Versatility of Cyclooctadiene Ligands in Iridium Chemistry and Catalysis

Marta Martín, Eduardo Sola,* Olga Torres, Pablo Plou, and Luis A. Oro*

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

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In the presence of reactants such as acetonitrile, trimethylphosphine, and diphenylacetylene, the 1,5-cyclooctadiene iridium(I) complex [Ir(1,2,5,6-η-C_8H_{12})($NCCH_3$)(PMe_3)]BF_4 (**1**) has been found to transform into compounds containing cyclooctadiene or cyclooctadienyl ligands in η^3,η^2-; κ,η^3-; κ^2,η^2-; and η^3-coordination modes. All these reactions are initiated by an intramolecular C−H activation of the COD ligand and followed by either inter- or intramolecular insertion, or reductive elimination and further C−H activation elementary steps. Compound **1** has also been observed to undergo facile intermolecular oxidative additions of dihydrogen, hydrosilanes, and phenylacetylene to afford iridium(III) hydride complexes. Evidence for the insertion of COD into the Ir−H bonds of these new complexes has been obtained from the isolation of a monohydride complex containing a κ,η^2-cyclooctenyl ligand, from the isomerization of a silyl derivative into analogues containing 1,4- and 1,3-cycloctadiene ligands, and from the occurrence of H/D scrambling among Ir−H and COD C−H sites in the product of DC≡CPh oxidative addition. Si−Si coupling reactions to give disilanes and C−C coupling reactions to give an iridacyclopentadiene complex and 1,2,4-triphenylbenzene have also been observed in silane and phenylacetylene excess, respectively. Competition of all these intra- and intermolecular reactions under the conditions of phenylacetylene hydrosilylation has been found to result in catalytic reactions, the selectivity of which depends on the presence of introduced acetonitrile and its concentration.

Introduction

1,5-Cyclooctadiene (COD) rhodium and iridium complexes are readily accessible compounds and common starting materials in the chemistry of these metals.[1] As a result of their accessibility, complexes such as [M(μ-X)(COD)]$_2$ (M = Rh, Ir; X = Cl, OMe) are often the chosen catalyst precursors for a variety of homogeneous catalytic reactions.[2] In many of these applications, it is assumed that cyclooctadiene is readily released from the metal coordination sphere by the action of added ligands or substrates; hence its presence in the reaction is often considered irrelevant. Nevertheless, while this assumption has been sufficiently verified in catalytic transformations such as hydrogenations, hydroformylations, or carbonylations,[3] it does not seem fully justified in other processes involving milder reaction conditions and less coordinating substrates. In this context, the selected reactivity of the cationic iridium(I) complex [Ir(COD)($NCCH_3$)(PMe_3)]BF_4 described in this study intends to substantiate that the presence or absence of cyclooctadiene ligands in the metal coordination sphere is far from irrelevant in catalytic reactions that use COD compounds as precursors. This is illustrated by showing the potential of this ligand as a reversible source of hydrides and coordination vacancies and its ability to accommodate the electronic and steric demands of metal fragments. Together, these capabilities confer to the nearly ubiquitous and often ignored cyclooctadiene highly interesting properties as an ancillary ligand, the consideration of which could be essential in understanding the reactivity and selectivity of systems generated from COD precursors.

* Corresponding author. E-mail: oro@unizar.es.

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(2) *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: Weinheim, 1996.

(3) (a) Chaloner, P. A.; Esteruelas, M. A.; Joó, F.; Oro, L. A. *Homogeneous Hydrogenation*; Kluwer: Dordrecht, 1993. (b) *Rhodium Catalyzed Hydroformylation*; van Leeuwen, P. W. M. N., Claver, C., Eds.; Kluwer: Dordrecht, 2000.

Results and Discussion

Intramolecular C−H Activation and Insertion. In $CDCl_3$ solution and in the presence of the 1,5-cyclooctadiene complex [Ir(1,2,5,6-η-C_8H_{12})($NCCH_3$)(PMe_3)]BF_4 (**1**), a kinetically stable olefin such as *cis*-stilbene was found to slowly isomerize into its thermodynamically stable trans isomer. No changes in complex **1** nor new iridium species were detected by NMR during the isomerization process, but when assuming the commonly accepted mechanism for olefin isomerization, the experiment suggests the formation of a reactive hydride intermediate (eq 1) from complex **1**. In an attempt to obtain further evidence for this postulated hydride compound, we replaced the alkene reactant by an alkyne, since the difficult hydrogen β-elimination from an alkenyl species was expected to stop at this intermediate the likely sequence of reversible reactions

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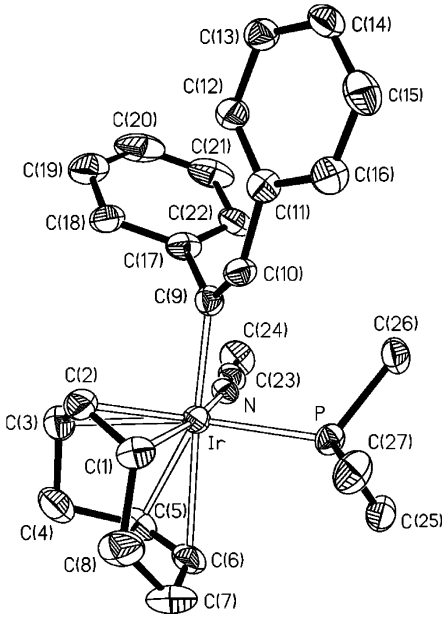
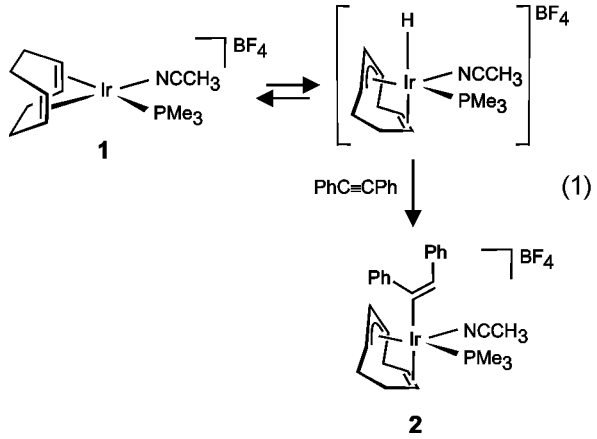


Figure 1. Molecular structure of the cation of complex **2**. Thermal ellipsoids are drawn at the 50% probability level.

involved in the isomerization process. Indeed, the treatment of **1** with 1 equiv of diphenylacetylene, in CH_2Cl_2 at room temperature, led to the formation of the alkenyl complex [Ir(1,2,3,5,6-η-C_8H_{11})(*Z*-C(Ph)═CHPh)($NCCH_3$)(PMe_3)]BF_4 (**2**), the X-ray structure of which is shown in Figure 1. Relevant bond distances and angles of the structure are collected in Table 1. A precedent for a closely related reaction has been reported,[4] and several compounds containing similar η^3,η^2-cyclooctadienyl ligands have been described for iridium[5] and other metals.[6]

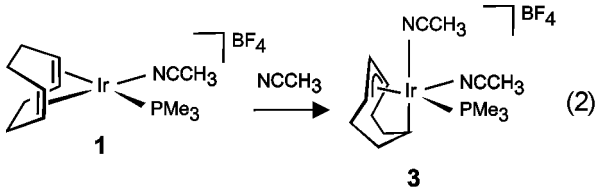


The ease with which complex **2** is formed and its structure together with the occurrence of the aforementioned alkene isomerization strongly suggest that the 1,5-cyclooctadiene ligand of **1** undergoes facile and reversible allylic C−H activation to give a labile Ir(III) hydride intermediate, the lifetime of which seems to be long enough to allow for intermolecular insertions with alkenes or alkynes. In the absence of such substrates, an intramolecular insertion with the remaining C═C double bond of the η^3,η^2-cyclooctadienyl ligand was observed instead, yielding the Ir(III) complex [Ir(1-κ-4,5,6-η-C_8H_{12})($NCCH_3$)$_2$(PMe_3)]BF_4 (**3**) (eq 2). Using 1,2-dichloroethane as solvent, this transformation was found to require the addition of 1 equiv of acetonitrile, since in its absence the solutions of **1** were perfectly stable. It is likely that this additional acetonitrile is required to stabilize the final insertion product as a coordinatively saturated compound, thus allowing for favorable thermodynamics.

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

Ir−P	2.3179(12)	Ir−C(6)	2.378(5)
Ir−N	2.070(3)	Ir−C(9)	2.072(4)
Ir−C(1)	2.101(5)	C(1)−C(2)	1.440(6)
Ir−C(2)	2.162(5)	C(2)−C(3)	1.369(7)
Ir−C(3)	2.344(5)	C(5)−C(6)	1.329(7)
Ir−C(5)	2.353(5)	C(9)−C(10)	1.345(6)
M[a]−Ir−P	100.3	N−Ir−C(3)	98.87(16)
M−Ir−N	90.3	N−Ir−C(9)	89.82(14)
M−Ir−C(1)	84.6	C(1)−Ir−C(2)	39.45(17)
M−Ir−C(2)	91.8	C(1)−Ir−C(3)	68.01(19)
M−Ir−C(3)	72.5	C(1)−Ir−C(9)	93.49(17)
M−Ir−C(9)	171.6	C(2)−Ir−C(3)	35.07(18)
P−Ir−N	92.08(10)	C(2)−Ir−C(9)	81.70(18)
P−Ir−C(1)	100.77(14)	C(3)−Ir−C(9)	99.16(17)
P−Ir−C(2)	137.30(14)	Ir−N−C(23)	172.8(3)
P−Ir−C(3)	166.84(13)	Ir−C(9)−C(10)	124.0(3)
P−Ir−C(9)	88.09(12)	C(10)−C(9)−C(17)	120.5(4)
N−Ir−C(1)	166.82(16)	C(9)−C(10)−C(11)	130.9(4)
N−Ir−C(2)	128.96(16)		

[a] M is the midpoint of the C(5)−C(6) double bond.



The analytic data of **3** agree with the proposed stoichiometry, and its NMR spectra are consistent with the presence of a κ,η^3-cyclooctadiene ligand,[7] indicating an asymmetric structure. The proposed relative position of the phosphine in this structure, trans to allyl, can be inferred from the J_{CP} coupling constant of 30.0 Hz in the $^{13}C\{^1H\}$ NMR signal attributable to one of the allylic carbons at δ 81.16. Our attempts to corroborate the proposed structure of **3** by X-ray diffraction were unsuccessful due to the poor quality of its crystals. Neverthe-

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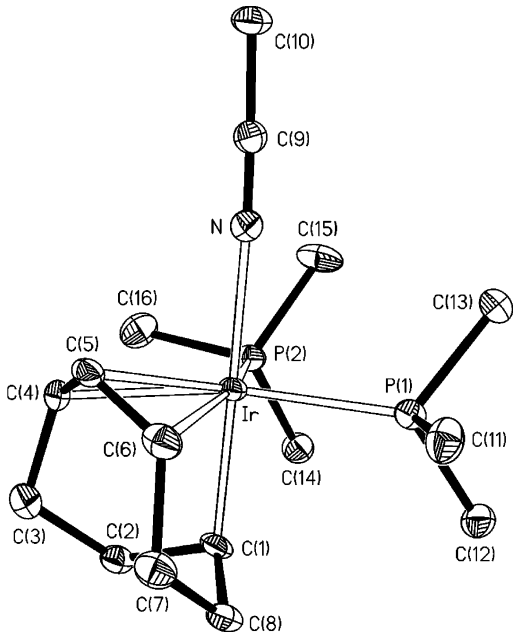


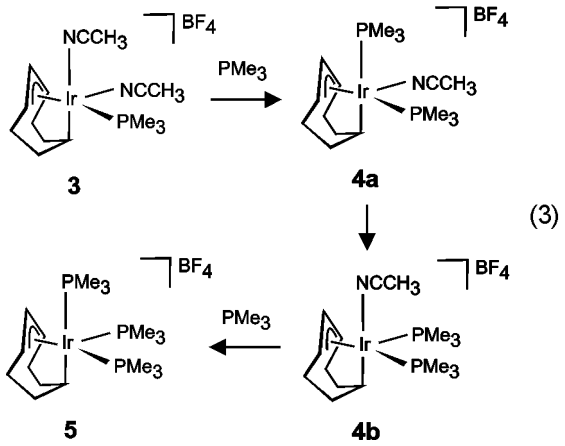
Figure 2. Molecular structure of the cation of complex **4b**. Thermal ellipsoids are drawn at the 50% probability level.

less, crystals allowing for an X-ray diffraction experiment could be obtained for derivatives of **3** when prepared by ligand substitution. Figure 2 shows the molecular structure of the cation of complex [Ir(1-κ-4,5,6-η-C_8H_{12})($NCCH_3$)(PMe_3)$_2$]BF_4 (**4**), which was prepared by treatment of **3** with 1 equiv of PMe_3. The structure corresponds to the thermodynamically stable isomer of this compound (**4b** in eq 3), which resulted from the slow isomerization of the substitution kinetic product **4a**. The characterization data of this latter kinetic isomer indicate a nonsymmetric structure with a phosphine ligand in the position trans to the σ-bonded carbon of the cyclic ligand. The sequence of reactions leading to **4b**, depicted in eq **3**, is consistent with the large trans effect and influence that this σ-bonded carbon is expected to exert.[8] This large trans influence also results in a long Ir−N bond distance of 2.115(3) Å for the acetonitrile ligand of compound **4b** (Table 2).

Consistently with this long bond distance, the remaining acetonitrile ligand of **4b** could be readily substituted by another equivalent of PMe_3, yielding the complex [Ir(1-κ-4,5,6-η-C_8H_{12})(PMe_3)$_3$]BF_4 (**5**). Interestingly, this compound is an Ir(III) isomer of the already reported Ir(I) derivative [Ir(COD)(PMe_3)$_3$]BF_4 (**6**), which contains a 1,2,5,6-η-C_8H_{12} ligand (eq 4).[9] This indicates that both coordination modes of the cyclooctadiene ligand are compatible with the $[Ir(PMe_3)_3]^+$ metal fragment, permitting the isolation of complexes in both Ir(I) and Ir(III) formal oxidation states.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 4b

Ir−P(1)	2.3085(9)	Ir−C(5)	2.186(3)
Ir−P(2)	2.3085(9)	Ir−C(6)	2.239(4)
Ir−N	2.115(3)	C(4)−C(5)	1.419(5)
Ir−C(1)	2.079(3)	C(5)−C(6)	1.414(5)
Ir−C(4)	2.238(3)		
P(1)−Ir−P(2)	98.92(3)	P(2)−Ir−C(6)	163.02(10)
P(1)−Ir−N	90.34(8)	N−Ir−C(1)	178.82(13)
P(1)−Ir−C(1)	90.31(10)	N−Ir−C(4)	96.89(12)
P(1)−Ir−C(4)	163.27(10)	N−Ir−C(5)	81.77(12)
P(1)−Ir−C(5)	130.14(10)	C(1)−Ir−C(4)	82.23(14)
P(1)−Ir−C(6)	96.33(10)	C(1)−Ir−C(5)	97.06(14)
P(2)−Ir−N	90.52(8)	C(1)−Ir−C(6)	82.12(14)
P(2)−Ir−C(1)	90.36(10)	C(4)−Ir−C(6)	67.90(14)
P(2)−Ir−C(5)	130.09(10)	Ir−N−C(9)	176.5(3)



The thermal behavior in solution of complexes **5** and **6** was investigated in order to determine whether these two isomers can convert into each other and thus evaluate their relative thermodynamic stability. The solutions of **5** in 1,2-dichloroethane were found to be stable, even after heating them at 333 K for 6 h. On the contrary and under the same conditions, compound **6** afforded a mixture containing two new products in approximately 1:1 molar ratio, along with significant amounts of the starting compound. Although these two new products could not be separated from the reaction mixture and independently characterized, the combination of ^{1}H-COSY, ^{13}C-DEPT, ^{1}H,^{13}C-HSQC, and ^{1}H-NOESY NMR experiments on the mixture (see Supporting Information) permitted their identification as two new isomers of **5** and **6**, [Ir(1,4-κ-2,3-η-C_8H_{12})(PMe_3)$_3$]BF_4 (**7**) and [IrH(1,2,3-η-C_8H_{11})(PMe_3)$_3$]BF_4 (**8**) (eq 4).

The ^{31}P{^{1}H} NMR spectrum of compound **7** in CD_2Cl_2 displays two broad signals of relative intensity 2 to 1. As in the starting complex **6**, the broadening can be attributed to the presence of a small unresolved J_{PP} mutual coupling constant. This spectrum indicates a structure with two equivalent phosphines, although it is compatible with both *fac* and *mer* arrangements of the PMe_3 ligands. The two ^{1}H NMR signals of **7** at lowest field, being two multiplets at δ 4.91 and 3.15, correlate in the ^{1}H,^{13}C-HSQC spectrum with two ^{13}C-{^{1}H} signals corresponding to CH carbons, a doublet of triplets at δ 89.12 with J_{CP} coupling constants of 5.6 and 2.1 Hz, and the multiplet at δ 43.19 shown in Figure

(7) For precedents of this coordination mode of COD and functionalized COD ligands see: (a) Flood, T. C.; Iimura, M.; Perotti, J. M.; Rheingold, A. L.; Concolino, T. E. *Chem. Commun.* **2000**, 1681−1682. (b) Burrows, A. D.; Green, M.; Jeffrey, J. C.; Lynam, J. M.; Mahon, M. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 3043−3045. (c) de Bruin, B.; Brands, J. A.; Donners, J. J. J. M.; Donners, M. P. J.; de Gelder, R.; Smits, J. M. M.; Gal, A. W.; Spek, A. L. *Chem. Eur. J.* **1999**, *5*, 2921−2936. (d) Day, V. W.; Eberspacher, T. A.; Klemperer, W. G.; Zhong, B. *J. Am. Chem. Soc.* **1994**, *116*, 3119−3120. (e) Esteruelas, M. A.; Oliván, M.; Oro, L. A.; Schulz, M.; Sola, E.; Werner, H. *Organometallics* **1992**, *11*, 3659−3664. (f) Day, V. W.; Klemperer, W. G.; Lockledge, S. P.; Main, D. J. *J. Am. Chem. Soc.* **1990**, *112*, 2031−2033. (g) Bönnemann, H.; Goddard, R.; Grub, J.; Mynott, R.; Raabe, E.; Wendel, S. *Organometallics* **1989**, *8*, 1941−1958. (h) Cotton, F. A.; LaPrade, M. D. *J. Organomet. Chem.* **1972**, *39*, 345−354.

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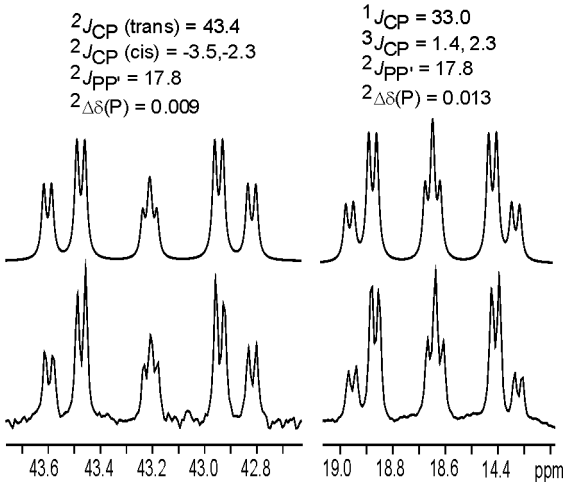
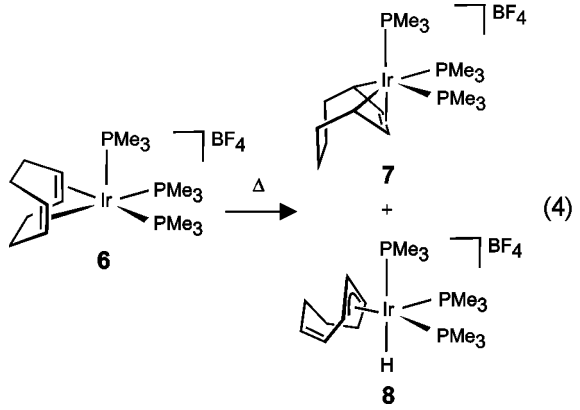


Figure 3. $^{13}C\{^1H\}$ NMR signals corresponding to two equivalent CH carbons of the cyclooctadiene (left) and two equivalent PMe_3 (right) ligands of complex **7**; experimental (below) and simulated (above).

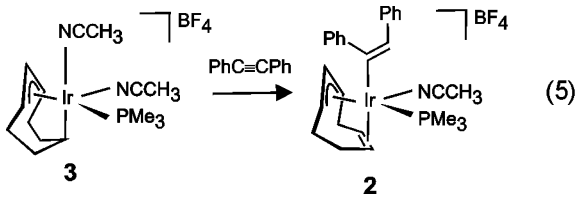
3, respectively. This latter $^{13}C\{^1H\}$ NMR multiplet is similar to that at δ 18.62, also shown in Figure 3, which is attributable to the methyl groups of the two equivalent phosphine ligands. Both multiplets could be successfully simulated as corresponding to atoms coupled to three ^{31}P nuclei, two of which were nonequivalent just as the result of different $^{12}C/^{13}C$ isotopic shifts. Both simulated spectra agreed in a coupling constant of 17.8 Hz between these latter "equivalent" phosphorus atoms, which indicates the *fac* arrangement of the three phosphine ligands of **7**.



The ^{1}H-COSY and NOESY NMR spectra of **7** also suggest that the former 1,5-cyclooctadiene ligand has been transformed into its 1,3-isomer, since the ^{1}H NMR signal at lower field does not show either scalar coupling or NOE effect with any of the signals attributable to CH_2 groups. Moreover, the aforementioned $^{13}C\{^1H\}$ NMR data suggest that the ligand adopts the 1,4-κ-2,3-η-coordination mode rather than the 1,2,3,4-η-alternative. This is inferred from the large $^2J_{CP}$(trans) coupling constant obtained in the simulation of Figure 3 (43.4 Hz), much larger than those observed in the other CH $^{13}C\{^1H\}$ NMR signal of the complex (5.6 and 2.1 Hz). Moreover, the magnitude of the ^{13}C isotopic shift induced by this CH group in the trans phosphorus nuclei ($^2\Delta\delta = \pm 0.009$) is comparable to that caused by the direct isotopic substitution at the phosphorus atom ($^1\Delta\delta = \pm 0.013$).[10]

The $^{31}P\{^1H\}$ NMR spectrum of compound **8** consists of three signals, a doublet of doublets at δ −55.51 with J_{PP} coupling constants of 20.5 and 20.8 Hz, and two broad doublets at δ −50.04 and −52.85. The high-field region of the ^{1}H NMR spectrum shows a doublet of triplets at δ −14.11 with J_{HP} coupling constants of 148.2 and 21.9 Hz respectively, confirming the *fac* arrangement of the three PMe_3 ligands in this hydride complex. The low-field region of the proton spectrum shows five multiplets which correlate in the ^{1}H,^{13}C-HSQC spectrum with five $^{13}C\{^1H\}$ signals corresponding to CH carbons. The ^{1}H-COSY and NOESY NMR spectra indicate that these five proton multiplets correspond to hydrogens occupying consecutive positions in the cyclic ligand. Together, this spectroscopic information points to the structure depicted in eq 4 as the most likely for complex **8**.

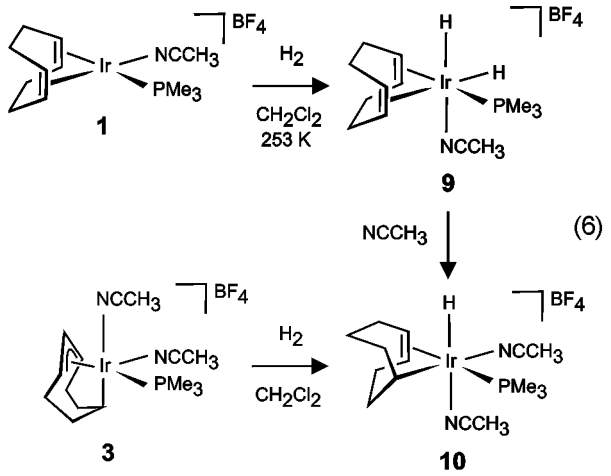
The above experiments involving the isomeric compounds **5**−**8** suggest that, although the iridium(I) complex **6** initiates its thermal transformation into the thermodynamic stable isomer **5**, the process cannot be completed in the presence of three PMe_3 ligands, which in turn drive the reaction to the alternative Ir(III) compounds **7** and **8**. A plausible explanation for this behavior results from taking into account the larger coordination capability of PMe_3 when compared to that of acetonitrile. This may favor the release of the C=C double bond from the iridium center of the postulated hydride intermediate of eq 1, thus precluding the subsequent intramolecular insertion. Under these circumstances, the only possible elementary steps on the cyclooctadiene moiety would be C−H reductive eliminations and activations, which still allow for the migration of the double bond, thus eventually leading to compounds **7** and **8**. This transformation indicates that the sequence of intramolecular reactions leading to cyclooctadiene ligand isomerization can be altered by intermolecular competing processes such as the coordination of strong ligands. A related conclusion is inferred from the formation of the alkenyl complex **2**, in which the COD isomerization sequence is intercepted by an intermolecular insertion reaction. Interestingly, compound **2** could also be prepared by reaction of the iridium(III) complex **3** with diphenylacetylene (eq 5), suggesting that all steps involved in the 1,2,5,6-η- to 1-κ-4,5,6-η-isomerization of the cyclooctadiene ligand are reversible under relatively mild reaction conditions. Further examples for the reversibility of these elementary steps are given in the following section.



Intermolecular Oxidative Additions and Insertion. Cationic cyclooctadiene complexes of iridium similar to **1** are known to be excellent catalyst precursors in homogeneous hydrogenation reactions.[11] Under hydrogenation conditions these compounds have been

(10) Hansen, P. E. *Prog. NMR Spectrosc.* **1988**, *20*, 207−255.

reported to undergo partial or total hydrogenation of the cyclooctadiene ligand to yield the catalytic active species.[12] Consistent with this proposal and previous studies in related compounds,[13] we observed that the treatment of **1** with dihydrogen in CH_2Cl_2 at 253 K afforded, in good yield, the dihydride complex $[IrH_2(1,2,5,6\text{-}\eta\text{-}C_8H_{12})(NCCH_3)(PMe_3)]BF_4$ (**9**) (eq 6).



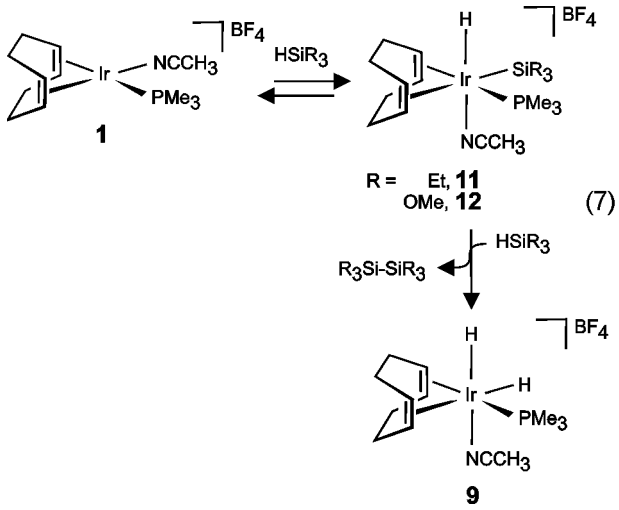
The ^1H NMR spectrum of **9** in CD_2Cl_2 at 243 K shows two hydride resonances at δ −17.01 and −12.70, with J_{HP} coupling constants of 18.0 and 21.0 Hz, respectively, without appreciable J_{HH} mutual coupling. This is consistent with a *fac* arrangement of the two hydrides and the phosphine. The structural assignment of this compound can be completed after observing that the $^{13}C\{^1H\}$ NMR resonance due to the acetonitrile quaternary carbon, a singlet at δ 123.63, splits into a doublet under off-resonance conditions due to a coupling of 9.0 Hz with the trans-located hydride ligand.

The addition of 1 equiv of acetonitrile to a solution of **9** in CD_2Cl_2 readily led to the formation of a monohydride compound. This new compound could be prepared as a pale yellow solid by precipitation in diethyl ether at room temperature, although the solid was found to transform into an oil upon drying. The NMR spectra at 233 K of the $CDCl_3$ solutions obtained from this oil allowed the characterization of the new compound as complex $[IrH(1\text{-}\kappa\text{-}4,5\text{-}\eta\text{-}C_8H_{13})(NCCH_3)_2(PMe_3)]BF_4$ (**10**) (eq 6). Compound **10** was also found to be the reaction product after treatment of the Ir(III) complex **3** with dihydrogen at room temperature. The formation of a common reaction product from complexes containing isomeric C_8H_{12} ligands again suggests the facility and reversibility of the elementary steps involved in the exchange of hydrogens between the cyclic ligand and the iridium center.

The $1\text{-}\kappa\text{-}4,5\text{-}\eta\text{-}C_8H_{13}$ ligand of **10** gives rise to eight separate signals in the $^{13}C\{^1H\}$ DEPT NMR spectrum, five corresponding to CH_2 carbons and three due to CH ones. The latter are doublets at δ 87.40, 84.32, and 4.81, with J_{CP} coupling constants of 14.7, 10.1, and 3.7 Hz, respectively. These chemical shifts and couplings constants are consistent with the presence of a C=C double bond coordinated trans to the phosphine and a σ-bonded CH cis to this ligand. The $^{13}C\{^1H\}$ NMR spectrum also shows two singlets at δ 118.36 and 121.48 corresponding to acetonitrile quaternary carbons. Under off-resonance conditions, the signal at δ 121.48 splits into a doublet due to a J_{CH} coupling constant of 9.0 Hz with the trans-located hydride ligand, in agreement with the structural proposal for **10** depicted in eq 6.

Compound **1** was also found to undergo facile oxidative addition of hydrosilanes such as $HSiEt_3$ and $HSi(OMe)_3$ to give the corresponding hydride-silyl iridium(III) derivatives $[IrH(SiR_3)(1,2,5,6\text{-}\eta\text{-}C_8H_{12})(NCCH_3)(PMe_3)]BF_4$ (**11**, **12**) (eq 7). Both complexes could be conveniently obtained by reaction of **1** with 1 equiv of the silane in CH_2Cl_2 at 233 K, followed by precipitation with diethyl ether.

The two hydride-silyl compounds **11** and **12** were found to significantly differ in stability. Whereas the solutions of the latter remained unchanged after several hours at room temperature, the triethylsilyl compound **11** was observed to readily disproportionate into the starting compound **1**, the dihydride **9**, and disilane. This reaction indicates the oxidative addition of $HSiEt_3$ to be reversible and also shows that compound **11** is capable of reacting with a second equivalent of silane to give an irreversible Si−Si coupling reaction. In fact, both **11** and **12** were found to react with a second equivalent of silane to give **9** and the corresponding disilane (eq 7). In CH_2Cl_2 at 233 K, both reactions were completed after several minutes.



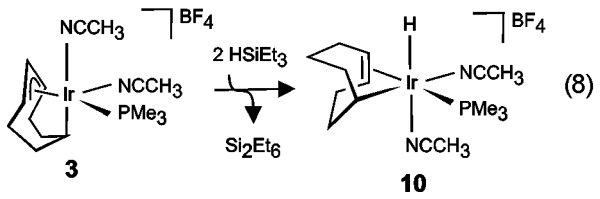
The Si−Si coupling reaction was also observed when the Ir(III) precursor **3** was used instead of **1**. In this case, due to the presence of an additional acetonitrile ligand in the starting complex, the final reaction products were disilane and the monohydride complex **10** (eq 8). The reaction in CH_2Cl_2 at 233 K seemed to be nearly instantaneous, and no reaction intermediates could be detected even when silane was scarce and at lower temperatures. This suggests that a different and faster reaction sequence, without participation of Ir(1,2,5,6-

(11) (a) Crabtree, R. H. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; pp 285−316. (b) Oro, L. A.; Cabeza, J. A.; Cativiela, C.; Díaz de Villegas, M. D.; Meléndez, E. *J. Chem. Soc., Chem. Commun.* **1983**, 1383−1384. (c) Cabeza, J. A.; Cativiela, C.; Díaz de Villegas, M. D.; Oro, L. A. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1881−1884. (d) Oro, L. A.; Sola, E.; Navarro, J. In *Perspectives in Organometallic Chemistry*; Screttas, C. G., Steele, B. R., Eds.; RSC: Cambridge, 2003; pp 297−305.

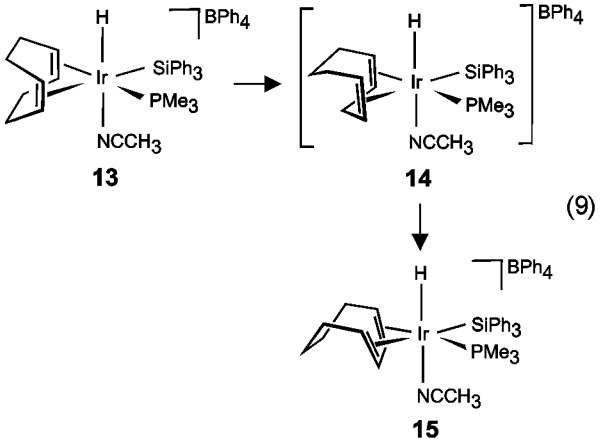
(12) Crabtree, R. H. *Acc. Chem. Res.* **1979**, *12*, 331−338.

(13) Kimmich, B. F. M.; Somsook, E.; Landis, C. R. *J. Am. Chem. Soc.* **1998**, *120*, 10115−10125.

η-C_8H_{12}) intermediates, may operate when the Si−Si coupling process starts from complex **3**.

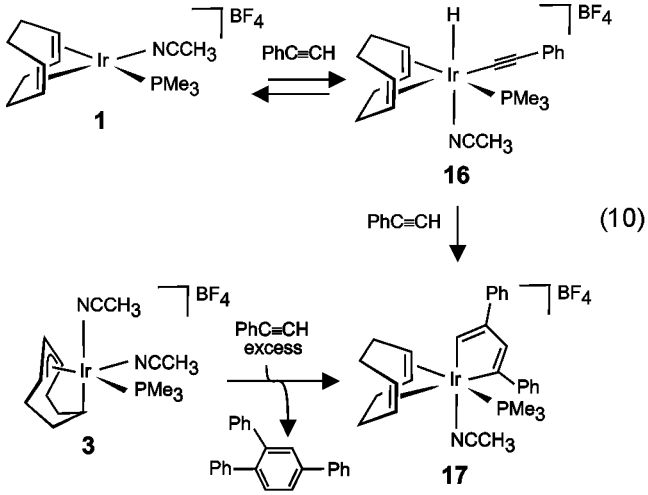


The NMR characterization data of the hydride-silyl compounds **11** and **12** indicate similar structures. Out of the five possible isomers of a concerted silane oxidative addition to **1**, only that displaying a trans arrangement of hydride and acetonitrile was formed. The identity of this isomer was confirmed, in both compounds, by the splitting into a doublet of the ^{13}C NMR signal corresponding to the acetonitrile quaternary carbon under off-resonance conditions. Note that all bulky ligands in this isomer share the same equatorial plane, a feature that allowed for an interesting observation as the steric demands of the ligands were increased. Thus, the oxidative addition of the bulky $HSiPh_3$ was observed to give a kinetic product, isostructural to **11** and **12**, which could be conveniently isolated as the tetraphenylborate salt [IrH($SiPh_3$)(1,2,5,6-η-C_8H_{12})($NCCH_3$)(PMe_3)]BPh_4 (**13**) (eq 9). Although no disproportionation of this compound was observed by NMR in CD_2Cl_2 at room temperature, it sequentially evolved to two new compounds. The final product of the transformation was isolated and characterized as the complex [IrH($SiPh_3$)(1,2,3,4-η-C_8H_{12})($NCCH_3$)(PMe_3)]BPh_4 (**15**), which retains the trans arrangement of hydride and acetonitrile but contains a 1,3-cyclooctadiene ligand.



The isomerization of the COD ligand is again deduced from the information in the ^1H-COSY and NOESY spectra. Due to its transient nature, the intermediate compound of this transformation could not be isolated and fully characterized. Nevertheless, its NMR data are compatible with the formulation [IrH($SiPh_3$)(1,2,4,5-η-C_8H_{12})($NCCH_3$)(PMe_3)]BPh_4 (**14**), which corresponds to an expected intermediate along the **13** to **15** isomerization containing a 1,4-cyclooctadiene ligand. Taking into account the smaller size of the 1,3-cyclooctadiene ligand compared with that of the 1,5-isomer, the observed isomerization can be rationalized as the cyclooctadiene response to the steric demands introduced into the complex by the bulky triphenylsilyl ligand.[14] In line with previous mechanistic proposals for similar isomerizations of COD ligands,[15] insertion processes similar to that in eq 6 followed by β-elimination steps would constitute the likely mechanism for this transformation.

Phenylacetylene has also been found to undergo oxidative addition to complex **1**, yielding the complex [IrH(C≡CPh)(1,2,5,6-η-C_8H_{12})($NCCH_3$)(PMe_3)]BF_4 (**16**). The characterization data of this compound indicate a structure analogue to those of the previously described kinetic oxidative addition products **9** and **11**−**13** (eq 10). The use of DC≡CPh as reactant provided evidence for the occurrence of an insertion step after oxidative addition, in the form of H/D exchange among Ir−H and COD C−H sites. The kinetic isotopomer of this reaction, which contains a deuteride ligand, shows characteristic downfield isotopic shifts[16] affecting, inter alia, the $^{31}P\{^1H\}$ NMR signal ($\Delta\delta$ = 0.12 ppm) and the $^{13}C\{^1H\}$ NMR resonance due to the alkynyl α carbon ($\Delta\delta$ = 0.17 ppm). In CD_2Cl_2 at 233 K, this isotopomer slowly transformed into others containing a hydride ligand. The $^{13}C\{^1H\}$ NMR of the isotopomeric mixture generated from this H/D scrambling did not reveal a preferred position for deuterium incorporation into the COD ligand. Instead, only very small signals next to the resonances of COD carbons could be detected.



The behavior of **16** was found to be related to that of the triethylsilyl analogue **11**, since at room temperature it was observed to disproportionate into the stating complex **1** and the iridacyclopentadiene complex [Ir(1,4-κ-CH=C(Ph)CH=CPh)(1,2,5,6-η-C_8H_{12})($NCCH_3$)(PMe_3)]BF_4 (**17**). The latter complex could be obtained as a single isomer by treatment of **1** with 2 equiv of the alkyne at 273 K. The structure of this compound is shown in Figure 4, and its bond distances and angles are collected in Table 3. Despite the fact that metallacyclopentadiene complexes are frequently observed as intermediates in alkyne cyclotrimerization reactions,[17]

(14) Similar steric arguments have been previously used to rationalize related COD isomerizations, see: Ashworth, T. V.; Chalmers, A. A.; Meitjies, E.; Oosthuizen, H. E.; Singleton, E. *Organometallics* **1984**, *3*, 1485−1491.

(15) See for example refs 7e and 14, and: Bennet, M. A.; McMahon, I. J.; Pelling, S.; Brookhart, M.; Lincoln, D. M. *Organometallics* **1992**, *11*, 127−138.

(16) (a) Torres, F.; Sola, E.; Martín, M.; López, J. A.; Lahoz, F. J.; Oro, L. A. *J. Am. Chem. Soc.* **1999**, *121*, 10632−10633. (b) Jiménez, M. V.; Sola, E.; Martínez, A.; Lahoz, F. J.; Oro, L. A. *Organometallics* **1999**, *18*, 1125−1136.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex 17

	a[a]	b		a	b
Ir−P	2.305(3)	2.317(2)	N−C(25)	1.111(12)	1.133(12)
Ir−N	2.100(8)	2.093(9)	C(1)−C(2)	1.339(12)	1.371(15)
Ir−C(1)	2.053(9)	2.025(12)	C(2)−C(3)	1.442(12)	1.449(13)
Ir−C(4)	2.061(9)	2.061(11)	C(3)−C(4)	1.337(12)	1.371(15)
Ir−C(17)	2.260(11)	2.293(10)	C(17)−C(18)	1.368(12)	1.359(16)
Ir−C(18)	2.296(10)	2.283(10)	C(21)−C(22)	1.370(13)	1.341(15)
Ir−C(21)	2.332(9)	2.319(10)			
Ir−C(22)	2.336(8)	2.316(11)			
M(1)−Ir−M(2)[b]	81.8	82.2	Ir−N−C(25)	172.7(11)	174.8(8)
M(1)−Ir−P	176.5	176.5	Ir−C(1)−C(2)	116.5(7)	116.5(7)
M(1)−Ir−N	94.2	94.9	Ir−C(4)−C(3)	114.1(7)	113.9(7)
M(1)−Ir−C(1)	94.2	95.4	Ir−C(4)−C(11)	126.2(6)	125.8(8)
M(1)−Ir−C(4)	90.6	90.1	C(1)−C(2)−C(3)	113.6(8)	113.8(10)
M(2)−Ir−P	95.7	95.1	C(1)−C(2)−C(5)	124.7(8)	123.8(9)
M(2)−Ir−N	95.6	96.6	C(2)−C(3)−C(4)	117.4(8)	116.3(11)
M(2)−Ir−C(1)	96.9	171.0	C(3)−C(2)−C(5)	121.7(8)	122.4(10)
M(2)−Ir−C(4)	170.7	81.0	C(3)−C(4)−C(11)	118.9(8)	119.5(10)
P−Ir−N	88.4(3)	87.6(2)			
P−Ir−C(1)	83.4(3)	82.6(3)			
P−Ir−C(4)	91.7(3)	92.4(3)			
N−Ir−C(1)	165.7(3)	165.4(4)			
N−Ir−C(4)	90.4(3)	90.2(4)			
C(1)−Ir−C(4)	78.2(4)	79.4(4)			

[a] The asymmetric unit is formed by two independent but chemically equivalent molecules. [b] M(1) and M(2) are the midpoints of the C(17)−C(18) and C(21)−C(22) double bonds.

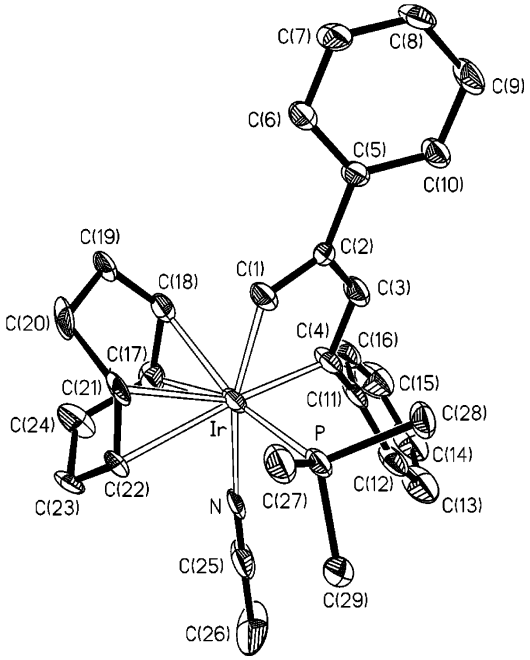


Figure 4. Molecular structure of the cation of complex **17**. Thermal ellipsoids are drawn at the 50% probability level.

compound **17** has been found to be inert in phenylacetylene excess. However, a product of phenylacetylene cyclotrimerization was observed when the synthesis of **17** was attempted from complex **3** (eq 10). This reaction was less selective than that starting from **1**, affording several byproducts detectable by ^{31}P NMR. The formation of **17** as the major reaction product was found to require the use of ca. 6 equiv of the alkyne and, in route to **17**, the alkyne excess was converted into 1,2,4-triphenylbenzene. Only traces of the other possible cyclotrimerization product, the 1,3,5-triphenylbenzene, were detected in the GC−MS and NMR analysis of the reaction products. Again, this reaction suggests that the achievement of a common reaction product from **1** and **3** may involve rather different reaction pathways.

Influence of COD Versatility in Catalysis. The previous paragraphs have described several intra- and intermolecular transformations of complex **1** that take place under relatively mild conditions. All these reactions, and possibly others, are expected to directly compete with each other in a catalytic process such as phenylacetylene hydrosilylation.[18] Considering the variety of possible reactions, their comparable kinetics, and the dependence of the observed equilibria on the nature of reactants and the presence of added ligands, it could be expected that such a catalytic process would be rather unselective and strongly dependent on the actual substrates and reaction conditions. Our exploration of **1** as hydrosilylation catalyst has indeed confirmed these expectations, since in general, these catalytic reactions have been found to yield alkenylsilanes (gem, trans, and cis), the products of alkyne dehydrogenative silylation and those of silane dehydrodimerization. Moreover, the selectivity of the processes catalyzed by **1** was found to depend on the concentration of added ligands such as acetonitrile, as illustrated by the selected reactions between triethylsilane and phenylacetylene in Table 4.

Under the conditions of Table 4, complex **1** was found to be a fast hydrosilylation catalysts, affording *cis*-alkenylsilane as the major product.[19] The addition of acetonitrile to the catalytic reaction was found to lower

(17) See for example: (a) Takeuchi, R. *Synlett.* **2002**, *12*, 1954−1965. (b) Calhorda, M. J.; Hirchner, K.; Veiros, L. F. In *Perspectives in Organometallic Chemistry*; Screttas, C. G., Steele, B. R., Eds., RSC: Cambridge, 2003; pp 111−119. (c) O'Connor, J. M.; Closson, A.; Hiibner, K.; Mervin, R.; Gantzel, P. *Organometallics* **2001**, *20*, 3710−3717. (d) Baxter, R. J.; Knox, G. R.; Pauson, P. L.; Spicer, M. D. *Organometallics* **1999**, *18*, 197−205. (e) Diercks, R.; Eaton, B. E.; Gürtzen, S.; Jalisatgi, S.; Matzger, A. J.; Radde, R. H.; Volhardt, K. P. C. *J. Am. Chem. Soc.* **1998**, *120*, 8247−8248.

(18) Several iridium complexes related to **1** have been previously described as efficient alkyne hydrosilylation catalysts. See: Ojima, I.; Zhaoyang, L.; Zhu, J. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley and Sons: New York, 1998; Vol. 2, pp 1687−1792.

Table 4. Reactions between $HSiEt_3$ and PhC≡CH Catalyzed by the Cationic Iridium Compounds $[Ir(COD)(NCCH_3)(PMe_3)]BF_4$ (1), $[Ir(TFB)(NCCH_3)(PiPr_3)]BF_4$ (18), and $[IrH_2(NCCH_3)_3(PiPr_3)]BF_4$ (19)[a]

				product distribution (%)					
				alkenylsilanes					
complex	$[NCCH_3]$ (M)	time (h)	yield[b] (%)	gem	trans	cis	styrene	$PhC{\equiv}CSiEt_3$	Si_2Et_6
1		1	100	2	9	74	7	8	0
1	0.25	2	90	3	21	50	13	10	3
1	2.5	2	47	6	27	35	16	8	8
18		1	100	5	24	47	12	12	0
18	2.5	3	74	6	23	45	13	13	0
19		0.2	100	9	26	35	15	15	0
19	2.5	1.3	61	7	25	37	18	13	0

[a] Conditions: [**complex**] = 2.5×10^{-3} M, [PhC≡CH] = $[HSiEt_3]$ = 0.25 M, solvent = 1,2-dichloroethane, T = 333 K. [b] Based on silane consumption.

the yield of this product, while increasing the conversion to *trans*-alkenylsilane[20] and promoting the formation of disilane.[21] Since this effect on the selectivity was found to increase at higher acetonitrile concentrations, it might be attributed to an increasing participation in the catalysis of species such as **3** and **10**, which are those favored in acetonitrile excess. It is interesting to note that the product of triethylsilane dehydrodimerization could only be obtained from catalytic reactions in the presence of added acetonitrile. This observation correlates with that previously mentioned suggesting the faster formation of this Si−Si coupling product from the bis-acetonitrile Ir(III) derivative **3**. Moreover, the use of related catalyst precursors containing diolefin ligands which cannot participate in the versatile chemistry of COD has led to reactions in which selectivity remained unaffected by the addition of acetonitrile. This is the case, for example, of complex $[Ir(TFB)(NCCH_3)(PiPr_3)]BF_4$ (**18**), which contains the diolefin tetrafluorobenzobarrelene (5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene) as ligand.[22] The selectivity of this catalytic transformation also remained insensitive to acetonitrile concentration when using the catalyst precursor $[IrH_2(NCCH_3)_3(PiPr_3)]BF_4$ (**19**), which can be obtained from **18** or the $PiPr_3$ analogue of **1** after removal of the diolefin ligand by hydrogenation.[23]

Conclusions

The reactions of complex $[Ir(COD)(NCCH_3)(PMe_3)]BF_4$ (**1**) toward reactants such as acetonitrile, trimethylphosphine, hydrosilanes, and alkynes have led, under mild conditions, to compounds containing cyclooctadiene, cyclooctadienyl, or cyclooctenyl ligands in eight different coordination modes. This versatility of the COD ligand in the presence of an iridium center is due to the facile and reversible exchange of hydrogens between Ir−H and COD ligand sites. Such an exchange can involve elementary steps of C−H oxidative addition, C−H reductive elimination, insertion, and hydrogen β-elimination and is driven by the electronic and steric demands of the metal fragment. Given that such elementary steps generate reactive hydride ligands and/or coordination vacancies, the equilibria among the various kinetically accessible species can be shifted or intercepted at a given species, by the action of introduced ligands or reactants. This fact seems to be responsible, at least in part, for the variety of reactions and products observed under the conditions of catalytic hydrosilylation of phenylacetylene. Even though the understanding of this unselective catalytic system will require a more profound mechanistic investigation, the observed selectivity dependence due to acetonitrile concentration suggests that COD versatility may well be turned into an advantageous property as a means of achieving versatile and selective catalysts, provided that the various transformations affecting the COD ligand and those involved in the catalytic reactions could be correctly synchronized.

Experimental Section

Equipment. Infrared spectra were recorded in KBr 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 Bruker Avance 300 MHz spectrometer. ^1H (300.13 MHz) and ^{13}C (75.47 MHz) NMR chemical shifts were measured relative to partially deuterated solvent peaks but are reported in ppm relative to tetramethylsilane. ^{31}P (121.48 MHz) and ^{19}F (282 MHz) NMR chemical shifts were measured relative to H_3PO_4 (85%) and $CFCl_3$, respectively. Coupling constants, J, are given in hertz. Generally, spectral assignments were achieved by ^1H 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 the Cs^+ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used as the matrix. Conductivities were measured in ca. 5×10^{-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.[24] The complexes $[Ir(\mu\text{-OMe})(COD)]_2$,[25] $[Ir(\mu\text{-OMe})(TFB)]_2$,[26] and $[IrH_2(NCCH_3)_3(PiPr_3)]BF_4$ (**19**)[23] and the phosphonium salt

(19) The formation of this type of product, formally involving a trans addition of the silane across the C≡C bond, seems to be relatively favored in the presence of late transition metal catalysts (ref 18), although its mechanism remains controversial. See: (a) Crabtree, R. H. *New J. Chem.* **2003**, *27*, 771−772. (b) Trost, B. M.; Ball, T. Z. *J. Am. Chem. Soc.* **2003**, *125*, 30. (c) Martín, M.; Sola, E.; Lahoz, F. J.; Oro, L. A. *Organometallics* **2002**, *21*, 4027−4029.

(20) The cis/trans isomerization of the alkenylsilanes has been found to require very prolonged reaction times under the conditions of this catalysis, and therefore it is nonrelevant for the selectivity.

(21) Silane dehydrodimerization, which constitutes the main reaction catalyzed by **1** in the presence of phenylacetylene and other silanes such as $HSi(OMe)_3$ or $HSi(OEt)_3$, requires the presence of alkyne as hydrogen acceptor. It is worth noting that all previously reported silane dehydrocoupling reactions catalyzed by early or late transition metal complexes are acceptorless. See for example: (a) Harrod, J. F. *Coord. Chem. Rev.* **2000**, *206−207*, 493−531. (b) Gauvin, F.; Harrod, J. F.; Woo, H. G. *Adv. Organomet. Chem.* **1998**, *42*, 363−405. (c) Rosenberg, L.; Davies, C. W.; Yao, J. *J. Am. Chem. Soc.* **2001**, *123*, 5120−5121. (d) Rosenberg, L.; Fryzuk, M. D.; Rettig, S. J. *Organometallics* **1999**, *18*, 958−969. (e) Fontaine, F.-G.; Kadkhodazadeh, T.; Zargarian, D. *Chem. Commun.* **1998**, 1253−1254.

(22) Esteruelas, M. A.; Oro, L. A. *Coord. Chem. Rev.* **1999**, *193−195*, 557−618.

(23) Sola, E.; Navarro, J.; López, J. A.; Lahoz, F. J.; Oro, L. A.; Werner, H. *Organometallics* **1999**, *18*, 3534−3546.

$[HP^iPr_3]BF_4$[23] were prepared by known procedures. $[HPMe_3]BF_4$ was prepared in quantitative yield by slow addition of a solution of HBF_4 (54% in diethyl ether) to a diethyl ether solution of PMe_3. The white solid obtained was filtered, washed with ether, and dried in vacuo. ^{1}H NMR (CD_2Cl_2, 293 K): δ 1.95 (dd, J_{HP} = 15.6, J_{HH} = 5.4, 9H, PC*H*$_3$), 6.44 (dm, J_{HP} = 510.2, J_{HH} = 5.4, 1H, PH). ^{31}P{^{1}H} NMR (CD_2Cl_2, 293 K): δ −4.32 (s). All other reagents were obtained from commercial sources and were used as received. All the compounds whose preparations are described below are air-sensitive in solution.

Preparation of [Ir(1,2,5,6-η-C_8H_{12})(NCCH$_3$)(PMe$_3$)]BF$_4$ (1). A solution of [Ir(μ-OMe)(1,2,5,6-η-C_8H_{12})]$_2$ (150 mg, 0.22 mmol) in acetone/acetonitrile (10/1, 8 mL) was treated with $[HPMe_3]BF_4$ (68 mg, 0.44 mmol) and stirred for 10 min at room temperature. The resulting solution was concentrated to ca. 0.5 mL, and diethyl ether was slowly added to give an orange solid. The solid was separated by decantation, washed with diethyl ether, and dried in vacuo: yield 137 mg (62%). Anal. Calcd for $C_{13}H_{24}BF_4IrNP$: C, 30.96; H, 4.80; N, 2.78. Found: C, 31.06; H, 5.10; N, 3.01. IR (cm^{-1}): 2251 ν(C≡N). ^{1}H NMR ($CDCl_3$, 293 K): δ 1.47 (d, J_{HP} = 9.9, 9H, PCH_3), 1.93 (m, 4H, CH_2), 2.22 (m, 4H, CH_2), 2.68 (s, 3H, $NCCH_3$), 4.0−5.0 (m, 4H, CH). ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): δ −18.06 (s).

Preparation of [Ir(1,2,3,5,6-η-C_8H_{11})(*Z*-C(Ph)=CHPh)(NCCH$_3$)(PMe$_3$)]BF$_4$ (2). A solution of **1** (100 mg, 0.20 mmol) in CH_2Cl_2 (8 mL) was treated with diphenylacetylene (35.6 mg, 0.20 mmol), and the mixture was stirred for 40 min at room temperature. The resulting solution was concentrated to ca. 0.5 mL, and diethyl ether was slowly added to give a pale yellow solid. The solid was separated by decantation, washed with diethyl ether, and dried in vacuo: yield 113 mg (83%). Anal. Calcd for $C_{27}H_{34}NPIrBF_4$: C, 47.51; H, 5.02; N, 2.05. Found: C, 47.32; H, 5.00; N, 1.99. Λ_M (acetone) = 88 Ω^{-1} cm^2 mol^{-1} (1:1). IR (cm^{-1}): 1636, 1595, 1562 ν(C=C). ^{1}H NMR (CD_2Cl_2, 293 K): δ 1.89 (m, 1H, CH_2), 1.96 (d, J_{HP} = 10.5, 9H, PCH_3), 2.01 (s, $NCCH_3$), 2.25 (m, 1H, CH_2), 2.48, 3.64 (both m, 2H each, CH_2), 3.77, 3.93, 4.54, 4.74, 5.05 (all m, 1H each, CH), 6.04 (s, 1H, IrC(Ph)=C*H*Ph), 6.71, 6.84 (both m, 2H each, CH), 6.97 (m, 1H, CH), 7.03 (m, 2H, CH), 7.17 (m, 1H, CH), 7.26 (m, 2H, CH). ^{31}P{^{1}H} NMR (CD_2Cl_2, 293 K): δ −35.87 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2, 293 K): δ 2.67 (s, $NCCH_3$), 16.85 (d, J_{CP} = 39.1, PCH_3), 20.82 (d, J_{CP} = 4.2, CH_2), 27.81 (d, J_{CP} = 1.6, CH_2), 31.30 (s, CH_2), 47.61 (s, CH), 51.63 (d, J_{CP} = 16.9, CH), 68.97 (d, J_{CP} = 5.8, CH), 102.55 (d, J_{CP} = 0.8, CH), 103.32, 125.46, 125.55, 126.49, 127.61, 128.18 (all s, CH) 126.0 (s, N*C*CH$_3$), 131.20 (d, J_{CP} = 10.0, Ir*C*(Ph)=CHPh), 132.50 (d, J_{CP} = 7.3, IrC(Ph)=*C*HPh), 139.32, 148.13 (both s, C).

Preparation of [Ir(1-κ-4,5,6-η-C_8H_{12})(NCCH$_3$)$_2$(PMe$_3$)]BF$_4$ (3). A solution of **1** (200 mg, 0.40 mmol) in 1,2-dichloroethane (8 mL) was treated with 1 mL of acetonitrile, and the mixture was stirred for 12 h at 333 K. The resulting solution was concentrated to ca. 0.5 mL, and diethyl ether was slowly added to give a pale yellow solid. The solid was separated by decantation, washed with diethyl ether, and dried in vacuo: yield 169 mg (78%). Anal. Calcd for $C_{15}H_{27}N_2PIrBF_4$: C, 33.03; H, 4.99; N, 5.14. Found: C, 32.54; H, 4.79; N, 4.95. ^{1}H NMR ($CDCl_3$, 293 K): δ 1.00, 1.08, 1.24, 1.33, 1.66, (all m, 1H each, CH_2), 1.68 (d, J_{HP} = 10.0, 9H, PCH_3), 1.70, 1.76, 1.78 (all m, 1H each, CH_2), 1.93 (m, 1H, CH), 2.26 (s, 3H, $NCCH_3$), 2.60 (d, J_{HP} = 1.4, 3H, $NCCH_3$), 4.05 (m, 1H, CH), 4.32 (td, J_{HH} = 8.1, J_{HP} = 1.5, 1H, CH), 5.39 (m, 1H, CH). ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): δ −34.65 (s). ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K): δ 2.65, 3.64 (both s, N*C*CH$_3$), 15.62 (d J_{CP} = 34.9, PCH_3), 22.61 (d, J_{CP} = 3.7, CH_2), 22.74 (d, J_{CP} = 4.4, CH), 27.21 (s, CH_2), 45.28 (d, J_{CP} = 2.3, CH_2), 50.62 (d, J_{CP} = 9.7, CH_2), 54.41 (d, J_{CP} = 1.4, CH), 81.16 (d, J_{CP} = 30.0, CH), 96.35 (d, J_{CP} = 0.8, CH), 119.00, 122.11 (both s, N*C*CH$_3$).

Preparation of [Ir(1-κ-4,5,6-η-C_8H_{12})(NCCH$_3$)(PMe$_3$)$_2$]BF$_4$ (4a). A solution of **3** (100 mg, 0.18 mmol) in CH_2Cl_2 (2 mL) at 258 K was treated with PMe_3 (20 mL, 0.18 mmol), and the mixture was stirred for 5 min. Diethyl ether was slowly added to produce a pale yellow solid. The solid was separated by decantation, washed with diethyl ether, and dried in vacuo: yield 89 mg (83%). Anal. Calcd for $C_{16}H_{33}NP_2IrBF_4$: C, 33.11; H, 5.73; N, 2.41. Found: C, 32.94; H, 5.61; N, 2.48. Λ_M (acetone) = 96 Ω^{-1} cm^2 mol^{-1} (1:1). MS (FAB+, *m*/*z* (%)): 494 (10) [M$^+$]. ^{1}H NMR ($CDCl_3$, 293 K): δ 1.31 (d, J_{HP} = 7.5, 9H, PCH_3), 1.62 (m, 2H, CH_2), 1.68 (m, 1H, CH), 1.75 (d, J_{HP} = 9.6, 9H, PCH_3), 1.97, 2.04, 2.31 (all m, 2H each, CH_2), 2.67 (s, 3H, $NCCH_3$), 3.74, 4.22, 5.00 (all m, 1H each, CH). ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): δ −51.60, −40.91 (both d, J_{PP} = 19.9). ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K): δ 4.11 (s, N*C*CH$_3$), 13.62 (d, J_{CP} = 26.7, PCH_3), 18.24 (dd, J_{CP} = 35.3, 3.4, PCH_3), 24.14 (dd, J_{CP} = 5.8, 3.5, CH_2), 30.32 (d, J_{CP} = 8.5, CH_2), 36.44 (dd, J_{CP} = 74.1, 5.1, CH), 43.27 (s, CH_2), 52.06 (d, J_{CP} = 10.7, CH_2), 55.42 (s, CH), 78.18 (d, J_{CP} = 30.2, CH), 90.21 (s, CH), 121.85 (s, N*C*CH$_3$).

Preparation of [Ir(1-κ-4,5,6-η-C_8H_{12})(NCCH$_3$)(PMe$_3$)$_2$]BF$_4$ (4b). A solution of **3** (100 mg, 0.18 mmol) in CH_2Cl_2 (8 mL) was treated with PMe_3 (19 mL, 0.18 mmol), and the mixture was stirred for 24 h at room temperature. The resulting solution was filtered through Celite and concentrated to ca. 0.5 mL. Addition of diethyl ether produced a pale yellow solid, which was separated by decantation, washed with diethyl ether, and dried in vacuo: yield 80 mg (73%). Anal. Calcd for $C_{16}H_{33}NP_2IrBF_4$: C, 33.11; H, 5.73; N, 2.41. Found: C, 32.91; H, 5.65; N, 2.17. Λ_M (acetone) = 95 Ω^{-1} cm^2 mol^{-1} (1:1). ^{1}H NMR (CD_2Cl_2, 293 K): δ 1.45, 1.48 (both m, 2H each, CH_2), 1.65 (m, 1H, CH), 1.75 (d, J_{HP} = 9.3, 18H, PCH_3), 1.81, 1.90 (both m, 2H each, CH_2), 2.37 (s, 3H, $NCCH_3$), 4.42 (m, 1H, CH), 5.00 (m, 2H, CH). ^{31}P{^{1}H} NMR (CD_2Cl_2, 293 K): δ −46.35 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2, 293 K): δ 2.80 (s, N*C*CH$_3$), 18.04 (dd, J_{CP} = 34.5, 1.6, PCH_3), 20.16 (t, J_{CP} = 4.2, CH), 23.72, 51.26 (both m, CH_2), 75.43 (dd, J_{CP} = 30.9, 1.5, CH), 102.43 (t, J_{CP} = 1.8, CH), 118.64 (s, N*C*CH$_3$).

Preparation of [Ir(1-κ-4,5,6-η-C_8H_{12})(PMe$_3$)$_3$]BF$_4$ (5). A solution of **3** (100 mg, 0.18 mmol) in CH_2Cl_2 (8 mL) was treated with PMe_3 (38 mL, 0.36 mmol) and the mixture was stirred for 24 h at room temperature. The resulting solution was filtered through Celite and concentrated to ca. 0.5 mL. Addition of diethyl ether produced a white solid, which was separated by decantation, washed with diethyl ether, and dried in vacuo: yield 84 mg (76%). Anal. Calcd for $C_{17}H_{39}P_3IrBF_4$: C, 33.18; H, 6.38. Found: C, 33.03; H, 6.45. Λ_M (acetone) = 89 Ω^{-1} cm^2 mol^{-1} (1:1). MS (FAB+, *m*/*z* (%)): 529 (100) [M$^+$]. ^{1}H NMR ($CDCl_3$, 293 K): δ 1.16 (d, J_{HP} = 12.3, 9H, PCH_3), 1.39 (m, 2H, CH_2), 1.68 (d, J_{HP} = 9.3, 18H, PCH_3), 1.78, 1.87 (both m, 2H each, CH_2), 1.95 (m, 1H, CH), 2.01 (m, 2H, CH_2), 4.15 (m, 1H, CH), 4.48 (m, 2H, CH). ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): δ −59.52 (t, J_{PP} = 20.3), −53.23 (d, J_{PP} = 20.3). ^{13}C{^{1}H} RMN ($CDCl_3$, 293 K): δ 16.21 (dt, J_{CP} = 27.8, 1.0, PCH_3), 20.93 (ddd, J_{CP} = 35.4, 3.2, 2.0, PCH_3), 26.13 (ddd, J_{CP} = 6.6, 3.3, 0.8, CH_2), 33.05 (dt, J_{CP} = 67.7, 5.0, CH), 51.51 (dd, J_{CP} = 9.9, 4.7, CH_2), 74.48 (dd, J_{CP} = 30.2, 1.3, CH), 96.07 (t, J_{CP} = 1.7, CH).

[Ir(1,4-κ-,2,3-η-C_8H_{12})(PMe$_3$)$_3$]BF$_4$ (7) and [IrH(1,2,3-η-C_8H_{11})(PMe$_3$)$_3$]BF$_4$ (8). A solution of **6** (100 mg, 0.16 mmol) in 1,2-dichloroethane (8 mL) was stirred for 3 h at 333 K. The resulting solution was evaporated to dryness, and the residue was dissolved in CD_2Cl_2. The spectroscopic analysis of the resulting solution revealed the presence of compounds **6**, **7**, and **8** in molar ratio 2:1:1. Partial data for **7**: ^{1}H NMR (CD_2-

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Cl_2, 293 K): δ 1.52 (d, J_{HP} = 8.2, 18H, PCH_3), 1.82 (d, J_{HP} = 9.2, 9H, PCH_3), 3.15, 4.91 (both m, 2H each, CH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ −56.48, −46.60 (both br). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ 18.62 (m, PCH_3), 20.91 (dt, J_{CP} = 34.6, 2.7, PCH_3), 43.19 (m, CH), 89.12 (dt, J_{CP} = 5.6, 2.1, CH). Partial data for **8**: ^1H NMR (CD_2Cl_2, 293 K): δ −14.11 (dt, J_{HP} = 148.2, 21.9, 1H, Ir−H), 1.38 (dd, J_{HP} = 7.7, 0.9, 9H, PCH_3), 1.85 (d, J_{HP} = 9.7, 18H, PCH_3), 3.63, 4.15, 4.30, 5.04, 6.31 (all m, 1H each, CH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ −55.51 (dd, J_{PP} = 20.5, 20.8), −52.85 (d, J_{PP} = 20.5), −51.04 (d, J_{PP} = 20.8). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ 15.39 (dt, J_{CP} = 28.8, 1.7, PCH_3), 23.45 (ddd, J_{CP} = 36.9, 3.9, 1.7, PCH_3), 23.54 (ddd, J_{CP} = 37.1, 3.8, 1.7, PCH_3), 52.92 (d, J_{CP} = 24.7, CH), 55.13 (d, J_{CP} = 26.9, CH), 93.02 (d, J_{CP} = 0.9, CH), 122.92 (d, J_{CP} = 4.8, CH), 135.84 (dd, J_{CP} = 4.4, 0.8, CH).

Preparation of [IrH$_2$(1,2,5,6-η-C$_8$H$_{12}$)(NCCH$_3$)(PMe$_3$)]BF$_4$ (9). A solution of **1** (125 mg, 0.20 mmol) in acetone (4 mL) was stirred under dihydrogen atmosphere (P = 1 atm) for 1 h at 253 K. The resulting pale yellow solution was concentrated to ca. 0.5 mL, and diethyl ether was slowly added to give a white solid. The solid was separated by decantation, washed with ether, and dried in vacuo: yield 59 mg (70%). Anal. Calcd for $C_{13}H_{26}BF_4IrNP$: C, 30.84; H, 5.18; N, 2.77. Found: C, 31.14; H, 4.98; N, 2.33. IR (cm^{-1}): 2330 ν(C≡N), 2209 ν(Ir−H). ^1H NMR (CD_2Cl_2, 243 K): δ −17.01 (d, J_{HP} = 18.0, 1H, Ir−H), −12.70 (d, J_{HP} = 21.0, 1H, Ir−H), 1.62 (d, J_{HP} = 11.0, 9H, PCH_3), 1.98−2.58 (m, 8H, CH_2), 2.64 (s, 3H, $NCCH_3$), 4.57 (m, 2H, CH), 4.78 (m, 1H, CH), 5.33 (m, 1H, CH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 243 K): δ −34.21 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 243 K): δ 2.77 (s, NCCH_3), 18.22 (d, J_{CP} = 40.7, PCH_3), 27.75 (s, CH_2), 29.27 (d, J_{CP} = 1.2, CH_2), 29.47 (d, J_{CP} = 2.3, CH_2), 34.81 (s, CH_2), 88.65 (s, CH), 89.24 (d, J_{CP} = 7.6, CH), 89.68 (d, J_{CP} = 5.4, CH), 89.94 (s, CH), 123.63 (s, NCCH_3).

Preparation of [IrH(1-κ-4,5-η-C$_8$H$_{13}$)(NCCH$_3$)$_2$(PMe$_3$)]BF$_4$ (10). A solution of **1** (125 mg, 0.20 mmol) in acetonitrile (4 mL) was stirred under dihydrogen atmosphere (P = 1 atm) for 15 min at room temperature. The solution was concentrated to ca. 0.5 mL, and diethyl ether was added to give a yellow solid. When the solid was separated by decantation, washed with diethyl ether, and taken to dryness, it transformed into a yellow oil. This oil could be dissolved and precipitated as a yellow solid, although again it became an oil after isolation. The NMR analysis of this oil in $CDCl_3$ at 233 K showed the presence of **10** as the only reaction product. ^1H NMR ($CDCl_3$, 233 K): δ −20.35 (dd, J_{HP} = 22.2, J_{HH} = 3.9, 1H, Ir−H), 1.11 (m, 2H, CH_2), 1.55 (m, 1H, CH), 1.67 (d, J_{HP} = 8.7, 9H, PCH_3), 1.70, 1.80, 2.05 (all m, 2H each, CH_2), 2.24, 2.43 (both s, 3H each, $NCCH_3$), 2.45, 3.21 (both m, 1H each, CH_2), 4.75, 4.78 (both m, 1H each, CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 233 K): δ −29.79 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 233 K): δ 2.77, 3.14 (both s, NCCH_3), 4.81 (d, J_{CP} = 3.7, Ir−CH), 15.25 (d, J_{CP} = 38.7, PCH_3), 24.75, 30.59, 39.05 (all s, CH_2), 24.88 (d, J_{CP} = 2.3, CH_2), 41.23 (d, J_{CP} = 5.3, CH_2), 84.32 (d, J_{CP} = 10.1, CH), 87.40 (d, J_{CP} = 14.7, CH), 118.36, 121.48 (both s, NCCH_3).

Preparation of [IrH(SiEt$_3$)(1,2,5,6,-η-C$_8$H$_{12}$)(NCCH$_3$)(PMe$_3$)]BF$_4$ (11). A solution of **1** (125 mg, 0.20 mmol) in CH_2Cl_2 (2 mL) at 233 K was treated with $HSiEt_3$ (31 μL, 0.20 mmol) and stirred for 10 min. The resulting yellow solution was concentrated to ca. 0.5 mL, and diethyl ether was added to give a pale yellow solid. The solid was separated by decantation, washed with diethyl ether, and dried in vacuo: yield 83 mg (67%). Anal. Calcd for $C_{19}H_{40}BF_4IrNPSi$: C, 36.77; H, 6.50; N, 2.26. Found: C, 37.27; H, 6.91; N, 2.41. IR (cm^{-1}): 2206 ν(Ir−H). ^1H NMR ($CDCl_3$, 233 K): δ −17.19 (d, J_{HP} = 18.0, 1H, Ir−H), 0.51, 0.68 (both m, 3H each, SiCH_2CH_3), 0.87 (m, 9H, $SiCH_2CH_3$), 1.65 (d, J_{HP} = 10.3, 9H, PCH_3), 2.00 (m, 1H, CH_2), 2.24−2.60 (m, 4H, CH_2), 2.63 (s, 3H, $NCCH_3$), 2.67 (m, 2H, CH_2), 3.08 (m, 1H, CH_2), 4.39, 5.11, 5.19, 5.29 (all m, 1H each, CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 233 K): δ −35.4 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 233 K): δ 4.77 (s, NCCH_3), 7.65 (m, SiCH_2-CH_3), 9.39 (s, $SiCH_2CH_3$), 17.40 (d, J_{CP} = 40.2, PCH_3), 29.41, 28.59, 36.72 (all s, CH_2), 87.56 (d, J_{CP} = 11.9, CH), 89.60 (s, CH), 101.65 (d, J_{CP} = 9.6, CH), 102.93 (s, CH), 125.03 (s, NCCH_3).

Preparation of [IrH{Si(OMe)$_3$}(1,2,5,6-η-C$_8$H$_{12}$)(NCCH$_3$)(PMe$_3$)]BF$_4$ (12). The compound was prepared as a pale yellow solid following the procedure described for **11**, by using **1** (125 mg, 0.25 mmol) and $HSi(OMe)_3$ (63 μL, 0.50 mmol): yield 76 mg (61%). Anal. Calcd for $C_{16}H_{34}BF_4IrNO_3PSi$: C, 30.67; H, 5.47; N, 2.24. Found: C, 30.57; H, 5.46; N, 2.14. IR (cm^{-1}): 2202 ν(Ir−H). ^1H NMR (CD_2Cl_2, 293 K): δ −17.36 (d, J_{HP} = 15.9, 1H, Ir−H), 1.68 (d, J_{HP} = 11.1, 9H, PCH_3), 2.61 (d, J_{CP} = 1.2, 3H, $NCCH_3$), 2.30−2.90 (m, 8H, CH_2), 3.50 (s, 9H, $SiOCH_3$), 4.76, 5.11, 5.35, 5.45 (all m, 1H each, CH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ −33.88 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 293 K): δ 3.75 (s, NCCH_3), 17.15 (d, J_{CP} = 40.0, PMe_3), 27.28 (d, J_{CP} = 3.0, CH_2), 30.11 (s, CH_2), 30.38 (d, J_{CP} = 2.5, CH_2), 33.94 (s, CH_2), 50.45 (s, $SiOCH_3$), 90.36 (d, J_{CP} = 11.0, CH), 91.92 (d, J_{CP} = 9.0, CH), 103.21, 103.65 (both s, CH), 124.51 (s, NCCH_3).

Preparation of [IrH(SiPh$_3$)(1,2,5,6-η-C$_8$H$_{12}$)(NCCH$_3$)(PMe$_3$)]BPh$_4$ (13). The procedure described for **11**, using compound **1** (125 mg, 0.25 mmol) and $HSiPh_3$ (64.5 mg, 0.25 mmol) as starting materials, afforded a yellow oil. This oil was dissolved in methanol at 233 K and treated with an excess of $NaBPh_4$ to afford a yellow solid. The solid was separated by decantation, washed with methanol, and dried in vacuo: yield 127 mg (51%). Anal. Calcd for $C_{55}H_{60}BIrNPSi$: C, 66.25; H, 6.06; N, 1.40. Found: C, 66.67; H, 6.32; N, 1.89. IR (cm^{-1}): 2264 ν(Ir−H). ^1H NMR (CD_2Cl_2, 243 K): δ −16.53 (d, J_{HP} = 18.0, 1H, Ir−H), 0.93 (d, J_{HP} = 10.4, 9H, PCH_3), 1.60 (m, 2H, CH_2), 1.80 (s, 3H, $NCCH_3$), 2.02, 2.14, 2.39, 2.49, 2.78, 3.13 (all m, 1H each, CH_2), 3.58 (m, 1H, CH), 4.75 (m, 2H, CH), 5.16 (m, 1H, CH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 243 K): δ −39.93 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 243 K): δ 2.86 (s, NCCH_3), 16.00 (d, J_{CP} = 41.0, PCH_3), 25.85, 25.97, 30.34, 38.20 (all s, CH_2), 91.55 (d, J_{CP} = 8.0, CH), 92.48 (d, J_{CP} = 11.8, CH), 98.70, 103.02 (both s, CH), 124.55 (s, NCCH_3). The NMR signals corresponding to phenyl groups have been omitted.

[IrH(SiPh$_3$)(1,2,4,5-η-C$_8$H$_{12}$)(NCCH$_3$)(PMe$_3$)]BPh$_4$ (14). A NMR tube containing a solution of **13** in CD_2Cl_2 (0.5 mL) was placed at 273 K for 4 h. After this period of time the NMR spectra of the resulting solution revealed the presence of a mixture containing compound **13** (ca. 50% of the reaction mixture) and two new species **14** and **15** in approximately 1:1 molar ratio. The evolution of this solution at 293 K for 1 h quantitatively produced complex **15**. Partial data for **14**: ^1H NMR (CD_2Cl_2, 233 K): δ −16.51 (d, J_{HP} = 18.0, 1H, Ir−H), 1.53 (d, J_{HP} = 10.9, 9H, PCH_3), 2.11 (s, 3H, $NCCH_3$), 3.60, 4.36 (both m, 1H each, CH), 4.90 (m, 2H, CH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 233 K): δ −35.46 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 233 K): δ 3.28 (s, NCCH_3), 16.79 (d, J_{CP} = 40.9, PCH_3), 26.79, 27.06, 29.56, 36.86 (all s, CH_2), 90.03 (d, J_{CP} = 9.4, CH), 91.61 (d, J_{CP} = 11.4, CH), 99.45, 103.59 (both s, CH), 123.41 (s, NCCH_3).

Preparation of [IrH(SiPh$_3$)(1,2,3,4-η-C$_8$H$_{12}$)(NCCH$_3$)(PMe$_3$)]BPh$_4$ (15). A solution of **13** (100 mg, 0.10 mmol) in CH_2Cl_2 (2 mL) was allowed to react at room temperature for 1 h. The resulting solution was concentrated to ca. 0.5 mL, and diethyl ether was added to give a pale yellow solid. The solid was separated by decantation, washed with diethyl ether, and dried in vacuo: yield 83 mg (83%). Anal. Calcd for $C_{55}H_{60}$-$BIrNPSi$: C, 66.25; H, 6.06; N, 1.40. Found: C, 66.05; H, 5.74; N, 1.20. ^1H NMR (CD_2Cl_2, 233 K): δ −16.46 (d, J_{HP} = 12.9, 1H, Ir−H), 1.31 (d, J_{HP} = 10.8, 9H, PCH_3), 1.83 (s, 3H, $NCCH_3$), 2.25−2.65 (m, 8H, CH_2), 4.40 (m, 2H, CH), 4.81, 4.98 (both m, 1H each, CH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 233 K): δ −32.88 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 233 K): δ 2.56 (s, NCCH_3), 14.41 (d, J_{CP} = 40.6, PCH_3), 27.76, 29.60, 30.89, 33.05 (all s, CH_2), 91.23, 92.65 (both s, CH), 93.91 (d, J_{CP} = 13.9, CH), 98.15 (d, J_{CP} =

11.5, CH), 122.90 (s, N*C*CH$_3$). The NMR signals corresponding to phenyl groups have been omitted.

Preparation of [IrH(C≡CPh)(1,2,5,6-η-C$_8$H$_{12}$)(NCCH$_3$)(PMe$_3$)]BF$_4$ (16). A solution of **1** (125 mg, 0.20 mmol) in CH_2Cl_2 (2 mL) at 253 K was treated with phenylacetylene (22 μL, 0.20 mmol) and allowed to react for 30 min. The resulting solution was concentrated to ca. 0.5 mL, and diethyl ether was added to give a pale yellow solid. The solid was separated by decantation, washed with diethyl ether, and dried in vacuo: yield 87 mg (72%). Anal. Calcd for $C_{21}H_{30}BF_4IrNP$: C, 41.60; H, 4.99; N, 2.31. Found: C, 42.01; H, 5.25; N, 2.25. IR (cm^{-1}): 2212 ν(Ir−H), 2124 ν(C≡C). ^{1}H NMR (CD_2Cl_2, 233 K): δ −16.90 (d, J_{HP} = 13.2, 1H, Ir−H), 1.75 (d, J_{HP} = 11.7, 9H, PC*H*$_3$), 2.20−2.60 (m, 8H, C*H*$_2$), 2.64 (s, 3H, NCC*H*$_3$), 4.76, 4.83, 4.98, 5.55 (all m, 1H each, CH), 7.10−7.40 (m, 5H, CH). ^{31}P{^{1}H} NMR (CD_2Cl_2, 233 K): δ −30.12 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2, 233 K): δ 4.71 (s, NC*C*H$_3$), 15.42 (d, J_{CP} = 41.9, PC*H*$_3$), 28.03, 31.74, 32.01, 33.50 (all s, C*H*$_2$), 79.91 (d, J_{CP} = 13.6, Ir−*C*≡CPh), 89.22 (s, CH), 98.03 100.93 (both d, J_{CP} = 11.3, CH), 102.21 (s, Ir−C≡*C*Ph), 122.91 (s, N*C*CH$_3$), 126.89 (s, CH), 127.21 (s, C), 128.69, 131.90 (both s, CH).

Preparation of [Ir(1,4-κ-CH=C(Ph)CH=CPh)(1,2,5,6-η-C$_8$H$_{12}$)(NCCH$_3$)(PMe$_3$)]BF$_4$ (17). A solution **16** (120 mg, 0.20 mmol) in CH_2Cl_2 (2 mL) was treated with phenylacetylene (22 μL, 0.20 mmol), and the mixture was stirred for 4 h at 273 K. The resulting solution was concentrated to ca. 1 mL, and diethyl ether was slowly added to produce a white microcrystalline solid. The solid was separated by decantation, washed with diethyl ether, and dried in vacuo. Yield: 85 mg (60%). Anal. Calcd for $C_{29}H_{36}BF_4IrNP\cdot0.5\ C_3H_6O$: C, 49.67; H, 5.33; N, 1.90. Found: C, 50.16; H, 5.51; N, 2.18. ^{1}H NMR ($CDCl_3$, 293 K): δ 1.47 (d, J_{HP} = 10.8, 9H, PC*H*$_3$), 2.22 (d, J_{HP} = 0.9, 3H, NCC*H*$_3$), 2.3−2.8 (m, 8H, C*H*$_2$), 4.63, 4.73, 5.19, 5.47 (all m, 1H each, CH), 6.77 (dd, J_{HH} = 3.0, J_{HP} = 0.9, 1H, CH=C(Ph)C*H*=CPh), 6.94 (m, 2H, CH), 7.18 (m, 2H, CH), 7.28 (m, 4H, CH), 7.42 (m, 2H, CH), 7.49 (dd, J_{HP} = 6.0, J_{HH} = 3.0, 1H, C*H*=C(Ph)CH=CPh). ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): δ −32.05 (s). ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K): δ 3.77 (s, NC*C*H$_3$), 12.65 (d, J_{CP} = 42.3, PC*H*$_3$), 27.54 (s, C*H*$_2$), 28.01 (d, J_{CP} = 3.0, C*H*$_2$), 30.65 (d, J_{CP} = 4.1, C*H*$_2$), 31.91 (s, C*H*$_2$), 100.53 (s, CH), 101.22 (d, J_{CP} = 11.0, CH), 101.75 (s, CH), 111.58 (d, J_{CP} = 11.5, CH), 123.75 (s, N*C*CH$_3$), 125.21, 126.01, 126.53, 126.84, 128.00 (all s, CH), 128.01 (d, J_{CP} = 15.0, *C*H=C(Ph)-CH=CPh), 128.70 (s, CH), 139.25 (s, CH=C(Ph)*C*H=CPh), 139.64, 148.32 (both s, C), 155.68 (d, J_{CP} = 3.5, CH=*C*(Ph)-CH=CPh), 158.57 (d, J_{CP} = 11.1, CH=C(Ph)CH=*C*Ph).

Preparation of [Ir(TFB)(NCCH$_3$)(P*i*Pr$_3$)]BF$_4$ (18). The compound was prepared following the procedure described for **1** by using [Ir(μ-OMe)(TFB)]$_2$ (150.0 mg, 0.17 mmol) and [HP*i*Pr$_3$]BF$_4$ (82.8 mg, 0.33 mmol): yield 188 mg (80%). Anal. Calcd for $C_{23}H_{30}BF_8IrNP$: C, 39.10; H, 4.28; N, 1.98. Found: C, 38.72; H, 4.08; N, 1.89. ^{1}H NMR (acetone-d_6, 293 K): δ 1.28 (dd, J_{HP} = 14.1, J_{HH} = 7.2, 9H, PCHC*H*$_3$), 2.30 (m, 3H, PC*H*CH$_3$), 2.68 (s, 3H, NCCH$_3$), 3.45 (br, 2H, CH), 4.45 (br, 2H, CH), 5.81 (m, 2H, CH). ^{31}P{^{1}H} NMR (acetone-d_6, 293 K): δ 32.62 (s). ^{19}F NMR (acetone-d_6, 293 K): δ −162.53 (m, 2F, TFB), −152.83, −152.78 (both s, ^{11}BF$_4$ and ^{10}BF$_4$), −149.29 (m, 2F, TFB).

Catalytic Experiments. The reactions were carried out under argon in 1,2-dichloroethane with magnetic stirring. The equipment consisted of a 50 mL two-necked flask fitted with a condenser and a septum to allow sampling without opening the system. In a typical procedure, 4 mL of reactants solution (PhC≡CH and silane) in 1,2-dichloroethane was injected into a solution of the catalyst precursor in 4 mL of the same solvent. The flask was then immersed in a thermostated bath. Positive pressure of argon (ca. 1.1 atm) was maintained in the reaction mixture during the runs to exclude the penetration of oxygen during sampling. The progress of the reactions was followed by GC on a Hewlett-Packard HP-5890-Series II gas chromatograph with a FID detector and using a HP-Ultra 1 column (cross-linked methyl silicone gum, 25 m × 0.32 mm × 0.17 μm) at an initial temperature of 353 K for 4.5 min followed by a rate ramp of 22 K/min to a final temperature of 493 K. Calibration of the detector response to the substrates and products was made by comparing the GC integrals with those obtained in the same samples by ^{13}C{^{1}H} NMR, setting the relaxation delay between pulses to 20 s. Products were identified by ^{1}H NMR and GC−MS analysis on the mixtures of reaction products.

Structural Analysis of Complexes 2, 4b, and 17. X-ray data were collected at 100.0(2) K on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using ω scans (0.3°). Data were collected over the complete sphere by a combination of four sets and corrected for absorption using a multiscan method applied with the SADABS program.[27] The structures were solved by the Patterson method. Refinement, by full-matrix least squares on F^2 using SHELXL97,[28] was similar for all complexes, including isotropic and subsequently anisotropic displacement parameters for all non-hydrogen nondisordered atoms. Particular details concerning the presence of solvent, static disorder, and hydrogen refinement are listed below. All the highest electronic residuals were observed in close proximity of the Ir centers and make no chemical sense.

Crystal Data for 2. $C_{27}H_{34}BF_4IrNP$, M = 682.53; colorless plate, 0.22 × 0.10 × 0.02 mm^3; monoclinic, $P2_1/n$; a = 16.711(3) Å, b = 13.970(3) Å, c = 11.966(2) Å, β = 110.471(8)°; Z = 4; V = 2617.1(8) Å^3; D_c = 1.732 g cm^{-3}; μ = 5.208 mm^{-1}, minimum and maximum transmission factors 0.474 and 0.652; $2\theta_{max}$ = 56.9°; 30 313 reflections collected, 6197 unique [R(int) = 0.0503]; number of data/restraints/parameters 6197/0/344; final GoF 0.944, R1 = 0.0309 [4717 reflns $I > 2\sigma(I)$], wR2 = 0.0622 for all data; largest difference peak 2.097 e Å^{-3}. Hydrogen atoms were included in calculated positions and refined riding on carbon atoms with the thermal parameter related to bonded atoms, or in observed positions and refined freely.

Crystal Data for 4b. $C_{16}H_{33}BF_4IrNP_2$, M = 580.38; colorless irregular block, 0.20 × 0.10 × 0.08 mm^3; monoclinic, $P2_1/c$; a = 9.9665(8) Å, b = 12.3631(10) Å, c = 16.6245(14) Å, β = 90.775(1)°; Z = 4; V = 2048.2(3) Å^3; D_c = 1.882 g cm^{-3}; μ = 6.710 mm^{-1}, minimum and maximum transmission factors 0.388 and 0.545; $2\theta_{max}$ = 57.8°; 24 476 reflections collected, 4937 unique [R(int) = 0.0382]; number of data/restraints/parameters 4937/0/245; final GoF 0.900, R1 = 0.0251 [4168 reflns $I > 2\sigma(I)$], wR2 = 0.0492 for all data; largest difference peak 2.820 e Å^{-3}. Hydrogen atoms were included in calculated positions and refined riding on carbon atoms, or in observed positions and refined freely with the thermal parameter related to bonded atoms.

Crystal Data for 17. $C_{29}H_{36}BF_4IrNP\cdot0.5\ C_3H_6O$, M = 737.61; colorless irregular block, 0.14 × 0.12 × 0.10 mm^3; monoclinic, $C2/c$; a = 33.404(3) Å, b = 11.7355(11) Å, c = 32.244(3) Å, β = 90.264(2)°; Z = 16; V = 12640(2) Å^3; D_c = 1.550 g cm^{-3}; μ = 4.321 mm^{-1}, minimum and maximum transmission factors 0.307 and 0.684; $2\theta_{max}$ = 55°; 69 711 reflections collected, 14 435 unique [R(int) = 0.1322]; number of data/restraints/parameters 69 711/226/779; final GoF 1.023, R1 = 0.0674 [8953 reflns $I > 2\sigma(I)$], wR2 = 0.1484 for all data; largest difference peak 2.355 e Å^{-3}. A BF$_4$ anion was found to be disordered by rotation around a B−F bond. This anion and the two solvent molecules were refined with retraints in the geometry and in the thermal parameters. Hydrogen atoms were included in calculated positions and refined riding on the

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corresponding carbon atoms, or in observed positions and refined freely.

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Supporting Information Available: ^{1}H-COSY, ^{1}H-NOESY, and ^{1}H,^{13}C-HSQC NMR spectra of a mixture of **6**, **7**, and **8**, and details of the X-ray crystallographic study of **2**, **4b**, and **17** (PDF). A crystallographic information file (CIF) on the structural analysis of complexes **2**, **4b**, and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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