} = 6.9, 6.9, 1H, =CH), 2.34 (dqd, J_{HH} = 6.9, 6.3, J_{HP} = 7.2, 1H, =CH), 3.84, 5.97 (both br, 1H each, NH), 6.63 (d, J_{HH} = 7.2, 1H, CH), 6.75 (d, J_{HH} = 7.5, 1H, CH), 7.10 (dd, J_{HH} = 7.5, 7.2, 1H, CH), 7.15 (dd, J_{HH} = 8.4, 8.1, 1H, CH), 7.41 (d, J_{HH} = 8.1, 1H, CH), 7.46 (d, J_{HH} = 8.4, 1H, CH). ^{31}P\{^{1}H\} NMR (C_6D_6, 293 K): δ 13.88, 39.84 (both s). ^{13}C\{^{1}H\} NMR (C_6D_6, 293 K): δ 12.70, 14.70 (both s, CH$_3$), 19.67, 19.80, 19.89, 20.18 (all s, P*C*HCH$_3$), 22.29 (d, J_{CP} = 26.9, P*C*HCH$_3$), 26.61 (d, J_{CP} = 29.2, P*C*HCH$_3$), 28.32 (s, =CH), 39.69 (d, J_{CP} = 2.1, =CH), 108.07 (d, J_{CP} = 3.0, CH), 108.42 (d, J_{CP} = 2.3, CH), 118.86, 119.10 (both s, CH), 122.52 (s, C), 125.64, 126.83 (both s, CH), 135.62 (s, C), 151.01, 152.01 (both d, J_{CP} = 3.8, C), 180.69 (d, J_{CP} = 12.7, CO).

Preparation of [Ir$_2$\{μ-1,8-(NH)$_2$C$_{10}$H$_6$\}(μ-H)H\{CH=C(Me)SiMe$_3$\}$_2$(NCMe)(P*i*Pr$_3$)$_2$] (9). A solution of **1** (100 mg, 0.11 mmol) in toluene (5 mL) was treated with 1-trimethylsilyl-1-propyne (32.6 μL, 0.22 mmol) and stirred for 10 h at room temperature. The resulting white solution was taken to dryness and the residue treated with pentane to give a white solid. The solid was separated by decantation, washed with pentane, and dried in vacuo: yield 126 mg (51%). Anal. Calcd for $C_{42}H_{81}Ir_2N_3P_2Si_2$: C, 44.61; H, 7.22; N, 3.72. Found: C, 44.28; H, 7.16; N, 3.25. IR (Nujol, cm^{-1}): 3338, 3317 ν(NH), 2232 ν(IrH), 1817 ν(IrHIr). ^{1}H NMR (CD_2Cl_2, 293 K): δ −22.71 (d, J_{HP} = 25.8, 1H, IrH), −19.80 (d, J_{HP} = 11.1, 1H, IrHIr), −0.11 (br, 3H, NCCH$_3$), −0.10, −0.07 (both s, 9H each, SiCH$_3$), 1.05 (dd, J_{HP} = 12.9, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 1.14 (dd, J_{HP} = 12.6, J_{HH} = 8.4, 9H, PCHC*H*$_3$), 1.21 (dd, J_{HP} = 12.6, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 1.22 (dd, J_{HP} = 12.6, J_{HP} = 6.9, 9H, PCHC*H*$_3$), 1.68, 1.71 (both d, J_{HH} = 0.9, 3H each, CH$_3$), 2.03, 2.29 (both m, 3H each, PC*H*CH$_3$), 3.27, 3.42 (both br, 1H each, NH), 6.77 (d, J_{HH} = 7.5, 2H, CH), 6.98 (dd, J_{HH} = 8.1, 7.5, 2H, CH), 7.23, 7.24 (both d, J_{HH} = 8.1, 1H each, CH), 8.41, 9.11 (both m, 1H each, =CH). The ^{1}H NOESY spectrum shows NOE effects between the signals at δ −0.10, −0.07 and the multiplets at δ 8.41, 9.11, respectively. ^{31}P\{^{1}H\} NMR (CD_2Cl_2, 293 K): δ 12.03, 26.34 (both s). ^{13}C\{^{1}H\} NMR (C_6D_6, 293 K): δ −0.62, −0.42 (both s, SiCH$_3$), 1.10 (s, NC*C*H$_3$), 19.14, 19.28, 19.32, 19.51 (all s, PC*H*C*H*$_3$), 23.12, 23.95 (both s, CH$_3$), 24.91 (d, J_{CP} = 28.3, P*C*HCH$_3$), 25.18 (d, J_{CP} = 27.4, P*C*HCH$_3$), 108.50 (d, J_{CP} = 4.4, CH), 108.70 (d, J_{CP} = 3.8, CH), 113.77 (s, =C), 116.85, 117.24, 121.56 (all s, CH), 121.98 (d, J_{CP} = 7.8, =CH), 124.01 (s, C), 126.94 (s, CH), 136.38, 136.90 (both s, C and =C), 143.47 (d, J_{CP} = 7.4, =CH), 155.08 (d, J_{CP} = 3.2, C), 156.09 (d, J_{CP} = 2.3, C).

[Ir$_2$\{μ-1,8-(NH)$_2$C$_{10}$H$_6$\}\{η^2-CH$_2$=C(Me)SiMe$_3$\}$_2$(P*i*Pr$_3$)$_2$] (10). A solution of **9** (100 mg, 0.088 mmol) in toluene was heated at 333 K for 24 h, filtered through an alumina column, and taken to dryness. The resulting red oil was dissolved in hexane and stored at 233 K during several days to give a red solid. The solid was separated by decantation and dried in vacuo: yield 46 mg (48%). Anal. Calcd for $C_{40}H_{78}Ir_2N_2P_2$: C, 44.09; H, 7.21; N, 2.57. Found: C, 43.98; H, 7.15; N, 2.62. IR (Nujol, cm^{-1}): 3325 ν(NH), 1568 ν(C=C). ^{1}H NMR (C_6D_6, 293 K): δ 0.10 (s, 18H, SiCH$_3$), 1.21 (dd, J_{HP} = 13.8, J_{HH} = 8.1,

18H, PCHC*H*$_3$), 1.28 (d, J_{HH} = 5.7, 6H, CH$_3$), 1.36 (dd, J_{HP} = 12.3, J_{HH} = 7.2, 18H, PCHC*H*$_3$), 2.00 (m, 6H, PC*H*CH$_3$), 2.22 (m, 2H, =CH$_2$), 2.95 (m, 2H, =CH$_2$), 4.59 (br, 2H, NH), 6.64 (d, J_{HH} = 7.2, 2H, CH), 7.12 (dd, J_{HH} = 8.1, 7.2, 2H, CH), 7.41 (d, J_{HH} = 8.1, 2H, CH). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 293 K): δ 15.86 (s). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 293 K): δ 1.77 (s, SiCH$_3$), 19.41, 19.88 (both s, PCH*C*H$_3$), 20.22 (s, CH$_3$), 22.92 (d, J_{CP} = 26.7, P*C*HCH$_3$), 29.62 (s, =CH$_2$), 29.92 (s, =C), 108.26 (d, J_{CP} = 2.9, CH), 122.38 (s, C), 125.64, 129.28 (both s, CH), 135.67 (s, C), 151.91 (d, J_{CP} = 4.1, C).

Preparation of [Ir$_2$\{μ-1,8-(NH)$_2$C$_{10}$H$_6$\}\{C=C(SiMe$_3$)$_2$\}$_2$-(P*i*Pr$_3$)$_2$] (11). A solution of **1** (160 mg, 0.17 mmol) in toluene (10 mL) was treated with bis(trimethylsilyl)acetylene (160 μL, 0.68 mmol) and stirred for 48 h at 323 K. The resulting purple solution was concentrated to ca. 1 mL and treated with diethyl ether to give a purple solid. The solid was separated by decantation, washed with diethyl ether, and dried in vacuo: yield 121 mg (62%). Anal. Calcd for C$_{44}$H$_{86}$Ir$_2$N$_2$P$_2$Si$_4$: C, 46.97; H, 7.21; N, 2.33. Found: C, 46.23; H, 7.34; N, 2.47. IR (cm^{-1}): 3356, 3339 ν(NH). ^{1}H NMR (C$_6$D$_6$, 293 K): δ 0.12 (s, 18H, SiCH$_3$), 0.29 (s, 18H, SiCH$_3$), 1.27, 1.29 (both dd, J_{HP} = 13.5, J_{HH} = 6.9, 18H each, PCHC*H*$_3$), 2.39 (m, 6H, PC*H*CH$_3$), 4.68 (br, 2H, NH), 6.89 (d, J_{HH} = 7.2, 2H, CH), 7.09 (dd, J_{HH} = 7.2, 8.1, 2H, CH), 7.36 (d, J_{HH} = 8.1, 2H, CH). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 293 K): δ 29.97 (s). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 293 K): δ 2.36, 2.51 (both s, SiCH$_3$), 19.83, 20.96 (both s, PCH*C*H$_3$), 26.11 (d, J_{CP} = 28.5, P*C*HCH$_3$), 88.28 (s, Ir=C=*C*), 108.60, 119.25 (both s, CH), 121.62 (s, C), 126.88 (s, CH), 135.82 (s, C), 152.21 (d, J_{CP} = 3.6, C), 256.26 (d, J_{CP} = 11.1, Ir=*C*=C).

Preparation of [Ir$_2$\{μ-1,8-(NH)$_2$C$_{10}$H$_6$\}H\{CH=C(Me)-SiMe$_3$\}(CO)(P*i*Pr$_3$)$_2$] (12). A solution of **2** (100 mg, 0.11 mmol) in toluene (10 mL) was treated with 1-trimethylsilyl-1-propyne (0.22 mmol, 33.2 μL) and stirred for 24 h at 343 K. The resulting red solution was concentrated to ca. 0.5 mL, and hexane was added to give a red solid. The solid was separated by decantation, washed with hexane, and dried in vacuo: yield 79 mg (72%). Anal. Calcd for C$_{35}$H$_{64}$Ir$_2$N$_2$OP$_2$Si: C, 41.90; H, 6.43; N, 2.79. Found; C, 41.53; H, 6.29; N, 2.48. IR (toluene, cm^{-1}): 1942 ν(CO). ^{1}H NMR (C$_6$D$_6$, 293 K): δ −38.08 (ddd, J_{HP} = 26.4, 2.0, J_{HH} = 2.5, 1H, IrH), 0.37 (s, 9H, SiCH$_3$), 1.02 (dd, J_{HP} = 14.1, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 1.10 (dd, J_{HP} = 13.5, J_{HH} = 6.3, 9H, PCHC*H*$_3$), 1.18 (dd, J_{HP} = 13.2, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 1.19 (dd, J_{HP} = 13.5, J_{HH} = 7.5, 9H, PCHC*H*$_3$), 2.07 (m, 3H, PC*H*CH$_3$), 2.11 (m, 3H, CH$_3$), 2.18 (m, 3H, PC*H*CH$_3$), 4.70, 5.26 (both br, 1H each, NH), 6.80 (d, J_{HH} = 7.5, 1H, CH), 6.98 (d, J_{HH} = 6.9, 1H, CH), 7.14 (m, 2H, CH), 7.49, 7.54 (both d, J_{HH} = 8.4, 1H each, CH), 9.27 (m, 1H, =CH). The ^{1}H NOESY spectrum shows a NOE effect between the signal at δ 0.37 and that at δ 9.27. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 293 K): δ 27.75, 38.38 (both s). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 293 K): δ −2.36 (s, SiCH$_3$), −0.84 (s, CH$_3$), 19.14, 19.44, 19.55, 19.79 (all s, PCH*C*H$_3$), 24.77 (d, J_{CP} = 29.2, P*C*HCH$_3$), 24.86 (d, J_{CP} = 29.4, P*C*HCH$_3$), 107.89, 108.24 (both d, J_{CP} = 3.2, CH), 118.83, 119.73 (both s, CH), 124.60 (s, C), 126.93, 127.27 (both s, CH), 136.13, 137.65 (both s, =C and C), 147.09 (d, J_{CP} = 8.0, =CH), 151.11, 152.53 (both d, J_{CP} = 3.2, C), 179.90 (d, J_{CP} = 10.4, CO).

Preparation of [Ir$_2$\{μ-1,8-(NH)$_2$C$_{10}$H$_6$\}\{C=C(SiMe$_3$)$_2$\}-(CO)(P*i*Pr$_3$)$_2$] (13). A suspension of **2** (100 mg, 0.11 mmol) in toluene (5 mL) was treated with bis(trimethylsilyl)acetylene (76.12 μL, 0.33 mmol) and reacted for 48 h at 343 K. The resulting red solution was concentrated to ca. 0.5 mL, and methanol was added to provoke the precipitation of a red solid. The solid was separated by decantation, washed with methanol, and dried in vacuo: yield 52 mg (45%). Anal. Calcd for C$_{37}$H$_{68}$Ir$_2$N$_2$OP$_2$Si$_2$: C, 41.94; H, 6.47; N, 2.64. Found: C, 41.67; H, 6.47; N, 2.31. IR (toluene, cm^{-1}): 1931 ν(CO). ^{1}H NMR (C$_6$D$_6$, 293 K): δ 0.28, 0.30 (both s, SiCH$_3$), 1.10 (dd, J_{HP} = 13.8, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 1.24 (m, 27H, PCHC*H*$_3$), 2.27 (m, 6H, PC*H*CH$_3$), 4.65, 4.80 (both br, 1H each, NH), 6.55 (d, J_{HH} = 7.2, 1H, CH), 6.96 (m, 2H, CH), 7.14 (dd, 1H, J_{HH} = 8.1, 7.2, CH), 7.35 (d, J_{HH} = 8.4, 1H, CH), 7.44 (d, J_{HH} = 8.1, 1H, CH). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 293 K): δ 30.34, 38.24 (both s). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 293 K): δ 2.32, 1.91 (both s, SiCH$_3$), 19.16, 19.48, 19.79, 20.51 (all s, PCH*C*H$_3$), 25.64 (d, J_{CP} = 29.5, P*C*HCH$_3$), 25.86 (d, J_{CP} = 29.0, P*C*HCH$_3$), 88.82 (s, Ir=C=*C*), 108.32, 108.98 (both d, J_{CP} = 3.2, CH), 119.36, 119.70 (both s, CH), 121.56 (s, C), 126.77, 127.43 (both s, CH), 135.75 (s, C), 151.02 (d, J_{CP} = 3.2, C), 151.33 (d, J_{CP} = 3.7, C), 180.52 (d, J_{CP} = 11.0, CO), 255.08 (d, J_{CP} = 11.0, s, Ir=*C*=C).

Catalytic Reactions. The reactions were carried out in a ca. 10 mL two-necked Schlenk tube provided with a septum to allow sampling without opening the system. In a typical reaction, the catalyst (0.02 mmol) and the alkyne substrate (1 mmol) were dissolved in toluene (4 mL) under argon. Then, the Schlenk was closed and placed into an oil bath at the desired reaction temperature. The progress of the reactions was followed at intervals by GC-MS by using an Agilent 6890 Series GC with a 5973 Network mass selective detector and a HP-Innowax cross-linked poly(ethylene glycol) column (30 m $\times$ 0.53 mm $\times$ 1.0 μm). At the end of each reaction, the volatile compounds were evaporated and the residues were dissolved in CDCl$_3$ to accomplish the NMR characterization of the final products. The 1,4-disubstituted-*Z*-1-en-3-yne dimers **14a**−**c** (R = Ph, **a**; R = *t*Bu, **b**; R = SiMe$_3$, **c**) were identified by comparison of their NMR data with those previously reported.[19] The dimer *Z*-1,4-bis-triethylsilyl-but-1-en-3-yne (**14d**) and the hexadienyne trimers **15a** (R = Ph) and **15b** (R = tBu) were identified by a combination of COSY and NOESY ^{1}H, ^{13}C DEPT, and C,H-heterocorrelation NMR experiments. Data for **14d**: MS (EI, *m/z* (%)): 280 (100) [M$^+$]. ^{1}H NMR (CDCl$_3$, 293 K): δ 1.07−0.61 (m, 30H, CH$_2$ and CH$_3$), 5.94 (d, J_{HH} = 15.3, 1H, CH), 6.33 (d, J_{HH} = 1H, CH). A NOE effect was observed between the signals at δ 5.94 and 6.33. ^{13}C{^{1}H} NMR (CDCl$_3$, 293 K, all s): δ 3.57, 4.17 (both CH$_2$), 7.19, 7.26 (both CH), 95.75, 106.31 (both C), 125.98, 142.56 (both CH). Data for **15a**: MS (EI, *m/z* (%)): 306 (100) [M$^+$]. ^{1}H NMR (CDCl$_3$, 293 K): δ 6.94 (s, 1H, CH), 7.05 (d, J_{HH} = 15.9, 1H, CH), 7.34 (d, J_{HH} = 15.9, 1H, CH), 7.36−8.11 (m, 15H). A NOE effect was observed between the signals at δ 6.94 and 7.05. The signals at δ 7.05 and 7.34 do not show a NOE effect between them, but they both show NOE with the same aromatic signal. ^{13}C{^{1}H} NMR (CDCl$_3$, 293 K, all s): δ 85.89, 97.92, 120.79, 123.21 (all C), 126.80, 127.74, 128.36, 128.53, 128.69, 129.21, 130.46, 131.47, 131.63 (all CH), 136.62, 137.08 (both C), 137.49 (CH). Data for **15b**: MS (EI, *m/z* (%)): 246 (100) [M$^+$]. ^{1}H NMR (CDCl$_3$, 293 K): δ 1.00, 1.17, 1.26 (all s, 9H each, CCH$_3$), 5.71 (s, 1H, CH), 5.81 (d, J_{HH} = 15.4, 1H, CH), 5.99 (d, J_{HH} = 15.4, 1H, CH). A NOE effect was observed between the signals at δ 5.71 and 5.81. The signals at δ 5.71 and 5.81 do not show a NOE effect between them, but they both show a NOE with the singlet at δ 1.00. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 293 K, all s): δ 28.40 (C), 29.96, 30.28, 30.84 (all CH$_3$), 32.92, 33.24, 76.20, 106.77, 121.92 (all C), 127.92, 141.78, 148.16 (s, CH).

X-ray Structural Determination of Compounds 2 and 11. Suitable crystals for the X-ray diffraction experiments were obtained by slow evaporation of a saturated methanol solution of **2** at room temperature and by slow diffusion of methanol into a saturated toluene solution of **11**. Intensity data were collected at low temperature on a CCD Bruker SMART APEX diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) by using ω rotations (0.3°). Instrument and crystal stability were evaluated by measuring equivalent reflections at different times; no significant decay was observed. Data were corrected for Lorentz and polarization effects, and a semiempirical absorption correction was applied.[20] The structures were solved by Patterson and difference

(19) Yi, C. S.; Liu, N. *Organometallics* **1998**, *17*, 3158−3160.

(20) SAINT+ Software for CCD difractometers; Bruker AXS: Madison, WI, 2000. Sheldrick, G. M. *SADABS Program for Correction of Area Detector Data*; University of Göttingen: Göttingen, Germany, 1999.

Fourier methods.[21] Anisotropic displacement parameters were applied for all non-hydrogen atoms. Hydrogen atoms were introduced in the refinement in calculated positions and refined riding on carbon or nitrogen atoms with three common isotropic displacement parameters. Refinements were carried out by full-matrix least-squares on F^2 (SHELXL-97).[21] All residuals above 1.0 e·Å^{-3} were found in the proximity of metal centers and have no chemical sense.

Crystal data for 2. $C_{29}H_{54}Ir_2N_2OP_2$, M = 893.08; crystal size 0.111 × 0.103 × 0.037 mm^3; monoclinic, $P2_1/n$; a = 8.0028(7) Å, b = 18.7066(17) Å, c = 21.5672(19) Å, β = 100.095(2)°; Z = 4; V = 3178.7(5) Å^3; D_c = 1.866 g/cm^3; μ = 8.489 mm^{-1}, minimum and maximum transmission factors 0.423 and 0.718; $2\theta_{max}$ = 56.8°; temperature 100(2) K; 20 385 reflections collected, 7336 unique [R(int) = 0.0638]; number of data/restraints/parameters 7336/5/356; final GoF 1.068, R_1 = 0.0582 [5418 reflections $I > 2\sigma(I)$], wR_2 = 0.1090 for all data; largest difference peak 3.23 e·Å^{-3}. The hydride ligands were included from electrostatic potential calculations[8] and refined in the last cycles with weak restrictions in the Ir−H bond distances.

(21) Sheldrick, G. M. *SHELXS-97: Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

Crystal data for 11. $C_{44}H_{86}Ir_2N_2P_2Si_4$, M = 1201.85; crystal size 0.160 × 0.128 × 0.124 mm^3; triclinic, $P\bar{1}$; a = 12.0806(11) Å, b = 14.2020(13) Å, c = 16.3161(14) Å, α = 87.897(2)°, β = 77.029(2)°, γ = 84.659(2)°; Z = 2; V = 2715.7(4) Å^3; D_c = 1.470 g/cm^3; μ = 5.071 mm^{-1}, minimum and maximum transmission factors 0.429 and 0.523; $2\theta_{max}$ = 57.4°; temperature 173(2) K; 18 171 reflections collected, 12 193 unique [R(int) = 0.0557]; number of data/restraints/parameters 12 193/0/515; final GoF 0.806, R_1 = 0.0504 [7306 reflections $I > 2\sigma(I)$], wR_2 = 0.0862 for all data; largest difference peak 1.88 e·Å^{-3}.

Acknowledgment. Financial support for this research was provided by Plan Nacional de Investigación MEC/FEDER (Projects BQU2002-01729 and BQU2003-05412).

Supporting Information Available: Details of the X-ray crystallographic study of **2** and **11**, and a crystallographic information file (CIF) on these structural analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050044M