Binuclear Oxidative Addition of Hydrogen in Diamidonaphthalene-Bridged Diiridium Complexes

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

Abstract: The complex $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CO)_2(P\textit{i}Pr_3)_2]$ (**1**) reacts with triflic acid to give $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)H(CO)_2(P\textit{i}Pr_3)_2](CF_3SO_3)$ (**2**), which contains a terminal hydride. Complex **2** reacts with NEt_3 to reform **1**, but it can also react with a second equivalent of triflic acid to give the asymmetric dihydride complex $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(\mu\text{-}H)H(OSO_2CF_3)(CO)_2(P\textit{i}Pr_3)_2](CF_3SO_3)$ (**3**). The triflate ligand of **3** can be replaced by acetone or acetonitrile to give $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(\mu\text{-}H)H(OC(CH_3)_2)(CO)_2(P\textit{i}Pr_3)_2](CF_3SO_3)_2$ (**4**) and $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(\mu\text{-}H)H(NCCH_3)(CO)_2(P\textit{i}Pr_3)_2](CF_3SO_3)_2$ (**5**), respectively. The X-ray structure of **4** revealed the presence of a terminal and an asymmetric bridging hydride. The hydrido ligands of **2**–**4** undergo H/D exchange in D_2O or $[D_6]$acetone. The monohydride **2** reacts with H_2 to give two isomeric compounds of stoichiometry $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(\mu\text{-}H)H_2(CO)_2(P\textit{i}Pr_3)_2](CF_3SO_3)$ (**7a, 7b**), in which a molecule of hydrogen has been added to form a terminal and a bridging hydride. In the presence of NEt_3, **7a** and **7b** isomerize into the symmetric complex **8** which presents a *trans* arrangement of the hydrides. Oxidation of complex **1** allows the preparation of the iridium(II) species $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(OSO_2CF_3)_2(CO)_2(P\textit{i}Pr_3)_2]$ (**9**). The triflate ligands of **9** can be replaced by tetrahydrothiophene or acetonitrile to give complexes **10** and **11**, respectively. The acetonitrile complexes can exist as three different isomers: two have C_2 symmetry (**11a**, **11c**) and one is asymmetric (**11b**); the latter has been characterized by X-ray diffraction. The kinetic study of the isomerization reactions reveals these processes to be strictly intramolecular. The reaction of **9** with hydrogen gives different final products, depending on the solvent. Thus, in $CDCl_3$ the dihydride **3** is obtained, whereas in acetone a mixture of the trihydrides **7a** and **7b** is formed.

Keywords: hydrido complexes · iridium · metal–metal interactions · NMR spectroscopy

Introduction

The expected cooperation between metal atoms to perform novel chemical transformations is the basic idea that promotes most of the research in binuclear complexes.[1, 2] Such cooperation can result from electronic influences between metal centers behaving essentially as in mononuclear complexes[3, 4] or, alternatively, can be the consequence of an overall change in the reactivity due to the proximity of both metals.

Clear examples of the latter are found in the chemistry of binuclear rhodium and iridium compounds, which very frequently give rise to complexes in oxidation state II,[5] and which is very unusual for mononuclear species.[6] This may have a positive influence for some transformations but may also introduce limitations with regard to the mononuclear complexes. Thus, whilst the activation of molecules such as halogens or halocarbons by diiridium(I) complexes has been extensively documented,[7] the reported examples of concerted activations of H–H bonds are very scarce.[8] This is in contrast with the behavior of mononuclear Ir^I complexes, in which the oxidative addition of hydrogen is perhaps the most typical reaction. This lack of results in concerted oxidations coincides with early theoretical investigations which indicated that oxidative additions to diiridium d^8–d^8 centers are difficult processes,[9] which should preferably take place at a single metal atom. However, the same investigations proposed that these additions could be more favorable in d^7–d^7 species, as suggested by the calculations on iron(I) models.

Due to the importance of oxidative additions in homogeneous catalysis[10] and following our interest in the catalytic applications of binuclear complexes,[11] the present work focuses on the study of concerted oxidative additions in binuclear iridium complexes. From the variety of possible reactions and reactants, we have restricted ourselves to simple processes, such as protonations, oxidations, and additions of hydrogen, which can model the behavior of other small molecules of interest in homogeneous catalysis. The starting

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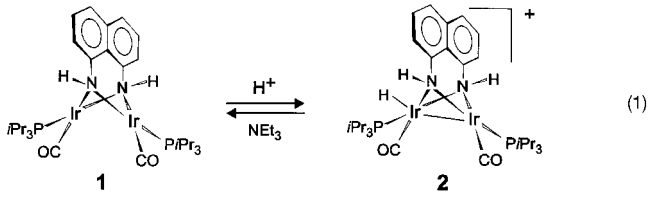
material employed in this study, the complex $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CO)_2(PiPr_3)_2]$ (**1**), contains a di-μ-amido bridge,[12, 13] which binds the metals in both bridging and chelating modes. This is advantageous not only since it reduces the possibility of fragmentation, but also since it allows short intermetallic distances to minimize structural strain. Furthermore, the combination of nitrogen donor ligands and very basic phosphanes, such as $PiPr_3$, allows the formation of stable nucleophilic iridium complexes.

Results and Discussion

Preparation of $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CO)_2(PiPr_3)_2]$ (1): Compound $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CO)_2(PiPr_3)_2]$ (**1**) can be obtained in good yield from the reaction of the tetracarbonyl complex $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CO)_4]$[13] with two equivalents of triisopropylphosphane. According to the spectroscopic data, the structure of **1** [Eq. (1); counterion $CF_3SO_3^-$] is



(1)

similar to that of its triphenylphosphane analogue, which we reported previously.[12] The $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 shows a singlet at $\delta = 37.40$ which may agree with either a C_s (*cisoid*) or with a C_2 (*transoid*) symmetry. The proton spectrum shows three resonances for the aromatic protons of the diamidonaphthalene bridge, together with a single broad peak for both NH protons at $\delta = 4.73$. This indicates C_2 symmetry [Eq. (1)]. The $^{13}C\{^1H\}$ NMR spectrum is also consistent with this symmetry. It is noteworthy that the signal corresponding to the C1 and C8 quaternary carbon atoms of the diamidonaphthalene bridge at $\delta = 150.55$ displays a $^3J(C,P)$ coupling of 3.0 Hz, which is attributed to the *trans* position of the phosphorus and nitrogen atoms. As will be shown below, the presence or absence of this $^3J(C,P)$ is a very useful indicator for the determination of the phosphane ligand positions within the binuclear framework.

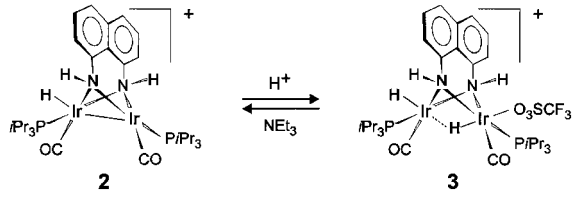
At first sight, complex **1** should contain very nucleophilic iridium(I) centers, provided that they coordinate very basic phosphanes and a nitrogen donor bridge. In spite of these apparently favorable conditions for oxidative addition, **1** does not react with hydrogen under normal reaction conditions.

Protonation of complex 1: Complex **1** reacts with strong acids, such as HBF_4 or HO_3SCF_3, to give protonation products. The reaction with one equivalent of trifluoromethylsulfonic acid in THF led to the cationic complex $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)H(CO)_2(PiPr_3)_2](CF_3SO_3)$ (**2**).[14] Conductivity measurements of solutions of **2** in nitromethane indicate a 1:1 electrolyte,[15] whereas the analytical data agree with the proposed stoichiometry.

Compound **2** is asymmetric, as evidenced by the $^{31}P\{^1H\}$ NMR spectrum, which shows two singlets at $\delta = 38.56$ and 33.94. The signal in the proton spectrum attributed to the hydrido ligand consists of a doublet of doublets at $\delta = -29.13$ with $J(H,P)$ couplings of 18.6 and 4.8 Hz. The former is typical for a terminal hydride *cis* to a phosphane, whereas the latter would suggest the presence of an Ir–Ir bond which would allow a $^3J(H,P)$ coupling. The resonances of the C1 and C8 carbons of the diamidonaphthalene bridge in the $^{13}C\{^1H\}$ spectrum, two doublets at $\delta = 147.68$ ($J(C,P) = 3.7$ Hz) and 147.71 ($J(C,P) = 1.5$ Hz), are consistent with a *transoid* arrangement of the phosphanes. In CD_2Cl_2, the triflate ^{19}F signal is a singlet at $\delta = -78.8$, which suggests that the anion is not coordinated to iridium. In agreement with this, the NMR signals of complex **2** in CD_2Cl_2 do not change in the presence of small amounts of coordinating solvents such as acetone or acetonitrile. The IR spectrum of **2** shows an absorption at 2197 cm^{-1}, which corresponds to a $\nu(Ir-H)$ mode of a terminal hydride. In view of the data mentioned above, the structure of **2** depicted in Equation (1) can be considered as the most plausible description of the compound.

Nevertheless, formulation of a structure for derivatives such as **2** is not obvious, due to the different possibilities for the assignment of charges and formal oxidation states. The previously reported complex $[Ir_2(\mu\text{-}Pz)_2(NO)(cod)_2]BF_4$ (cod = cycloocta-1,5-diene, PzH = pyrazole), which is isoelectronic to **2**, was discussed as being possibly a d^7-d^7 or d^6-d^8 complex,[14b] whereas, on the basis of theoretical calculations, isoelectronic reaction intermediates of rhodium have been described as $Rh^{III}-Rh^{I}$ derivatives containing a dative metal–metal bond.[5a] This particular aspect has also been extensively discussed in the chemistry of binuclear gold complexes.[16] In the case of complex **2**, some experimental observations suggest that the $Ir^{III}-Ir^{I}$ description could be more appropriate. In particular, the two infrared $\nu(CO)$ modes at 2025 and 1977 cm^{-1} are indicative of rather different iridium centers, and the difference between these two $\nu(CO)$ modes is comparable to that found in well defined $Ir^{III}-Ir^{I}$ compounds.[4, 7f] In addition, the lack of coordination of the triflate anion could be also claimed as an indication of d^6-d^8 character. In agreement with this, the structural and theoretical studies performed on the complex $[Ir_2(\mu\text{-}Pz)_2(CH_3)(CO)_2(PiPr_3)_2]ClO_4$, which is also isoelectronic to **2**, have indicated the presence of $Ir^{III}-Ir^{I}$ centers connected by a weak metal–metal bond.[7g]

Complex **2** can react with NEt_3 to reform **1**, but also with a second equivalent of triflic acid to give complex $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(\mu\text{-}H)H(OSO_2CF_3)(CO)_2(PiPr_3)_2](CF_3SO_3)$ (**3**) [Eq. (2); counterion in each case $CF_3SO_3^-$]. The ^{19}F NMR

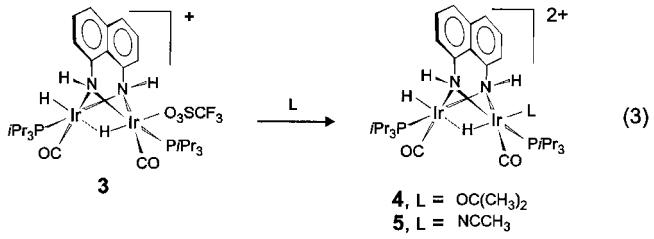


(2)

spectrum of **3** in CD_2Cl_2 shows two singlets at $\delta = -77.97$ and -78.85,[17, 18] which indicates that only one of the anions is coordinated to the bimetallic unit. In agreement with this, the

solutions of **3** in CH_2Cl_2 display molar conductivities consistent with a 1:1 electrolyte.[15] The $^{31}P\{^1H\}$ NMR of **3** in CD_2Cl_2 displays two singlets at $\delta = 24.09$ and 29.19, which under *off resonance* conditions split into two doublets with hydride couplings of $J = 9.6$ and 19.5 Hz respectively. The ^1H NMR spectrum contains two doublets corresponding to the hydride ligands at $\delta = -22.25$ ($J(H,P) = 9.6$ Hz) and at $\delta = -20.01$ ($J(H,P) = 19.5$ Hz). The $J(H,P)$ coupling of the latter is consistent with a terminal hydride *cis* to the phosphane ligand, whereas the small $J = 9.6$ Hz coupling suggests that this hydride may bridge the metal centers in an asymmetric fashion [Eq. (2)].[11, 19] A weak band in the IR spectrum at 2253 cm^{-1} can be attributed to the terminal hydride, whereas the carbonyl stretching frequencies at 2076 and 2056 cm^{-1} agree with an $Ir^{III}-Ir^{III}$ complex.[20]

The triflate ligand of **3** can be substituted by weak Lewis bases, such as acetone or acetonitrile, to give the solvato complexes $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(\mu\text{-}H)H(OC(CH_3)_2)(CO)_2(P\mathit{i}Pr_3)_2](CF_3SO_3)_2$ (**4**) and $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(\mu\text{-}H)H(NCCH_3)(CO)_2(P\mathit{i}Pr_3)_2](CF_3SO_3)_2$ (**5**) [Eq. (3); counterion: $CF_3SO_3^-$]. Conductivity measurements of solutions of



(3)

both complexes give typical values for 2:1 electrolytes. In agreement with this, the ^{19}F NMR spectra of **4** or **5** in [D_6]acetone give a singlet at $\delta = -78.32$, characteristic of a noncoordinated triflate. The other spectroscopic parameters of compounds **4** and **5** are very similar to those of complex **3** (see Experimental Section), which indicates that these three Ir^{III} dihydrides have similar structures. Figure 1 shows the structure of the cation of **4**, as determined by X-ray diffraction and Table 1 lists the relevant distances and angles.

The cation of **4** is an asymmetric species in which both metallic centers display approximately octahedral coordination environments. The binuclear unit presents *transoid* arrangements of both carbonyl and phosphane ligands. The intermetallic distance is 2.7659(5) Å, which is considerably shorter than that determined for the methylene-bridged derivative $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(\mu\text{-}CH_2)I_2(CO)_2(PPh_3)_2]$[12] (3.0306(4) Å). The hydride ligands were located in the difference Fourier maps. One of them (H101) occupies a terminal position with an Ir–H distance of 1.44 Å, and the other (H102) bridges the two metal centers with distances of 1.87 and 1.74 Å.

Although the hydride positions must be interpreted with some caution, they agree well with the interpretation of the solution NMR spectra. As in other cases where an asymmetric bridging hydride has been found,[11, 19] the asymmetry can be attributed to the different *trans* influences of the ligands *trans* to the bridge. The structural parameters of the acetone ligand of **4** are similar to those found in the mononuclear complex

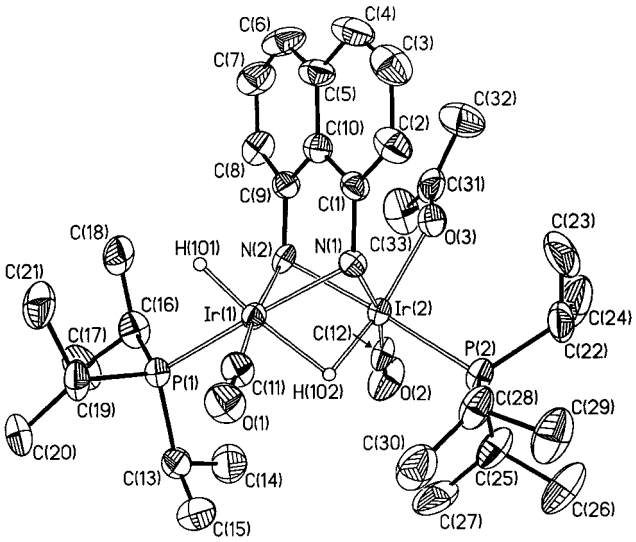


Figure 1. Molecular structure of the cation of complex **4**.

Table 1. Selected bond lengths [Å] and angles [°] for complex **4**.

Ir(1)–P(1)	2.338(2)	Ir(2)–P(2)	2.3693(19)
Ir(1)–N(1)	2.121(5)	Ir(2)–N(1)	2.155(6)
Ir(1)–N(2)	2.084(6)	Ir(2)–N(2)	2.149(5)
Ir(1)–C(11)	1.861(8)	Ir(2)–C(12)	1.870(9)
Ir(1)–H(101)	1.44[a]	Ir(2)–O(3)	2.127(6)
Ir(1)–H(102)	1.87[a]	Ir(2)–H(102)	1.74[a]
P(1)-Ir(1)-N(1)	172.53(17)	P(2)-Ir(2)-N(1)	97.17(16)
P(1)-Ir(1)-N(2)	99.05(18)	P(2)-Ir(2)-N(2)	168.49(17)
P(1)-Ir(1)-C(11)	88.7(2)	P(2)-Ir(2)-C(12)	90.4(2)
P(1)-Ir(1)-H(101)	80.33(5)	P(2)-Ir(2)-O(3)	95.28(15)
P(1)-Ir(1)-H(102)	103.84(5)	P(2)-Ir(2)-H(102)	87.54(5)
N(1)-Ir(1)-N(2)	74.8(2)	N(1)-Ir(2)-N(2)	72.8(2)
N(1)-Ir(1)-C(11)	97.3(3)	N(1)-Ir(2)-C(12)	168.5(3)
N(1)-Ir(1)-H(101)	103.96(15)	N(1)-Ir(2)-O(3)	89.3(2)
N(1)-Ir(1)-H(102)	71.55(15)	N(1)-Ir(2)-H(102)	73.08(16)
N(2)-Ir(1)-C(11)	171.9(3)	N(2)-Ir(2)-C(12)	98.7(3)
N(2)-Ir(1)-H(101)	93.32(16)	N(2)-Ir(2)-O(3)	90.3(2)
N(2)-Ir(1)-H(102)	82.92(16)	N(2)-Ir(2)-H(102)	84.16(17)
C(11)-Ir(1)-H(101)	90.1(3)	C(12)-Ir(2)-O(3)	98.7(3)
C(11)-Ir(1)-H(102)	93.2(3)	C(12)-Ir(2)-H(102)	98.7(3)
H(101)-Ir(1)-H(102)	175[a]	O(3)-Ir(2)-H(102)	162.38(14)
Ir(1)-N(1)-Ir(2)	80.61(19)	Ir(1)-N(2)-Ir(2)	81.6(2)
Ir(1)-H(102)-Ir(2)	99.891(15)		
Ir(1)-C(11)-O(1)	177.7(8)	Ir(2)-C(12)-O(2)	177.9(7)

[a] Hydride ligands were refined with a riding model

$[IrH_2(Me_2CO)_2(PPh_3)_2]BF_4$,[21] the previously sole example of an (acetone)Ir^{III} complex determined by X-ray diffraction. The Ir–O distance (2.127(6) Å) is considerably shorter than those found in the above-mentioned mononuclear complex (2.220(5) and 2.235(5) Å), where the acetone ligands are *trans* to terminal hydrides.

Complexes **3**–**5** can be also obtained directly by reaction of **1** with an excess of triflic acid in CH_2Cl_2, acetone, or acetonitrile, respectively. At short reaction times, the reaction of **1** in CD_2Cl_2 with a tenfold excess of acid yields **3** as a major product, together with a new species, **6**. The latter slowly isomerizes to give **3**, but can be maintained at temperatures below 273 K. On the basis of the data collected for **6**, the

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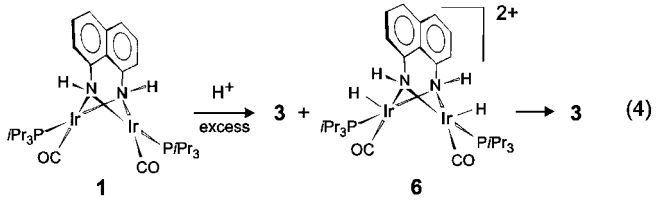
species can be formulated as the symmetric isomer of **3** [Eq. (4); counterion: $CF_3SO_3^-$]. The $^{31}P\{^1H\}$ NMR spectrum of **6** in CD_2Cl_2 consists of a singlet at $\delta = 22.76$. The proton



spectrum shows a doublet at $\delta = -26.86$ ($J(H,P) = 18.3$ Hz) which corresponds to two equivalent terminal hydrides, along with a single broad N–H resonance. The $^{13}C\{^1H\}$ spectrum at 253 K also agrees with the proposed C_2 structure.

Interestingly, in spite of the fact that **6** can easily be observed on treatment of **1** with excess acid, this species cannot be detected during protonation of the monohydride **2**. This fact suggests that **6** results from the simultaneous double protonation of **1** rather than from a stepwise reaction via **2**. In agreement with this proposal, it has been observed that the greater the excess of triflic acid employed, the more complex **6** is formed. Therefore, complex **3** should be considered to be not only the thermodynamic result of protonation of **2**, but also the kinetic product of this reaction. This indicates that, regardless the formal ambiguity in the electronic structure of **2**, the electron density of this complex is concentrated between the metal centers and it directs the electrophilic attack of H^+ to the intermetallic position.

The formation of complexes **3–5** constitutes a rare example of the double protonation of a binuclear complex, especially considering the fact that the monohydride **2** is itself acidic. Previously reported double protonations in dirhodium complexes led to H_2 elimination[22] or to the formation of symmetric dihydrides similar to **6**.[23] In addition, the double protonation of the complex $[Cp^*Ir(\mu\text{-}CO)]_2$ has been reported to give a symmetric bis(hydrido)-bridged complex.[8a] However, to the best of our knowledge, complexes **3–5** are the first examples of a double protonation of a symmetric binuclear complex leading to an asymmetric species.

H/D exchange reactions in polar deuterated solvents: In the presence of D_2O or [D_6]acetone, complex **2** undergoes H/D scrambling of the hydride ligand to produce the complex $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)D(CO)_2(PiPr_3)_2](CF_3SO_3)$ ([D]**2**). The deuterated complex is characterized by a downfield isotopic shift $\Delta\delta = +0.12$ ppm of the signal at $\delta = 33.94$ in the $^{31}P\{^1H\}$ NMR. Similar H/D scrambling processes with acetone have been previously observed,[17, 24] and attributed to the acidity of the hydride complexes.[25] In agreement with this proposal, **2** can be readily deprotonated by NEt_3 to yield **1**.

In an analogous manner to **2**, complexes **4** and **5** also undergo H/D scrambling in the presence of D_2O or [D_6]acetone. Initially, this scrambling affects only the terminal hydride, giving rise to monodeuterated complexes [D]**4** and [D]**5**. In both cases downfield isotopic shifts of $\Delta\delta = 0.12$ ppm are found for the singlet at lower field in the $^{31}P\{^1H\}$ NMR spectra. In addition, the bridging hydride signals display downfield isotopic shifts of $\Delta\delta = 0.022$ ppm in both complexes. Replacement of the bridging hydrides by deuterium occurs only after extended reaction times (up to 2 h), to give complexes [D_2]**4** and [D_2]**5**, which are deuterated in both hydrido positions. Deuteration of the bridging hydride results in nondetectable isotopic shifts in the $^{31}P\{^1H\}$ NMR spectra.[11]

The different rates of deuteration of the two hydrido ligands suggest that, for complexes **4** and **5**, the terminal hydrides are *kinetically* more acidic than the bridging ones. In contrast to this, treatment of complexes **3–5** with one equivalent of triethylamine yielded the terminal hydrido complex **2**. This result can be understood by assuming that the initial abstraction of the terminal hydride is followed by the isomerization of the resulting monohydride to give the thermodynamic stable complex **2**. In terms of Norton's definitions of kinetic and thermodynamic acidities,[25, 26] this implies that the *thermodynamic* acidity of the bridging hydride is larger than that of the terminal hydride, which is in agreement with previous observations.[25–27]

In order to support the above proposals, the spectroscopic detection of kinetic deprotonation products were attempted. During the treatment of solutions of **4** in [D_6]acetone with one equivalent of NEt_3, a reaction intermediate which readily gives complex **2** can be observed. This intermediate displays a triplet at $\delta = -17.84$ with $J(H,P) = 9.0$ Hz in the ^1H NMR spectrum, that may agree with a bridging hydride. Also, a single broad resonance at $\delta = 6.41$ can be clearly attributed to the two N–H protons of the intermediate, whereas in the $^{31}P\{^1H\}$ spectrum this species gives a broad signal at $\delta = 30.18$. Although this spectrocopic information is not enough to give a structural proposal, the data obtained qualitatively correlates with the expected product of a terminal hydride abstraction. Attempts to trap this intermediate by reaction with ligands such as CO or acetonitrile gave complex **1** together with other unidentified species which are probably disproportionation products.

Oxidative addition of hydrogen to complex 2: In contrast to complex **1**, which does not react with H_2, the red solutions of complex **2** in acetone rapidly turn yellow upon bubbling with hydrogen. From the resulting solutions, a pale yellow solid of stoichiometry $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(\mu\text{-}H)H_2(CO)_2(PiPr_3)_2](CF_3SO_3)$ (**7**) can be isolated in good yield. The spectroscopic analysis of this solid reveals that it consists of a mixture of two isomers, **7a** and **7b**, in approximately 0.4:0.6 molar ratio. The structures of both isomers, deduced from the NMR parameters, are those represented in Equation (5) (counterion: $CF_3SO_3^-$) .

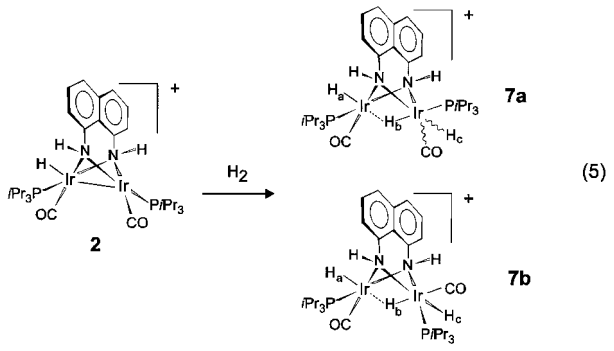


Figure 2 shows the hydride region of the ^{1}H NMR spectrum of the mixture **7** in [D$_6$]acetone. The minor isomer, **7a**, shows a lowfield signal at $\delta = -10.46$ (H$_b$) with a ddd pattern. This

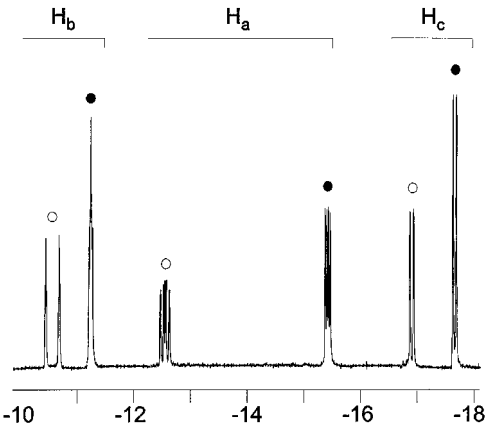


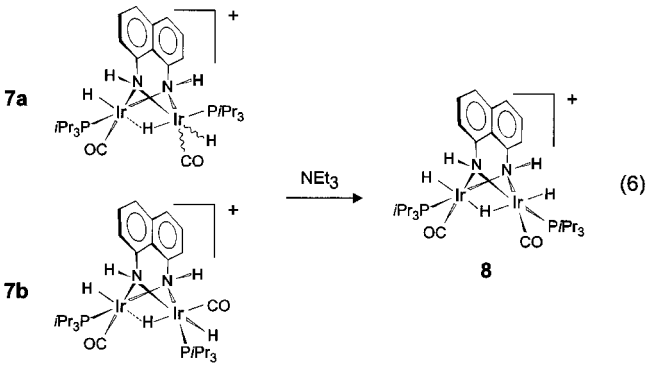
Figure 2. Highfield region of the ^{1}H NMR spectrum of the mixture **7**. White dots correspond to the minor isomer **7a**, and black dots to isomer **7b**.

signal displays unusual J(H,P) couplings of 70.2 and 3.6 Hz together with a J(H,H) of 3.3 Hz. The absence of a typical J(H,P) coupling for a terminal hydride *cis* to a phosphane ligand($\approx$18 Hz) suggests that the signal corresponds to a bridging hydride located *trans* to a P*i*Pr$_3$ ligand. The small value of the second J(H,P) coupling also suggests that, as in complexes **3**–**5**, this bridge is asymmetric. This observation is also supported by the small *trans* J(H,H) coupling of 3.3 Hz with H$_a$. The other two hydrido signals of **7a** display J(H,P) couplings typical of terminal hydrides located *cis* to a phosphane ligand: $J = 19.8$ Hz for H$_c$ and 18.9 for H$_a$. The latter also shows an unusual ^4J(H,P) coupling of 29.1 Hz, which may result from the all-*trans* H$_a$-Ir-H$_b$-Ir-P*i*Pr$_3$ arrangement.

Unfortunately, the NMR data of **7a** may agree with both *cisoid* and *transoid* dispositions of the carbonyl ligands, so that the structure of this isomer cannot be unambiguously determined. As a result of the loss of the *transoid* arrangement of the phosphane ligands in **7a**, the ^{13}C{^{1}H} NMR signals of the C1 and C8 carbon atoms of the diamidonaphthalene bridge consist of a doublet at $\delta = 149.95$ (J(C,P) = 3.5 Hz) and a singlet at $\delta = 152.73$, instead of the two doublets obtained for the *transoid* derivatives. On the other hand, the signals corresponding to these two carbon atoms in the major isomer, **7b**, consist of a doublet of doublets at $\delta = 149.54$ (J(C,P) = 3.5 and 2.3 Hz) and a singlet at $\delta = 152.77$, which suggests a *cisoid* arrangement of the P*i*Pr$_3$ ligands. The hydrido signal of **7b** at $\delta = -11.15$ displays H–P couplings of 6.3 and 3.3 Hz, in agreement with a semibridging hydride H$_b$. This signal also contains a H–H coupling of 9.3 Hz to the hydride H$_a$ located *trans*. Both H$_a$ and H$_c$ have J(H,P) coupling constants consistent with their terminal character, 17.4 and 15.9 Hz, respectively.

The reaction with H$_2$ of the deuterated complex [D]**2** gave an isomeric mixture of [D]**7a** and [D]**7b**, likewise in a 0.4:0.6 molar ratio. Both isomers are deuterated selectively at the position of H$_a$, and they did not undergo detectable H/D scrambling. Apart from the absence of the H$_a$ signal in the ^{1}H NMR spectra, isomer [D]**7a** is characterized by a downfield isotopic shift of the bridging hydride H$_b$ of $\Delta\delta = 0.047$ ppm. In addition, a ^4J(P,D) coupling of 3.8 Hz is observed in the ^{31}P{^{1}H} spectrum, which corresponds well with the ^4J(H,P) coupling of 29.1 Hz, observed for the H$_a$ signal of **7a**. The signal corresponding to the bridging hydride of [D]**7b** is also affected by a downfield shift of $\Delta\delta = 0.042$ ppm with regard to that of complex **7b**. Unfortunately, due to the close proximity of three of the four ^{31}P{^{1}H} signals of the isomeric mixture, the isotopic shifts of these signals cannot be clearly observed.

The 0.4:0.6 molar ratio of **7a**:**7b** found in the mixtures of **7** remains unaltered in solution, even after a period of days. The ratio is also not affected by heating or cooling the solution. This suggests that the mixture corresponds to a kinetic distribution rather than to an equilibrium. In contrast to the situation found for the hydrido complexes previously described, **7a** and **7b** do not undergo H/D scrambling in the presence of acetone or water. The above observations suggest that the trihydrido complexes **7a** and **7b** are less acidic than the previously described dihydrido and monohydrido complexes **2**–**5**. In agreement with this proposal, the addition of one equivalent of triethylamine to the mixture **7** did not yield observable deprotonated products of **7a** and **7b**, but an isomer, the complex **8**. Analytical and spectroscopic data of **8** support the structure depicted in Equation (6) (counterion: $CF_3SO_3^-$).



The mass spectra (FAB$^+$) of complex **8** are identical to those of the mixture **7**. In addition, conductivity measurements of its nitromethane solutions are consistent with a 1:1 electrolyte. The ^{31}P{^{1}H} NMR spectrum of **8** in [D$_6$]acetone exhibits a singlet at $\delta = 31.77$. The lowfield region of the proton spectrum shows three signals for the diamidonaphthalene ligand together with a single broad line for the N–H protons, thus confirming the C_2 symmetry. The highfield region of the ^{1}H spectrum (Figure 3) consists of two multiplets at $\delta = -13.59$ and -9.68, that can be assigned to the AA′ and M parts of an AA′MXX′ spin system (X = ^{31}P), respectively. In agreement with the structural proposal given in Equation (6), simulation of the spin system gave J(H,P) = 17.3 Hz for the terminal hydrides and 4.5 Hz for the bridging one, which is coupled to both phosphorus atoms. The latter is also coupled to both terminal hydrides with J(H,H) = 10.9 Hz, which confirms their relative *trans* positions. The other NMR parameters of **8** are consistent with the proposed symmetry.

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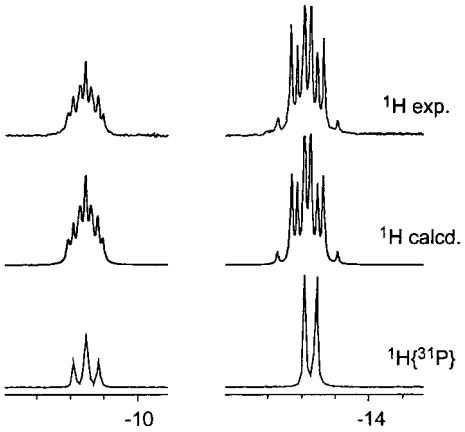


Figure 3. Hydride signals in the ^{1}H and ^{1}H{^{31}P} NMR spectra of complex **8** in [D$_6$]acetone.

The IR spectrum in Nujol has a single ν(CO) mode at 2027 cm^{-1} and a terminal ν(Ir–H) at 2129 cm^{-1}.

The features of these trihydrido complexes described above show that the oxidative addition of hydrogen to complex **2** occurs at the *pocket* of the binuclear framework and results in one bridging and two terminal hydrido ligands. As a consequence, either a phosphane or a carbonyl ligand is displaced to the *exo* coordination position to give rise to a kinetic mixture of **7a** and **7b**. The addition of NEt_3 to this mixture provokes the isomerization of **7a** and **7b** into the thermodynamic stable isomer **8**, most probably through the formation of deprotonated intermediates.

Oxidation of complex 1 to give diiridium(II) complexes: Cyclic voltammetry experiments in CH_2Cl_2 solutions of **1** (Figure 4) show that the complex can undergo several oxidation

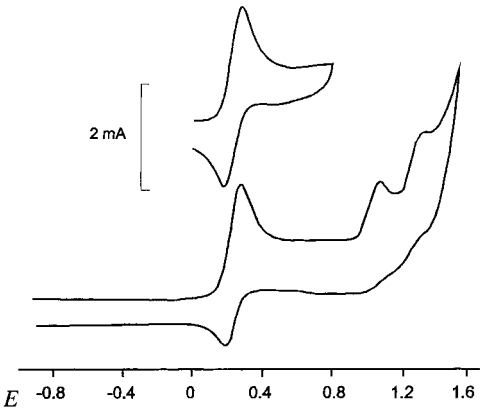
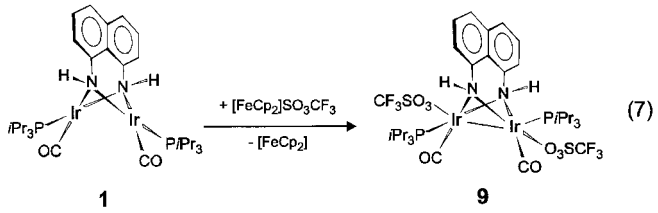


Figure 4. Cyclic voltammogram for the oxidation of complex **1** in CH_2Cl_2 at 20 mV s^{-1}.

processes: a two-electron reversible oxidation at $E = 0.23$ V and two irreversible one-electron oxidations at $E = 1.11$ and 1.22 V.

The low value of the first process indicates that the two-electron oxidation products of **1** could be easily obtained on treatment with mild oxidants. Thus, solutions of $[FeCp_2]CF_3SO_3$[28] in acetone readily react with **1** to give the complex $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(OSO_2CF_3)_2(CO)_2(P\mathit{i}Pr_3)_2]$ (**9**) [Eq. (7)].



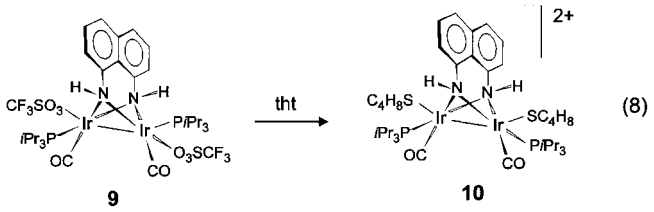
(7)

The IR spectrum of **9** in Nujol shows carbonyl stretching frequencies at 2054 and 2012 cm^{-1}, in agreement with a diiridium(II) complex. The ^{19}F NMR spectrum in $CDCl_3$ at 243 K consists of two singlets at $\delta = -77.39$ and -78.33, which shows that both triflate anions are coordinated to the metal centers. If the temperature is raised, the singlet at lowfield undergoes only a small highfield shift, whereas the signal at $\delta = -78.33$ shifts to higher field and broadens. This temperature-dependence of the chemical shifts indicates the existence of a fast equilibrium process. The shift of the highfield signal towards the chemical shift of the free triflate ($\delta = -79.17$ in $CDCl_3$) suggests that this equilibrium is established between a neutral and a cationic species which results from the dissociation of one triflate anion, whereas the second triflate remains coordinated. In agreement with this, **9** is soluble in nonpolar solvents such as toluene, but solutions of it in acetone show conductivities characteristic of 1:1 electrolytes.

In agreement with the existence of two different triflate ligands, the ^{31}P{^{1}H} NMR spectrum in CD_2Cl_2 at room temperature shows two doublets at $\delta = 0.18$ and 41.19 with a J(P,P) couling of 8.8 Hz. Also, the C1 and C8 carbon atoms of the bridging ligand give rise to a doublet at $\delta = 142.72$ (J(C,P) = 3.6 Hz) and a singlet at $\delta = 143.00$ in the ^{13}C{^{1}H} NMR spectrum. This indicates that the phosphane ligands are *not in a transoid* arrangement and would point to the structure depicted in Equation (7). This structure can also explain the existence of two different triflate ligands with different lability.

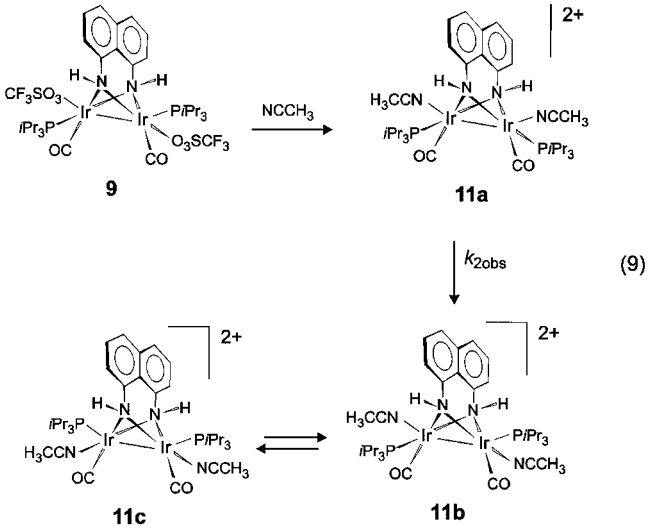
Treatment of complex **9** with an excess of the mild ligand tetrahydrothiophene (THT), produced the displacement of the coordinated triflate anions and formation of the compound $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CO)_2(P\mathit{i}Pr_3)_2(tht)_2](CF_3SO_3)_2$ (**10**). The analytical data confirm the incorporation of two THT ligands into the binuclear complex, and the conductivity measurements are consistent with a 1:2 electrolyte. The unique singlet ($\delta = 11.89$) found for **10** in the ^{31}P{^{1}H} NMR spectrum in $CDCl_3$ indicates that the complex is symmetric. Also, in the proton NMR, the sole broad signal at $\delta = 7.59$, corresponding to both NH protons, indicates C_2 symmetry. The other NMR parameters of **10** are those expected from this symmetry and the *transoid* arrangement of the phosphane ligands, and support the structural formulation given in Equation (8) (counterion for **10:** $CF_3SO_3^-$) .

The addition of acetonitrile to complex **9** gives rise to the immediate formation of complex $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CO)_2(P\mathit{i}Pr_3)_2(NCCH_3)_2](CF_3SO_3)_2$ (**11a**). The spectroscopic data collected for **11a** support its formulation as an acetoni-



(8)

trile analogue of complex **10** [Eq. (9); counterion in each case $CF_3SO_3^-$]. Thus, **11a** shows a singlet at $\delta = 21.63$ in the $^{31}P\{^1H\}$ NMR and a proton spectrum characteristic of a C_2 symmetry.



(9)

However, **11a** is not stable in solution; it disappears to give a mixture of the two complexes **11b** and **11c**. The final ratio of these two complexes strongly depends on the solvent, although **11b** is always the major component. Thus, in [D_6]acetone the proportion of **11b** is greater than 95%, whereas in $CDCl_3$ it is about $\approx 65\%$.

Crystals of **11b** suitable for single-crystal X-ray diffraction were obtained from solutions of the mixture in acetone. The structure is depicted in Figure 5 and important bond lengths and angles are listed in Table 2.

Complex **11b** is an asymmetric isomer of its precursor **11a**: both metal centers have the same ligands but in a different spatial arrangement. The ligands coordinate in a square-pyramidal mode about both iridium atoms, which complete their coordination spheres by means of a metal–metal bond to produce very distorted octahedrals environments around each Ir center. The intermetallic distance is 2.5770(5) Å, close to the shortest Ir–Ir bond length hitherto reported (2.518 Å),[29] and almost 0.2 Å shorter than that found in the hydrido-bridged complex **4**.

The structure allows a comparison between identical ligands bonded in different positions of the bimetallic complex. Comparison between both acetonitrile ligands and both P*i*Pr$_3$ clearly shows that the distances are longer when the ligands are *trans* to the metal–metal bond. This indicates a larger *structural trans effect* of the metal in comparison to that of the bridging nitrogen. Also, in spite of fact that both metals are surrounded by the same ligands, both metallic centers

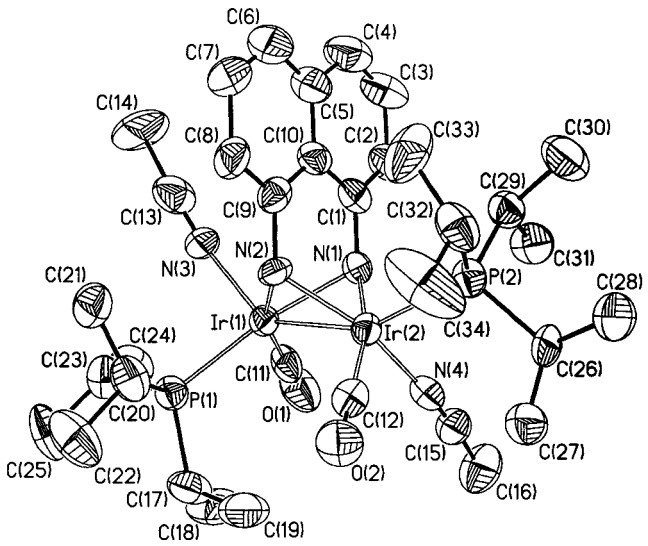


Figure 5. Molecular structure of the cation of complex **11b**.

Table 2. Selected bond lengths [Å] and angles [°] for complex **11b**.

Ir(1)–Ir(2)	2.5770(5)		
Ir(1)–P(1)	2.336(3)	Ir(2)–P(2)	2.398(3)
Ir(1)–N(1)	2.138(8)	Ir(2)–N(1)	2.079(8)
Ir(1)–N(2)	2.144(8)	Ir(2)–N(2)	2.066(7)
Ir(1)–N(3)	2.134(8)	Ir(2)–N(4)	2.018(9)
Ir(1)–C(11)	1.821(11)	Ir(2)–C(12)	1.886(11)
Ir(2)-Ir(1)-P(1)	116.52(7)	Ir(1)-Ir(2)-P(2)	152.51(7)
Ir(2)-Ir(1)-N(1)	51.32	Ir(1)-Ir(2)-N(1)	53.4(2)
Ir(2)-Ir(1)-N(2)	50.89(19)	Ir(1)-Ir(2)-N(2)	53.6(2)
Ir(2)-Ir(1)-N(3)	136.0(2)	Ir(1)-Ir(2)-N(4)	100.8(2)
Ir(2)-Ir(1)-C(11)	108.2(4)	Ir(1)-Ir(2)-C(12)	111.3(3)
P(1)-Ir(1)-N(1)	167.7(2)	P(2)-Ir(2)-N(1)	103.1(2)
P(1)-Ir(1)-N(2)	101.3(2)	P(2)-Ir(2)-N(2)	111.3(2)
P(1)-Ir(1)-N(3)	91.9(3)	P(2)-Ir(2)-N(4)	92.1(2)
P(1)-Ir(1)-C(11)	92.4(3)	P(2)-Ir(2)-C(12)	91.7(3)
N(1)-Ir(1)-N(2)	72.8(3)	N(1)-Ir(2)-N(2)	75.6(3)
N(1)-Ir(1)-N(3)	99.2(3)	N(1)-Ir(2)-N(4)	89.5(3)
N(1)-Ir(1)-C(11)	90.5(4)	N(1)-Ir(2)-C(12)	164.7(4)
N(2)-Ir(1)-N(3)	92.9(3)	N(2)-Ir(2)-N(4)	154.5(3)
N(2)-Ir(1)-C(11)	158.6(4)	N(2)-Ir(2)-C(12)	95.6(4)
N(3)-Ir(1)-C(11)	103.1(5)	N(4)-Ir(2)-C(12)	93.8(4)
Ir(1)-N(1)-Ir(2)	75.3(3)	Ir(1)-N(2)-Ir(2)	75.5(2)

have rather different bond lengths to the bridging ligand and to the carbonyl ligands, which shows that the different arrangements of the ligands may strongly influence electronic properties at the metal center. This observation is further supported by the IR spectrum, which shows two ν(CO) modes at rather different frequencies of 2042 and 2008 cm^{-1}. This effect is very similar to that found in the neutral complex **9**, which is also asymmetric.

The other spectroscopic data found for **11b** are as expected from the asymmetric structure found in solid state. On the other hand, the spectra of **11c** indicate that this species is a symmetric isomer of **11b**, and is different from **11a**. The $^{31}P\{^1H\}$ NMR spectrum in [D_6]acetone shows a singlet at $\delta =$ 9.19. The diamidonaphthalene ligand gives the ^1H resonances expected for C_2 symmetry, and the two acetonitrile ligands give a singlet at $\delta = 2.88$. The signals corresponding to the methyl groups of the P*i*Pr$_3$ ligands consist of two doublets of virtual triplets at $\delta = 0.85$ and 0.92, which, on decoupling of

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the CH isopropylic protons, give two virtual triplets. The existence of coupling between the methyl groups and both magnetically nonequivalent phosphorus atoms is typical of mononuclear complexes with two equivalent P*i*Pr$_3$ ligands *trans* each other. This suggests that in **11c** the phosphane ligands occupy the positions *trans* to the Ir–Ir bond. In agreement with the latter, the $^{13}C\{^1H\}$ spectrum displays for the CH carbon atoms of P*i*Pr$_3$ a virtual triplet at $\delta = 24.66$ with a C–P coupling $N = J(C,P) + J(C,P') = 23.3$ Hz, characteristic of an AA′XX′ system. The C1 and C8 carbon atoms of the bridge give rise to a singlet at $\delta = 145.15$. These observations support the structural formulation of **11c** as depicted in Equation (9).

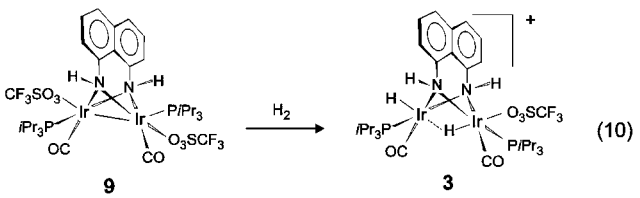
Dissolution of the crystals of **11b** in $CDCl_3$ produce a mixture of **11b** and **11c** in the same ratio which was found as a result of the isomerization of **11a**. Thus, isomers **11b** and **11c** are in equilibrium. The rates of isomerization ($k_{2,\,obs}$) of **11a** to give the equilibrium distribution of **11b** and **11c** in $CDCl_3$ were measured at different temperatures and acetonitrile concentrations by monitoring the disappearance of the $^{31}P\{^1H\}$ NMR signal of **11a**. In addition, the rates of exchange between free acetonitrile and the acetonitrile coordinated to **11a** ($k_{1,\,obs}$) were measured by spin-saturation transfer methods at 283 and 293 K. The pseudo-first-order rate constants obtained for these processes are given in Table 3.

Table 3. Acetonitrile dissociation rates from complex **11a** ($k_{1,\,obs}$) and rates of isomerization of **11a** ($k_{2,\,obs}$).

T [K]	$[NCCH_3]_{free}$ [M]	$k_{1,\,obs}$ [s^{-1}]	$k_{2,\,(obs)}$ [s^{-1}]
283	0.13	0.73	9.85×10^{-5}
293	0.13	1.99	5.05×10^{-4}
298	0.13		8.45×10^{-4}
303	0.08		1.56×10^{-3}
	0.13		1.47×10^{-3}
	1.04		1.45×10^{-3}
308	0.13		3.79×10^{-3}
313	0.13		7.13×10^{-3}

The results show that dissociation of acetonitrile from **11a** is more that three orders of magnitude faster than the isomerization of **11a**. In spite of this, the isomerization rates are independent of the acetonitrile concentration, which shows that the isomerization reaction does not require previous dissociation of the ligand. The Eyring plot, given in Figure 6, allows an estimation of the kinetic activation parameters for the isomerization: $\Delta S^{\neq} = 8.8\ (\pm 2)$ eu and $\Delta H^{\neq} = 24.2\ (\pm 1.6)$ kcal mol^{-1}, which are consistent with an intramolecular process.

Addition of hydrogen to the diiridium(II) complexes: The diiridium(II) complex **9** readily reacts under a hydrogen atmosphere in $CDCl_3$ to give complex **3** [Eq. (10); counter-



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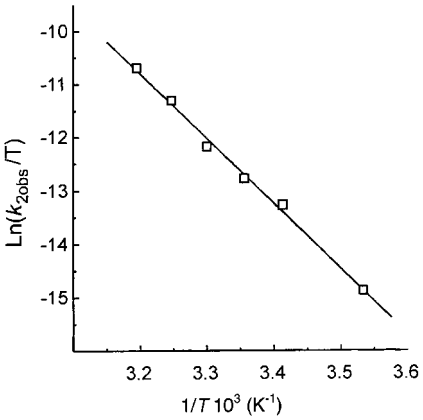
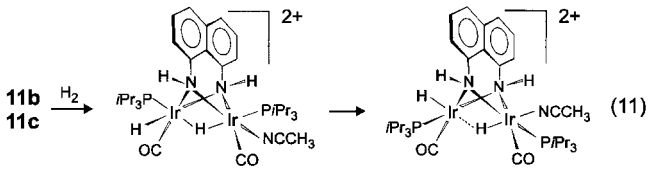


Figure 6. Eyring plot of the rate constants for the isomerization of **11a** into the mixture of **11b** and **11c** in $CDCl_3$.

ion: $CF_3SO_3^-$]. The reaction of the $CDCl_3$ equilibrium mixture of acetonitrile adducts **11b** and **11c** with hydrogen gave complex **5** as the final product; however, an intermediate that precedes formation of **5** was observed. Only partial NMR data could be collected for this intermediate, but the observed ^1H and ^{31}P signals support its formulation as the complex **12** [Eq. (11); counterion: $CF_3SO_3^-$]. The hydride region of the



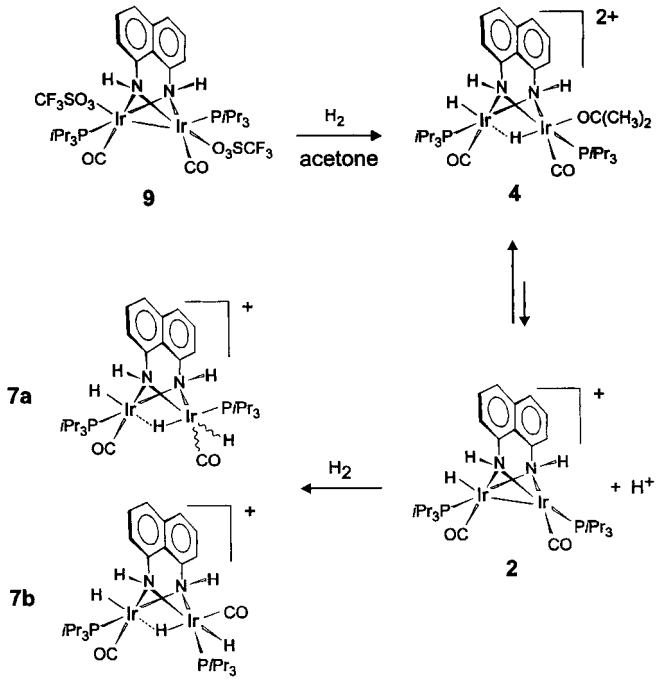
(11)

proton spectrum of **12** contains two signals: a doublet at $\delta = -16.31$ ($J(H,P) = 21.3$ Hz) and a doublet of doublets at $\delta = -11.75$ with $J(H,P) = 76.2$ and 46.2 Hz. These two unusual couplings suggest that this hydride bridges two metal atoms which have phosphane ligands in both *trans* positions. The other hydride is terminal and is *cis* with respect to one phosphane ligand. The $^{31}P\{^1H\}$ NMR spectrum displays two doublets at $\delta = 37.52$ and 23.51 with $J(P,P)$ coupling of 38.5 Hz, consistent with an all-*trans* P-Ir-H-Ir-P arrangement. Under *off resonance* conditions, the lowfield signal shows two $J(H,P)$ couplings of 21.3 and 46.2 Hz, whereas the signal at $\delta = 23.51$ is split by a $J(H,P)$ coupling of 76.2 Hz.

Equation (11) shows that H_2 adds to the diiridium(II) complexes **11** in the same way as that observed for the monohydride complex **2**. Rearrangement of **12** into the thermodynamic isomer **5** with *trans* hydrides occurs very rapidly, and is most probably favored by the dissociation of the acetonitrile ligand. Such a process is also very likely to occur for complex **9**, although in this case, the lability of the triflate ligand precludes detection of the kinetic intermediate.

Interestingly, when the reaction between **9** and H_2 is carried out in [D_6]acetone, the rapid formation of complex **4** is followed by its slow disappearance to give a mixture of the trihydrido complexes **7a** and **7b**. The reaction is complete within one hour at room temperature and 1 atm H_2 to give the same **7a**:**7b** ratio found for the reaction of the monohydrido complex **2** with hydrogen. On the basis of the Brønsted acid

properties of the dihydrido complexes **3–5** already discussed, this reaction most probably involves the sequence shown in Scheme 1. A related oxidative addition–deprotonation sequence has already been reported for the reaction of the dirhodium complex $[Rh_2(CO)_4(dppm)_2]^{2+}$ with H_2 to give $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(dppm)_2]^+$.[17]



Scheme 1. Probable sequence for the reaction between **9** and H_2

The fact that trihydride formation can be achieved in acetone but not in $CDCl_3$ is most probably related to the extension of the deprotonation equilibrium, which requires a polar medium to be established. The multistep process of Scheme 1 constitutes a heterolytic activation of molecular hydrogen[30] proceeding by classical oxidative addition and deprotonation steps.

Conclusions

Although the very basic Ir^I binuclear complex **1** does not react with hydrogen, its oxidized derivatives, obtained either by protonation (**2**) or by direct oxidation (**9** and **11**), readily undergo oxidative addition of H_2. This is in contrast with the behavior of mononuclear complexes, in which their ability to undergo oxidative addition is enhanced by increasing the electron density at the metal centers.[31] However, our experimental observations agree with the theoretical studies of bimetallic complexes: concerted addition of H_2 appears to be much easier for d^7-d^7 than for d^8-d^8 complexes.[9]

These H_2 oxidative additions occur at the *pocket* of the binuclear complex, where the available electronic density of the complex accumulates. The kinetic products resulting from these additions are asymmetric, and contain a terminal hydride ligand and a bridging one in mutually *cis* positions, as expected for a concerted process. Under appropriate conditions, these kinetic products isomerize to give the thermodynamically stable isomers, in which the hydrides are mutually *trans*.

The Ir^{III} dihydride complexes obtained by the oxidative addition of H_2, or alternatively by the unusual double protonation of **1**, display Brønsted acid properties. As a consequence, the treatment of the triflate complex **9** with H_2 in acetone gives trihydrides (**7a**, **7b**) as final products. This reaction represents a new example for the ability of transition metal complexes to perform the heterolytic cleavage of molecular hydrogen.

From the above results, we can also conclude that these binuclear Ir^{II} complexes present sites with different capabilities in oxidative addition reactions: the unreactive *axial* sites (*trans* to the neighboring metal) and the reactive *pocket* sites (*cis* to the metal). The studies carried out on the acetonitrile complexes **11** have shown the possibility of facile ligand exchange between axial and pocket sites, which suggests that these processes are intramolecular and do not require previous dissociation of the ligand.

Experimental Section

Physical measurements: Infrared spectra were recorded as Nujol mulls on polyethylene sheets with a Nicolet 550 spectrometer. C, H, N, and S analyses were carried out in a Perkin–Elmer 2400 CHNS/O analyzer. NMR spectra were recorded on a Varian UNITY, a Varian Gemini 2000 or a Bruker ARX 300 MHz spectrometer. The temperature was calibrated by ^1H NMR with a standard methanol sample. ^1H and ^{13}C chemical shifts were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane. ^{31}P and ^{19}F chemical shifts were measured relative to H_3PO_4 (85%) and $CFCl_3$, respectively. Coupling constants are given in Hz. Generally, spectral assignments were achieved by ^1H COSY and NOESY and ^{13}C DEPT experiments. The relaxation times T_1 were obtained by a conventional inversion–recovery method. The calculations of the relaxation times were made with the fitting routine of the Varian spectrometers. Cyclic voltammetric experiments were performed with an EG&GPARC Model 273 potentiostat. A three-electrode system was used, consisting of a platinum disk working electrode, a platinum wire auxiliary electrode, and a saturated calomel reference electrode. The measurements were carried out in CH_2Cl_2 solutions with 0.1M Bu_4NPF_6 as the supporting electrolyte. Under the present experimental conditions, the ferrocenium/ferrocene couple was located at $E = 0.47$ V. The reversibility of the first oxidation process was studied at scan rates of 20, 50, 100, and 200 $mV\,s^{-1}$. The ratio i_c/i_a remained close to unity and the magnitudes, $(E_{p,a} - E_{p,c})$ and $(i_{p,a})(\nu)^{-1/2}$ were constant for the different scan rates.[32]

Synthesis: All reactions were carried out with exclusion of air with standard Schlenk techniques. Solvents were dried by known procedures and distilled under Ar prior to use. The complex $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CO)_4]$ was prepared following the procedure described in reference [13b].

Preparation of $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CO)_2(P\mathit{i}Pr_3)_2]$ (1): A solution of $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CO)_4]$ (980 mg, 1.51 mmol) in diethyl ether (20 mL) was treated with triisopropylphosphane (577 μL, 3.02 mmol). After 30 min, the orange solid formed was decanted, washed with diethyl ether, and dried in vacuo. Yield: 1.15 g (83%); IR (Nujol): $\tilde{\nu} = 3358$ (N–H), 1929, 1911 (CO) cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2, 293 K): $\delta = 1.25$ (dd, $J(H,P) = 13.6$, $J(H,H) = 7.2$, 18H, $PCHCH_3$), 1.38 (dd, $J(H,P) = 13.6$, $J(H,H) = 7.2$, 18H, $PCHCH_3$), 2.40 (m, 6H, $PCHCH_3$), 4.68 (br, 2H, NH), 6.91 (d, $J(H,H) = 7.5$, 2H, CH), 7.11 (dd, $J(H,H) = 8.2$, 7.5, 2H, CH), 7.39 (d, $J(H,H) = 8.2$, 2H, CH); $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, 293 K): $\delta = 37.02$ (s); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 293 K): $\delta = 19.28$ (s, $PCHCH_3$), 19.91 (s, $PCHCH_3$), 25.95 (d, $J(C,P) = 30.1$, $PCHCH_3$), 108.97 (m, CH), 119.73 (s, CH), 120.96 (s, C), 127.50 (s, CH), 135.36 (s, C), 150.55 (AA′XX′ system, X = ^{31}P, $J(C,P) = 3.0$, $J(P,P) = 2.0$, C), 180.46 (d, $J(C,P) = 12.4$, CO); MS

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(FAB$^+$): *m/z* (%): 917 (100) [M^+], 889 (40) [$M^+ - CO$]; $C_{30}H_{50}N_2Ir_2P_2O_2$ (917.1): calcd C 39.29, H 5.49, N 3.05; found C 39.30, H 5.37, N 2.94.

Preparation of [Ir$_2$(μ-1,8-(NH)$_2$naphth)H(CO)$_2$(P*i*Pr$_3$)$_2$](CF$_3$SO$_3$) (2): A solution of **1** (150 mg, 0.16 mmol) in THF (10 mL) was treated with trifluoromethylsulfonic acid (14.6 μL, 0.16 mmol). After 30 min, the solution was concentrated ($\approx$2 mL) and the deep red solid formed was separated by decantation, washed with diethyl ether, and dried in vacuo. Yield: 143 mg (82%); IR (Nujol): $\tilde{\nu}$ = 3323 (N–H), 2197 (Ir–H), 2025, 1977 (CO) cm^{-1}; ^{1}H NMR (300 MHz, [D$_6$]acetone, 293 K): $\delta = -29.13$ (dd, J(H,P) = 18.6, J(H,P) = 4.8, 1H, Ir–H), 1.24 (dd, J(H,P) = 14.7, J(H,H) = 7.2, 9H, PCHC*H*$_3$), 1.42 (dd, J(H,P) = 15.3, J(H,H) = 7.2, 9H, PCHC*H*$_3$), 1.45 (dd, J(H,P) = 14.7, J(H,H) = 7.2, 18H, PCHC*H*$_3$), 2.88, 2.93 (m, 3H each, PC*H*CH$_3$), 7.09 (br, 1H, NH), 7.28 (br, 1H, NH), 7.34, 7.35 (t, J(H,H) = 7.5, 1H each, CH), 7.67, 7.72, 7.73, 7.76 (d, J(H,H) = 8.2, 1H each, CH); ^{31}P{^{1}H} NMR (121 MHz, [D$_6$]acetone, 293 K): δ = 38.56 (s), 33.94 (s); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]acetone, 293 K): δ = 19.14 (d, J(C,P) = 1.3, PCH*C*H$_3$), 19.99, 20.00, 20.12 (s, PCH*C*H$_3$), 25.79 (d, J(C,P) = 31.1, P*C*HCH$_3$), 26.59 (d, J(C,P) = 30.7, P*C*HCH$_3$), 112.13 (d, J(C,P) = 3.0, CH), 112.58 (d, J(C,P) = 3.2, CH), 121.95 (s,C), 122.92, 123.33, 128.50 (s, CH), 136.22 (s, C), 147.68 (d, J(C,P) = 3.7, C), 147.71 (d, J(C,P) = 1.5, C), 171.34 (d, J(C,P) = 6.9, CO), 178.96 (d, J(C,P) = 9.8, CO); ^{19}F NMR (282 MHz, [D$_6$]acetone, 293 K): $\delta = -78.32$ (s); MS (FAB+): *m/z* (%): 917 (30) [$M^+ - H$]; Λ_M (5×10^{-4} M, nitromethane) = 76 Ω^{-1}cm^{2}mol^{-1} (1:1); $C_{31}H_{51}N_2SIr_2P_2O_5F_3$ (1067.1): calcd C 34.89, H 4.72, N 2.62, S 3.00; found C 35.41, H 5.06, N 2.52, S 3.06.

Preparation of [Ir$_2$(μ-1,8-(NH)$_2$naphth)(μ-H)H(OSO$_2$CF$_3$)(CO)$_2$(P*i*Pr$_3$)$_2$](CF$_3$SO$_3$) (3): A solution of **1** (200 mg, 0.22 mmol) in CH_2Cl_2 (10 mL) was treated with trifluoromethylsulfonic acid (38.9 μL, 0.44 mmol). The color of the resulting solution slowly changed from orange to yellow. After 2 h, the solution was concentrated ($\approx$1 mL) and treated with diethyl ether to give a pale yellow solid, which was filtered off, washed with ether, and dried in vacuo. Yield: 183 mg (69%); IR (Nujol): $\tilde{\nu}$ = 3283 (N–H), 2076, 2056 (CO) cm^{-1}; ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): $\delta = -22.25$ (d, J(H,P) = 9.6, 1H, Ir—H$\cdots$Ir), -20.01 (d, J(H,P) = 19.5, 1H, Ir–H), 1.29 (dd, J(H,P) = 15.9, J(H,H) = 7.8, 18H, PCHC*H*$_3$), 1.35 (dd, J(H,P) = 16.5, J(H,H) = 6.9, 9H, PCHC*H*$_3$), 1.40 (dd, J(H,P) = 15.0, J(H,H) = 6.9, 9H, PCHC*H*$_3$), 2.51, 2.92 (m, 3H each, PC*H*CH$_3$), 5.39 (br, 1H, NH), 7.13 (dd, J(H,H) = 8.4, 8.1, 1H, CH), 7.17 (br, 1H, NH), 7.26 (t, J(H,H) = 7.8, 1H, CH), 7.50(d, J(H,H) = 7.8, 1H, CH), 7.73 (d, J(H,H) = 8.4, 1H, CH), 7.79 (d, J(H,H) = 8.1, 1H, CH), 7.88 (d, J(H,H) = 7.8, 1H, CH); ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2, 293 K): δ = 24.09 (s), 29.19 (s); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 293 K): δ = 18.99 (d, J(C,P) = 1.2, PCH*C*H$_3$), 19.54 (d, J(C,P) = 2.9, PCH*C*H$_3$), 19.65 (d, J(C,P) = 1.4, PCH*C*H$_3$), 19.80 (d, J(C,P) = 1.9, PCH*C*H$_3$), 25.46 (d, J(C,P) = 28.8, P*C*HCH$_3$), 25.47 (d, J(C,P) = 30.6, P*C*HCH$_3$), 114.44 (d, J(C,P) = 3.6, CH), 114.76 (d, J(C,P) = 3.9, CH), 122.98 (s, C), 123.66, 124.23, 127.15, 127.47 (s, CH), 135.38 (s, C), 142.94 (d, J(C,P) = 2.8, C), 143.07 (d, J(C,P) = 3.2, C), 164.53 (d, J(C,P) = 6.6, CO), 164.54 (d, J(C,P) = 7.3, CO); ^{19}F NMR (282 MHz, CD_2Cl_2, 293 K): $\delta = -77.97$ (s), -78.85 (s); MS (FAB$^+$): *m/z* (%): 918 (40) [$M^+ - HO_3SCF_3$]; Λ_M (5 E–4 M, CH_2Cl_2) = 10.5 Ω^{-1}cm^{2}mol^{-1} (1:1); $C_{32}H_{52}N_2S_2Ir_2P_2O_8F_6$ (1217.2): calcd C 31.58, H 4.31, N 2.30, S 5.27; found C 31.05, H 4.34, N 2.19, S 5.41.

Preparation of [Ir$_2$(μ-1,8-(NH)$_2$naphth)(μ-H)H(OC(CH$_3$)$_2$)(CO)$_2$(P*i*Pr$_3$)$_2$](CF$_3$SO$_3$)$_2$ (4): A suspension **1** (200 mg, 0.22 mmol) in acetone (10 mL) was treated with trifluoromethylsulfonic acid (38.9 μL, 0.44 mmol). The color of the resulting solution slowly changed from orange to yellow. After 2 h, the solution was concentrated to about 2 mL which led to a yellow solid. Precipitation of the compound was completed by addition of diethyl ether (10 mL). The solid was filtered off washed with ether and dried in vacuo. Yield: 210 mg (75%). IR (Nujol): $\tilde{\nu}$ = 3269 (N–H), 2250 (Ir–H), 2071, 2054 (CO), 1709 (C=O) cm^{-1}; ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): $\delta = -22.07$ (d, J(H,P) = 9.3, 1H, Ir–H$\cdots$Ir), -20.77 (dd, J(H,P) = 19.5, J(H,P) = 1.8, 1H, Ir–H), 1.28 (dd, J(H,P) = 15.6, J(H,H) = 6.6, 9H, PCHC*H*$_3$), 1.29 (dd, J(H,P) = 15.6, J(H,H) = 7.2, 9H, PCHC*H*$_3$), 1.31 (dd, J(H,P) = 15.3, J(H,H) = 6.6, 9H, PCHC*H*$_3$), 1.33 (dd, J(H,P) = 16.3, J(H,H) = 7.5, 9H, PCHC*H*$_3$), 1.77 (s, 6H, OC(CH$_3$)$_2$), 2.68, 2.95 (m, 3H each, PC*H*CH$_3$), 7.23 (br, 1H, NH), 7.28 (t, J(H,H) = 7.8, 1H, CH), 7.35 (t, J(H,H) = 8.1, 1H, CH), 7.62 (br, 1H, NH), 7.73 (d, J(H,H) = 8.1, 1H, CH), 7.81 (d, J(H,H) = 8.1, 1H, CH), 7.93 (d, J(H,H) = 7.8, 1H, CH), 8.07 (d, J(H,H) = 7.8, 1H, CH); ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2, 293 K): δ = 22.14 (s), 31.08 (s); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 293 K): δ = 19.04 (d, J(C,P) = 2.2, PCH*C*H$_3$), 19.19 (d, J(C,P) = 2.9, PCH*C*H$_3$), 19.24 (d, J(C,P) = 1.8, PCH*C*H$_3$), 19.79 (d, J(C,P) = 1.4, PCH*C*H$_3$), 25.71 (d, J(C,P) = 30.6, P*C*HCH$_3$), 26.64 (d, J(C,P) = 29.5, P*C*HCH$_3$), 32.25 (s, OC(*C*H$_3$)$_2$), 115.49 (d, J(C,P) = 3.4, CH), 115.72 (d, J(C,P) = 3.6, CH), 123.06 (s, C), 123.44, 123.99, 127.74, 128.52 (s, CH), 135.05 (s, C), 143.04 (d, J(C,P) = 3.4, C), 143.36 (d, J(C,P) = 3.0, C), 163.80 (d, J(C,P) = 8.2, CO), 164.59 (d, J(C,P) = 7.3, CO), 231.81 (s, O*C*(CH$_3$)$_2$); ^{19}F NMR (282 MHz, CD_2Cl_2, 293 K): $\delta = -78.85$ (s); Λ_M (5×10^{-4} M, nitromethane) = 136 Ω^{-1}cm^{2}mol^{-1} (1:2); $C_{35}H_{58}N_2S_2Ir_2P_2O_9F_6$ (1275.2): calcd C 32.96, H 4.58, N 2.21, S, 5.03; found C 33.02, H 4.90, N 2.15, S 5.20.

Preparation of [Ir$_2$(μ-1,8-(NH)$_2$naphth)(μ-H)H(NCCH$_3$)(CO)$_2$(P*i*Pr$_3$)$_2$](CF$_3$SO$_3$)$_2$ (5): A suspension of **1** (200 mg, 0.22 mmol) in acetone (10 mL) was treated with trifluoromethylsulfonic acid (38.9 μL, 0.44 mmol). After 2 h, the solution was treated with acetonitrile (excess, $\approx$50 μL) to give a pale yellow solution. Partial evaporation of this solution ($\approx$2 mL) followed by addition of diethyl ether (10 mL) resulted in the crystallization of a yellow solid. The solid was filtered off, washed with diethyl ether, and dried in vacuo. Yield: 186 mg (68%); IR (Nujol): $\tilde{\nu}$ = 3267 (N–H), 2253 (Ir–H), 2083, 2058 (CO) cm^{-1}; ^{1}H NMR (300 MHz, [D$_6$]acetone, 293 K): $\delta = -19.13$ (ddd, J(H,P) = 19.5, J(H,P) = 2.1, J(H,H) = 2.0, 1H, Ir–H), -18.03 (dd, J(H,P) = 7.8, J(H,H) = 2.0, 1H, Ir–H$\cdots$Ir), 1.39 (dd, J(H,P) = 16.2, J(H,H) = 7.2, 9H, PCHC*H*$_3$), 1.39 (dd, J(H,P) = 15.6, J(H,H) = 7.2, 9H, PCHC*H*$_3$), 1.41 (dd, J(H,P) = 15.3, J(H,H) = 7.2, 9H, PCHC*H*$_3$), 1.48 (dd, J(H,P) = 15.0, J(H,H) = 6.9, 9H, PCHC*H*$_3$), 1.75 (s, 3H, NCCH$_3$), 2.86, 3.10 (m, 3H each, PC*H*CH$_3$), 7.25 (br, 2H, NH), 7.41 (t, J(H,H) = 8.1, 1H, CH), 7.45 (t, J(H,H) = 7.8, 1H, CH), 7.95 (d, J(H,H) = 8.1, 1H, CH), 7.97 (d, J(H,H) = 8.1, 1H, CH), 8.00 (d, J(H,H) = 7.8, 1H, CH), 8.10 (d, J(H,H) = 7.8, 1H, CH); ^{31}P{^{1}H} NMR (121 MHz, [D$_6$]acetone, 293 K): δ = 25.75 (s), 32.48 (s); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]acetone, 293 K): δ = 1.66 (s, NC*C*H$_3$), 19.17, 19.22, 19.84, 19.89 (s, PCH*C*H$_3$), 25.97 (d, J(C,P) = 31.1, P*C*HCH$_3$), 26.59 (d, J(C,P) = 29.8, P*C*HCH$_3$), 114.86, 115.66 (d, J(C,P) = 4.0, CH), 121.78 (s, N*C*CH$_3$), 124.32 (s, C), 124.55, 124.61, 128.64 (s, CH), 135.83 (s, C), 144.83 (d, J(C,P) = 3.1, C), 145.26 (d, J(C,P) = 2.8, C), 161.36 (d, J(C,P) = 7.6, CO), 165.82 (d, J(C,P) = 7.3, CO); MS (FAB$^+$): *m/z* (%): 917 (55) [M^+ – NCCH$_3$ – 2H]; Λ_M (5×10^{-4} M, acetone) = 177 Ω^{-1}cm^{2}mol^{-1} (1:2); $C_{34}H_{55}N_3S_2Ir_2P_2O_8F_6$ (1258.3): calcd C 32.45, H 4.24, N 3.34, S 5.09; found C 32.76, H 4.74, N 3.41, S 5.33.

[Ir$_2$(μ-1,8-(NH)$_2$naphth)H$_2$(CO)$_2$(P*i*Pr$_3$)$_2$](CF$_3$SO$_3$)$_2$ (6): A solution of **1** (20 mg, 0.02 mmol) in CD_2Cl_2 (0.5 mL) was treated with excess trifluoromethylsulfonic acid (10.0 μL, 0.11 mmol). After 2 min at room temperature, the ^{1}H NMR spectrum of the reaction showed a mixture of complexes **3** and **6** in a 3:1 molar ratio. Partial NMR data for complex **6**: ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): $\delta = -26.86$ (d, J(H,P) = 18.3, 2H, Ir–H), 1.19 (dd, J(H,P) = 15.6, J(H,H) = 7.2, 18H, PCHC*H*$_3$), 2.58 (m, 6H, PC*H*CH$_3$), 5.49 (br, 2H, NH); ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2, 293 K): δ = 22.76 (s); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 253 K): δ = 18.56, 19.28 (s, PCH*C*H$_3$), 24.62 (d, J(C,P) = 33.7, P*C*HCH$_3$), 123.06 (s, C), 123.67, 127.32 (s, CH), 149.34 (d, J(C,P) = 2.8, C), 164.00 (d, J(C,P) = 7.5, CO).

Preparation of [Ir$_2$(μ-1,8-(NH)$_2$naphth)(μ-H)H$_2$(CO)$_2$(P*i*Pr$_3$)$_2$](CF$_3$SO$_3$) (7): Hydrogen was bubbled through a solution of complex **2** (200 mg, 0.22 mmol) in acetone (10 mL) for 5 min. The resulting pale yellow solution was concentrated ($\approx$1 mL) and diethyl ether was added which resulted in the precipitation of a pale yellow solid. The solid was separated by decantation, washed with diethyl ether, and dried in vacuo. Yield: 174 mg (87%); IR (Nujol): $\tilde{\nu}$ = 3290 (NH), 2154 (IrH), 2031 (CO) cm^{-1}; MS (FAB+): *m/z* (%): 919 (100) [$M^+ - H$]; Λ_M (5×10^{-4} M, acetone) = 82 Ω^{-1}cm^{2}mol^{-1} (1:1); $C_{31}H_{53}N_2SIr_2P_2O_5F_3$ (1069.1): calcd C 34.83, H 4.99, N 2.62, S 3.00; found C 34.81, H 4.53, N 2.38, S 3.12. Spectroscopic analysis of the solid obtained revealed a mixture of two isomers, **7a** and **7b**, in a 0.41:0.59 molar ratio.

Isomer ***7a***: ^{1}H NMR (300 MHz, [D$_6$]acetone, 293 K): $\delta = -16.82$ (d, J(H,P) = 19.8, 1H, Ir–H), -12.45 (ddd, J(H,P) = 29.1, J(H,P) = 18.9, J(H,H) = 3.3, 1H, Ir–H), -10.46 (ddd, J(H,P) = 70.2, J(H,P) = 3.6, J(H,H) = 3.3, 1H, Ir-H-Ir), 0.67 (dd, J(H,P) = 15.6, J(H,H) = 7.2, 9H, PCHC*H*$_3$), 1.18 (dd, J(H,P) = 15.6, J(H,H) = 6.9, 9H, PCHC*H*$_3$), 1.35 (dd, J(H,P) = 15.3, J(H,H) = 7.2, 18H, PCHC*H*$_3$), 1.82, 2.60 (m, 3H each, PC*H*CH$_3$), 5.40, 6.92 (br, 1H each, NH), 7.21 (dd, J(H,H) = 8.1, 7.5, 1H, CH), 7.25 (t, J(H,H) = 7.5, 1H, CH), 7.58 (d, J(H,H) = 7.5, 1H, CH), 7.64 (d, J(H,H) = 8.1, 1H, CH), 7.65 (d, J(H,H) = 7.5, 1H, CH), 7.71 (d, J(H,H) = 8.1, 1H, CH); ^{31}P{^{1}H} NMR (121 MHz, [D$_6$]acetone, 293 K): δ = 33.12 (s),

33.24 (s); $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]acetone, 293 K): $\delta = 18.75$ (d, $J(C,P) = 2.9$, PCHCH_3), 18.91 (d, $J(C,P) = 2.8$, PCHCH_3), 19.71 (s, PCHCH_3), 20.59 (d, $J(C,P) = 1.8$, PCHCH_3), 25.54 (d, $J(C,P) = 31.1$, PCHCH$_3$), 26.34 (d, $J(C,P) = 29.2$, PCHCH$_3$), 110.85 (d, $J(C,P) = 4.4$, CH), 111.57, 121.66, 122.56 (s, CH), 122.62 (s, C), 127.37, 127.51 (s, CH), 136.71 (s, C), 149.95 (d, $J(C,P) = 3.5$, 2.3, C), 152.73 (s, C), 167.60 (d, $J(C,P) = 10.5$, CO), 167.62 (s, CO).

Isomer ***7b***: ^1H NMR (300 MHz, [D$_6$]acetone, 293 K): $\delta = -17.57$ (d, $J(H,P) = 15.9$, 1H, Ir–H), -15.32 (dd, $J(H,P) = 17.4$, $J(H,H) = 9.3$, 1H, Ir–H), -11.15 (ddd, $J(H,P) = 6.3$, $J(H,P) = 3.3$, $J(H,H) = 9.3$, 1H, Ir-H-Ir), 1.32 (dd, $J(H,P) = 15.3$, $J(H,H) = 7.2$, 9H, PCHCH_3), 1.34 (dd, $J(H,P) = 15.6$, $J(H,H) = 7.2$, 9H, PCHCH_3), 1.35 (dd, $J(H,P) = 15.6$, $J(H,H) = 6.9$, 9H, PCHCH_3), 1.36 (dd, $J(H,P) = 15.0$, $J(H,H) = 6.9$, 9H, PCHCH_3), 2.68, 2.70 (m, 3H each, PCHCH$_3$), 5.88, 6.00 (br, 1H each, NH), 7.25 (t, $J(H,H) = 7.5$, 2H, CH), 7.61, 7.66, 7.67, 7.72 (d, $J(H,H) = 7.5$, 1H each, CH); $^{31}P\{^1H\}$ NMR (121 MHz, [D$_6$]acetone, 293 K): $\delta = 31.83$ (s), 33.02 (s); $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]acetone, 293 K): $\delta = 17.93$ (d, $J(C,P) = 2.1$, PCHCH_3), 19.09 (s, PCHCH_3), 19.59 (s, PCHCH_3), 20.39 (s, PCHCH_3), 25.95 (d, $J(C,P) = 30.7$, PCHCH$_3$), 26.70 (d, $J(C,P) = 32.0$, PCHCH$_3$), 109.95, 110.57 (d, $J(C,P) = 3.2$, CH), 121.49 (s, CH), 121.73 (s, C), 122.93 (s, CH), 127.13, 127.62 (s, CH), 136.67 (s, C), 149.54 (dd, $J(C,P) = 3.2$, 2.3, C), 152.77 (s), 165.50 (d, $J(C,P) = 8.7$, CO), 167.73 (d, $J(C,P) = 10.2$, CO).

Preparation of [Ir$_2$(μ-1,8-(NH)$_2$naphth)(μ-H)H$_2$(CO)$_2$(P*i*Pr$_3$)$_2$](CF$_3$SO$_3$) (8): Triethylamine (1 μL, 0.07 mmol) was added to a solution of **7** (60 mg, 0.06 mmol) in acetone (10 mL). After 5 h, the solution was taken to dryness, and the residue treated with diethyl ether to give a pale yellow microcrystalline solid. The solid was filtered off, washed with ether, and dried in vacuo. Yield: 98 mg (81 %); IR (Nujol): $\tilde{\nu} = 3292$ (N–H), 2129 (Ir–H), 2027 (CO) cm^{-1}; ^1H NMR (300 MHz, [D$_6$]acetone, 293 K): $\delta = -13.59$ (A part of an AA′MXX′ system (M = ^1H, X = ^{31}P), $J_{AM} = J_{A'M} = 10.9$, $J_{AX} = J_{A'X'} = 17.3$, $J_{A'X} = J_{AX'} = 0$, $J_{AA'} = 18.0$, 2H, Ir–H), -9.68 (M part of an AA′MXX′ system (M = ^1H, X = ^{31}P), $J_{AM} = J_{A'M} = 10.9$, $J_{MX} = J_{MX'} = 4.5$, 1H, Ir-H-Ir), 1.36, 1.39 (dd, $J(H,P) = 14.7$, $J(H,H) = 6.9$, 18H each, PCHCH_3), 2.70 (m, 6H, PCHCH$_3$), 5.78 (br, 2H, NH), 7.35 (t, $J(H,H) = 7.8$, 2H, CH), 7.56, 7.72, (d, $J(H,H) = 7.8$, 2H each, CH); $^{31}P\{^1H\}$ NMR (121 MHz, [D$_6$]acetone, 293 K): $\delta = 31.79$ (s); $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]acetone, 293 K): $\delta = 18.09$ (d, $J(C,P) = 1.5$, PCHCH_3), 18.90 (s, PCHCH_3), 25.06 (d, $J(C,P) = 31.1$, PCHCH$_3$), 110.60 (d, $J(C,P) = 1.3$, CH), 122.14 (s,C), 122.42, 126.63 (s, CH), 135.87 (s, C), 150.52 (d, $J(C,P) = 2.8$, C), 167.60 (dd, $J(C,P) = 9.2$, 1.1, CO); ^{19}F NMR (282 MHz, [D$_6$]acetone, 293 K): $\delta = -78.32$ (s); MS (FAB$^+$): *m/z* (%): 919 (100) [$M^+ - H$]; Λ_M (5×10^{-4} M, nitromethane) = 100 Ω^{-1}cm^{2}mol^{-1} (1:1); $C_{31}H_{53}N_2SIr_2P_2O_5F_3$ (1069.1): calcd C 34.83, H 4.99, N 2.62, S 3.00; found C 35.39, H 5.07, N 2.41, S 3.09.

Preparation of [Ir$_2$(μ-1,8-(NH)$_2$naphth)(OSO$_2$CF$_3$)$_2$(CO)$_2$(P*i*Pr$_3$)$_2$] (9): A solution containing [FeCp$_2$]CF$_3$SO$_3$[28] (0.43 mmol) in acetone was added to a suspension of **1** (200 mg, 0.22 mmol) in acetone (10 mL). After 30 min, the resulting orange solution was dried in vacuo, and the residue repeatedly washed with diethyl ether. The brown solid obtained was dissolved in toluene and treated with dry MgSO$_4$ for 1 h. The solution was then filtered through kieselgur and the solvent removed. Treatment of the residue with pentane gave a white solid, which was separated by decantation, washed with pentane, and dried in vacuo. Yield: 169 mg (64 %); IR (Nujol): $\tilde{\nu} = 3234$ (N–H), 2054, 2012 (CO) cm^{-1}; ^1H NMR (300 MHz, CD$_2$Cl$_2$, 293 K): $\delta = 0.81$ (dd, $J(H,P) = 15.0$, $J(H,H) = 7.2$, 9H, PCHCH_3), 1.21 (dd, $J(H,P) = 15.0$, $J(H,H) = 7.2$, 9H, PCHCH_3), 1.21 (dd, $J(H,P) = 16.8$, $J(H,H) = 7.2$, 9H, PCHCH_3), 1.71, 2.83 (m, 3H each, PCHCH$_3$), 7.31 (dd, $J(H,H) = 7.8$, 8.1 1H, CH), 7.35–7.45 (m, 2H, CH), 7.37 (br, 1H, NH), 7.74 (d, $J(H,H) = 7.8$, 1H, CH), 7.82 (d, $J(H,H) = 8.1$, 1H, CH), 7.98 (d, $J(H,H) = 7.5$, 1H, CH), 8.58 (br, 1H, NH); $^{31}P\{^1H\}$ NMR (121 MHz, CD$_2$Cl$_2$, 293 K): $\delta = 0.18$ (d, $J(P,P) = 8.8$), 41.19 (d, $J(P,P) = 8.8$); $^{13}C\{^1H\}$ NMR (75 MHz, CDCl$_3$, 293 K): $\delta = 17.61$ (d, $J(C,P) = 4.1$, PCHCH_3), 18.73, 19.85, 20.09 (s, PCHCH_3), 24.16 (d, $J(C,P) = 26.3$, PCHCH$_3$), 26.55 (d, $J(C,P) = 31.0$, PCHCH$_3$), 113.31 (d, $J(C,P) = 1.9$, CH), 117.12 (s, CH), 120.14 (s, C), 124.86, 125.66, 126.87, 127.92 (s, CH), 134.81 (s, C), 142.72 (d, $J(C,P) = 3.6$, C), 143.00 (s, C), 164.08 (d, $J(C,P) = 7.1$, CO), 177.89 (dd, $J(C,P) = 10.5$, 1.3, CO); ^{19}F NMR (282 MHz, CDCl$_3$, 293 K): $\delta = -77.60$ (s), -78.98 (br); MS (FAB$^+$): *m/z* (%): 1065 (25) [M^+], 917 (100) [$M^+ - CF_3SO_3$]; Λ_M (5×10^{-4} M, acetone) = 129 Ω^{-1}cm^{2}mol^{-1} (1:1); $C_{32}H_{50}N_2S_2Ir_2P_2O_8F_6$ (1215.2): calcd C 31.63, H 4.15, N 2.30, S 5.28; found C 31.76, H 4.76, N 2.14, S 4.84.

Preparation of [Ir$_2$(μ-1,8-(NH)$_2$naphth)(CO)$_2$(P*i*Pr$_3$)$_2$(tht)$_2$](CF$_3$SO$_3$)$_2$ (10): A solution of **9** (100 mg, 0.082 mmol) in toluene (10 mL) was treated with THT (22.4 μL, 0.25 mmol) to precipitate an orange solid. The solution was decanted, the solid washed with diethyl ether, and dried in vacuo. The product was recrystallized by slow diffusion of diethyl ether into a saturated solution in acetone. Yield: 101 mg (89 %); IR (Nujol): $\tilde{\nu} = 3270$ (N–H), 1927, 1917 (CO) cm^{-1}; ^1H NMR (300 MHz, CDCl$_3$, 293 K): $\delta = 0.63$, 1.20 (m, 4H each, CH$_2$), 1.41 (dd, $J(H,P) = 14.1$, $J(H,H) = 6.9$, 18H, PCHCH_3), 1.43 (dd, $J(H,P) = 14.7$, $J(H,H) = 7.2$, 18H, PCHCH_3), 1.65, 2.37 (m, 4H each, CH$_2$), 2.78 (m, 6H, PCHCH$_3$), 7.35 (dd, $J(H,H) = 7.2$, 8.1, 2H, CH), 7.59 (br, 2H, NH), 7.80 (d, $J(H,H) = 8.1$, 2H, CH), 8.16 (d, $J(H,H) = 7.2$, 2H, CH); $^{31}P\{^1H\}$ NMR (121 MHz, CDCl$_3$, 293 K): $\delta = 11.89$ (s); $^{13}C\{^1H\}$ NMR (75 MHz, CDCl$_3$, 293 K): $\delta = 19.23$ (d, $J(C,P) = 1.8$, PCHCH_3), 19.70 (d, $J(C,P) = 2.7$, PCHCH_3), 25.37 (d, $J(C,P) = 27.4$, PCHCH$_3$), 28.82, 34.47 (s, CH_2), 114.88 (d, $J(C,P) = 2.0$, CH), 120.54 (s, C), 122.87, 120.01 (s, CH), 135.64 (s, C), 146.54 (d, $J(C,P) = 2.7$, C), 169.72 (d, $J(C,P) = 9.1$, CO); ^{19}F NMR (282 MHz, CDCl$_3$, 293 K): $\delta = -79.17$ (s); MS (FAB$^+$): *m/z* (%): 1065 (70) [$M^+ - CO$], 917 (100) [$M^+ - 2(SC_4H_8)$]; Λ_M (5×10^{-4} M, acetone) = 161 Ω^{-1}cm^{2}mol^{-1} (1:2); $C_{40}H_{66}N_2S_4Ir_2P_2O_8F_6$ (1391.5): calcd C 34.52, H 4.78, N 2.01, S 9.22; found C 34.27, H 4.90, N 2.06, S, 9.33.

[Ir$_2$(μ-1,8-(NH)$_2$naphth)(CO)$_2$(P*i*Pr$_3$)$_2$(NCCH$_3$)$_2$](CF$_3$SO$_3$)$_2$ (11a): A solution of **9** (20 mg, 0.016 mmol) in CDCl$_3$ (0.5 mL) was treated with acetonitrile (1 μL). After 2 min at room temperature, the ^1H NMR spectrum of the reaction showed the presence of complex **11a** as the sole product. ^1H NMR (300 MHz, CDCl$_3$, 293 K): $\delta = 1.30$ (dd, $J(H,P) = 15.9$, $J(H,H) = 7.2$, 18H, PCHCH_3), 1.31 (dd, $J(H,P) = 13.8$, $J(H,H) = 7.2$, 18H, PCHCH_3), 1.51 (s, 6H, NCCH$_3$), 2.61 (m, 6H, PCHCH$_3$), 7.34 (t, $J(H,H) = 8.1$, 2H, CH), 7.49 (br, 2H, NH), 7.80, 8.25 (d, $J(H,H) = 8.1$, 2H each, CH); $^{31}P\{^1H\}$ NMR (121 MHz, CDCl$_3$, 293 K): $\delta = 21.63$ (s).

Preparation of [Ir$_2$(μ-1,8-(NH)$_2$naphth)(CO)$_2$(P*i*Pr$_3$)$_2$(NCCH$_3$)$_2$](CF$_3$SO$_3$)$_2$ (11b): A solution of **9** (200 mg, 0.16 mmol) in acetone (10 mL) was treated with acetonitrile (1 mL). After 1 h, the solution was concentrated and diethyl ether added, which caused the precipitation of a yellow solid. The solid was separated by decantation, washed with diethyl ether, and dried in vacuo. The product was recrystallized by slow diffusion of diethyl ether into a saturated solution in acetone. Yield: 178 mg (84 %); IR (Nujol): $\tilde{\nu} = 3252$, 3227 (N–H), 2042, 2008 (CO) cm^{-1}; ^1H NMR (300 MHz, [D$_6$]acetone, 293 K): $\delta = 0.80$ (dd, $J(H,P) = 14.4$, $J(H,H) = 7.2$, 9H, PCHCH_3), 1.25 (dd, $J(H,P) = 16.2$, $J(H,H) = 7.2$, 9H, PCHCH_3), 1.38 (dd, $J(H,P) = 15.3$, $J(H,H) = 7.2$, 9H, PCHCH_3), 1.41 (dd, $J(H,P) = 16.8$, $J(H,H) = 7.2$, 9H, PCHCH_3), 1.77 (s, 3H, NCCH$_3$), 1.85, 2.77 (m, 3H each, PCHCH$_3$), 3.01 (s, 3H, NCCH$_3$), 7.34, 7.40 (t, $J(H,H) = 7.6$, 1H each, CH), 7.86 (br, 1H, NH), 7.93, 7.95, 7.97, 8.11 (d, $J(H,H) = 7.6$, 1H each, CH), 8.33 (br, 1H, NH); $^{31}P\{^1H\}$ NMR (121 MHz, [D$_6$]acetone, 293 K): $\delta = -6.83$ (s), 29.70 (s); $^{13}C\{^1H\}$ NMR (75 MHz, [D$_6$]acetone, 293 K): $\delta = 1.13$, 4.37 (s, NCCH_3), 18.13 (d, $J(C,P) = 3.2$, PCHCH_3), 19.60 (d, $J(C,P) = 2.2$, PCHCH_3), 19.80, 20.1 (s, PCHCH_3), 24.94 (d, $J(C,P) = 23.3$, PCHCH$_3$), 25.90 (d, $J(C,P) = 29.8$, PCHCH$_3$), 114.87 (d, $J(C,P) = 1.7$, CH), 115.49 (s, CH), 120.18 (s, NCCH_3), 121.12 (s, NCCH_3), 123.68, 124.45 (s, CH), 127.70 (s, C), 128.68 (s, CH), 128.82 (s, CH), 136.33 (s, C), 144.77 (d, $J(C,P) = 3.5$, C), 146.8 (s, C), 170.16 (dd, $J(C,P) = 7.2$, 2.1, CO), 172.72 (d, $J(C,P) = 10.9$, CO); MS (FAB$^+$): *m/z* (%): 917 (100) [$M^+ - 2NCCH_3$]; Λ_M (5×10^{-4} M, acetone) = 150 Ω^{-1}cm^{2}mol^{-1} (1:2); $C_{36}H_{56}N_4S_2Ir_2P_2O_8F_6$ (1297.3): calcd C 33.33, H 4.35, N 4.35, S 4.94; found C 33.30, H 3.75, N 4.44, S 4.93.

[Ir$_2$(μ-1,8-(NH)$_2$naphth)(CO)$_2$(P*i*Pr$_3$)$_2$(NCCH$_3$)$_2$](CF$_3$SO$_3$)$_2$ (11c): Complex **11b** (20 mg, 0.016 mmol) was dissolved in CDCl$_3$ (0.5 mL). After 2 min at room temperature, the ^1H NMR spectrum of the solution showed the presence of a mixture of complexes **11b** and **11c** in a 2:1 molar ratio. Data for **11c**: ^1H NMR (300 MHz, CDCl$_3$, 293 K): $\delta = 0.85$ (dvt, $N = 15.3$, $J(H,H) = 7.2$, 18H, PCHCH_3), 0.92 (dvt, $N = 14.7$, $J(H,H) = 7.8$, 18H, PCHCH_3), 1.50 (m, 6H, PCHCH$_3$), 2.88 (s, 6H, NCCH_3), 7.30 (dd, $J(H,H) = 7.8$, 7.5, 2H, CH), 7.73 (d, $J(H,H) = 7.8$, 2H, CH), 8.18 (d, $J(H,H) = 7.5$, 2H, CH), 8.52 (br, 2H, NH); $^{31}P\{^1H\}$ NMR (121 MHz, CDCl$_3$, 293 K): $\delta = 9.19$ (s); $^{13}C\{^1H\}$ NMR (75 MHz, CDCl$_3$, 293 K): $\delta = 4.35$ (s, NCCH_3), 18.91, 19.20 (s, PCHCH_3), 24.66 (vt, $N = 23.3$, PCHCH$_3$), 114.87 (s, CH), 120.91 (s, NCCH_3), 122.15 (s, CH), 125.56 (s, C), 127.76 (s, CH), 134.76 (s, C), 145.15 (s, C), 170.94 (s, CO).

Kinetic analysis: The kinetics of the isomerization of **11a** into the mixture of **11b** and **11c** were measured in 0.22 M solutions of **11a** in CDCl$_3$. The decrease in the intensity of the $^{31}P\{^1H\}$ NMR signal of **11a** was measured automatically at intervals in a Varian Gemini 2000 spectrometer. The rate

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constants were obtained by fitting the data to an exponential decay function with the routine programs of the spectrometer. The activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, were obtained from a linear least-squares fit of $\ln(k/T)$ vs $1/T$ (Eyring equation). Errors were computed by published methods.[33] The error in temperature was assumed to be 1 K, error in k_{obs} was estimated as 10%.

The rate constants of acetonitrile exchange between **11a** and free acetonitrile were measured by spin-saturation transfer according to the Forsén–Hoffman method,[34] in 0.022 M $CDCl_3$ solutions of **11a**. Experiments were performed by irradiating the resonance of the free acetonitrile and measuring the integral of the coordinated acetonitrile resonance. The exchange rates k_{obs} were calculated from the equation[34] $k_{obs} = (1/T_1)((I/I') - 1)$, where I' and I are the integrals for the coordinated acetonitrile resonance with and without saturation of the free acetonitrile resonance, respectively. T_1 is the spin-lattice relaxation time of the coordinated acetonitrile signal obtained by the inversion-recovery method in the presence of the saturating field at the free acetonitrile signal.[35]

Crystal structure determinations of 4·$(CH_3)_2CO$ and 11b: A summary of the crystal data and refinement parameters is given in Table 4. Cell constants were obtained from the least-squares fit on the setting angles of 62 (**4**) or 48 (**11b**) reflections in the range $25 \le 2\theta \le 42^\circ$. Data were collected on a Siemens-P4 four-circle diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), with $\omega/2\theta$ (**4**) or ω (**11b**) scan methods. A set of three standard reflections was monitored every 97 measured reflections throughout the data collection; the weak decay of the intensity which was detected (1.15 (**4**) and 5.1% (**11b**)) was corrected according to standards. All data were corrected for Lorentz and polarization effects, and for absorption by using a semiempirical method (Ψ scans,[36] min. and max. transmission factors 0.105 and 0.189 for **4**, and 0.079 and 0.161 for **11b**). Both structures were solved by direct methods[37] and Fourier techniques, and refined by full-matrix least-squares on F^2(SHELXL-97).[38] Atomic scattering factors, corrected for anomalous dispersion, were used as implemented in the refinement program.

Table 4. Crystallographic data for complexes **4** and **11b**.

	4	**11b**
chem. formula	$C_{35}H_{58}F_6Ir_2N_2O_9P_2S_2 \cdot C_2H_6O$	$C_{36}H_{56}F_6Ir_2N_4O_8P_2S_2$
fw	1333.37	1297.31
T [K]	120.0(2)	200.0(2)
space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a [Å]	17.4764(19)	12.9068(11)
b [Å]	11.7935(14)	12.0318(9)
c [Å]	24.531(2)	31.608(3)
β [°]	94.259(8)	100.412(7))
V [Å^3]	5042.0(9)	4827.7(7))
Z	4	4
ρ_{calcd} [g cm^{-3}]	1.757	1.785
$\mu(Mo_{K\alpha})$ [mm^{-1}]	5.493	5.732
R(F) [$F^2 > 2\sigma(F^2)$][a]	0.0386	0.0498
$wR(F^2)$ [all data][b]	0.0875	0.1309
S [all data][c]	0.906	1.056

[a] $R(F) = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, for 6254 and 6208 observed reflections. [b] $wR(F^2) = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])^{1/2}$. [c] $S = [\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$; n = number of reflections, p = number of parameters.

Data for ***4***: A yellow prismatic block ($0.32 \times 0.28 \times 0.10$ mm) was indexed to monoclinic symmetry. Data was collected in the range $4 \le 2\theta \le 50^\circ$ ($-14 \le h \le 20$, $-9 \le k \le 14$, $-29 \le l \le 29$); 12820 measured reflections, 8818 unique ($R_{int} = 0.0336$). Anisotropic displacement parameters were used in the last cycles of refinement for all non-hydrogen atoms of the metal complex and of the crystallization acetone molecule. The two triflate anions were observed as statistically disordered. One was modeled with two groups of isotropic atoms with complementary occupancy factors (0.636 and 0.364(1)). The second anion showed a partial disorder affecting only the CF_3 group; this was also modeled with two moieties of identical occupancy (0.48 and 0.52(4)). Hydrogen atoms were included from difference Fourier maps for the amido groups and hydride ligands, and in calculated positions for the remaining hydrogens; all were refined with a riding model. The weighting scheme used was $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$ ($P = (F_o^2 + 2F_c^2)/3$) with $x = 0.0477$ and $y = 0.000$. Final agreement factors were $R(F)$ 0.0386 (6254 observed reflections, $F_o^2 < 2\sigma F_o^2$) and wR 0.0875 (all data) for 570 parameters. Largest peak in the final difference map is 1.69 e Å^{-3} and is situated close to a metal atom.

Data for ***11b***: A yellow prismatic crystal ($0.55 \times 0.46 \times 0.31$ mm) was mounted on the top of a glass fiber and a set of randomly searched reflections were indexed to monoclinic symmetry. Data was collected in the range $4 \le 2\theta \le 50^\circ$ ($-1 \le h \le 15$, $-1 \le k \le 14$, $-37 \le l \le 37$); 10623 measured reflections, 8426 unique ($R_{int} = 0.0280$). After refinement of all non-hydrogen atoms with anisotropic displacement parameters, the hydrogen atoms of the 1,8-diamidonaphthalene ligand and those of the tertiary carbon atoms of the phosphane ligand were positioned in calculated positions. These hydrogen atoms were treated in the refinement riding on the corresponding carbon or nitrogen atoms. The SO_3CF_3 anions were refined with several feeble geometric restrictions (SADI command). The weighting scheme used was analogous to that for **4** ($x = 0.0785$ and $y = 0.2651$). Final agreement factors were $R(F) = 0.0498$ (6208 observed reflections, $F_o^2 < 2\sigma F_o^2$) and $wR = 0.1309$ (all data) for 545 parameters and 61 restraints. Maximum residual peak in the final difference map was 1.498 e Å^{-3}.

Crystallographic data (excluding structure factors) for the structures reported have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100898. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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