

Articles

Facile and Reversible O–H and C–H Activation by a Chiral Iridium(I) Complex

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The reactivity of the dinuclear Ir(I) complexes *cis*- and *trans*-[Ir₂(μ-Cl)₂((*R*)-(*S*)-PPFPPh₂)₂] (**1**, (*R*)-(*S*)-PPFPPh₂ = (*R*)-1-(*S*)-2-(diphenylphosphino)ferrocenyl}ethyl)diphenylphosphine) toward O–H and C–H bonds has been studied (**1** was previously shown to be a catalyst precursor for the asymmetric addition of aniline to norbornene, via N–H activation). Compound **1** undergoes clean oxidative addition of water in toluene, affording a mixture of two isomeric, dinuclear hydroxo-bridged Ir(III) complexes. Isomerization to a single product, *syn-trans*-[(*R*)-(*S*)-PPFPPh₂)₂Ir₂Cl₂(H)₂(μ-OH)₂] (**3**), takes place upon dissolution in THF. *syn-trans*-**3** has been characterized by X-ray diffraction. Reaction of **1** with 2,6-dimethylaniline affords the corresponding sp³ C–H activation product **5**, the crystal structure of which has been determined. Both oxidative addition reactions are (partly) reversible at high temperature.

Introduction

The activation of the O–H group by transition metals is relevant to a variety of catalytic processes.¹ The oxidative addition of water onto a metal center leads, in a first step, to a hydrido–hydroxo derivative. However, well-characterized complexes obtained as primary products from such a reaction with water are quite rare;² more typically they are prepared by metathesis reactions.³ Furthermore, the crystal structures of only very few complexes of this type have been reported.^{2a,d,4,5} Similarly, despite the fact that homogeneous alkane

activation is still considered a “Holy Grail”, at least for the undirected intermolecular addition of unactivated C–H bonds,⁶ there are only few examples of structurally characterized complexes resulting from oxidative addition of sp³ C–H bonds.⁷

We recently reported the synthesis and characterization of chloride-bridged dinuclear Ir(I) complexes bearing chiral chelating ferrocenyl diphosphines [Ir₂(μ-Cl)₂(diphosphine)₂] of type **1** and demonstrated their catalytic activity in asymmetric hydroamination reactions in the presence of cocatalytic amounts of “naked” fluoride.⁸ As previously shown by Calabrese, Casalnuovo, and Milstein with a comparable Ir(I) system,⁹ a key feature of such a hydroamination reaction is amine

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(1) For the water gas shift reaction, see, e.g.: (a) Yoshida, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1973**, *100*, 3941. (b) Yoshida, T.; Okano, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 4311. For a recent report on Wacker-type chemistry, see: (c) Uozumi, Y.; Kato, K.; Hayashi, T. *J. Am. Chem. Soc.* **1997**, *119*, 5063. For nitrile and olefin hydration, see: (d) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1973**, *95*, 3030. (e) Jensen, C. M.; Troglor, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 723. For a preliminary report on transfer hydrogenation of alkyne, see: (f) Tani, K.; Iseki, A.; Yamagata, T. *Abstract of Papers, 9th IUPAC Symposium on Organometallic Chemistry Directed Towards Organic Synthesis*, Göttingen, Germany, 1997; Abstract 362.

(2) (a) Milstein, D.; Calabrese, J. C.; Williams, I. D. *J. Am. Chem. Soc.* **1986**, *108*, 6387. (b) Blum, O.; Milstein, D. *Angew. Chem.* **1995**, *107*, 210. (c) Ladipo, F. T.; Kooti, M.; Merola, J. S. *Inorg. Chem.* **1993**, *32*, 1681. (d) Burn, M. J.; Fickes, M. G.; Hartwig, J. F.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 5875. (e) Cole-Hamilton, D. J.; Wilkinson, G. *Nouv. J. Chim.* **1977**, *1*, 141. For the reactivity of Ir(I) species with NH₃, see: (f) Koelliker, R.; Milstein, D. *Angew. Chem.* **1991**, *103*, 724.

(3) (a) Edwards, A. J.; Elipse, S.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1997**, *16*, 3828. (b) Chaudret, B. N.; Cole-Hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1546. (c) Poulton, J. T.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 3190.

(4) Stevens, R. C.; Bau, R.; Milstein, D.; Blum, O.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1990**, 1429.

(5) As opposed to oxidative addition, usually to electron-rich late-transition-metal species, the reaction of water with early-transition-metal or lanthanide complexes proceeds more typically in a hydrolytic manner or with loss of molecular hydrogen, as the result of a water reduction process. See, e.g.: (a) Guggenberger, L. J.; Tebbe, F. N. *J. Am. Chem. Soc.* **1976**, *98*, 4137. (b) Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5472.

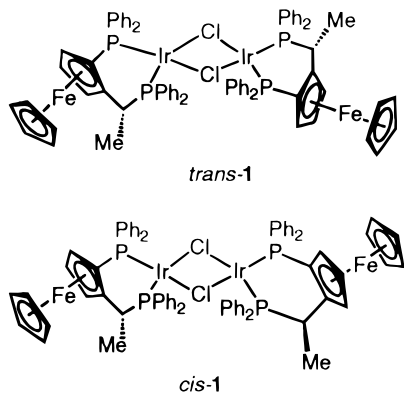
(6) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154. For a general review on C–H activation by metal complexes, see: Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879.

(7) For examples, see: (a) Liou, S.-Y.; Gozin, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 9774. (b) Hackett, M.; Ibers, J. A.; Jernakoff, P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1986**, *108*, 8094. (c) Bulls, A. R.; Schaefer, W. P.; Serfas, M.; Bercaw, J. E. *Organometallics* **1987**, *6*, 1219. (d) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537.

(8) (a) Dorta, R.; Egli, P.; Zürcher, F.; Togni, A. *J. Am. Chem. Soc.* **1997**, *119*, 10857. The synthesis and characterization of complexes of type **1** was also reported by Tani and co-workers. See: (b) Yamagata, T.; Iseki, A.; Tani, K. *Chem. Lett.* **1997**, 1215. For a derivative bearing a fluorinated trialkylphosphine, see: (c) Schnabel, R. C.; Roddick, D. M. *Inorg. Chem.* **1993**, *32*, 1513.

(9) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738.

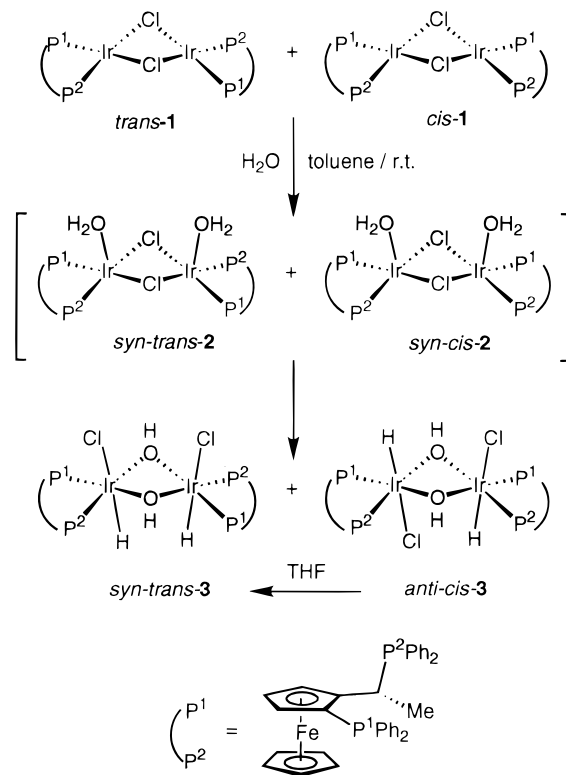
activation by N–H oxidative addition. We therefore reasoned that **1** might undergo analogous reactions with O–H and C–H bonds, and we report herein the results of the corresponding study comprising synthesis and structural characterization of the addition products of **1** with water and 2,6-dimethylaniline (C–H activation).



Results and Discussion

Reactivity Studies of 1. Addition of 2.2 equiv of water to an orange toluene slurry of the dinuclear complex **1** (ca. 60:40 cis/trans mixture) leads to the complete dissolution of the starting material within 90 min. The ^{31}P NMR spectrum of the reaction mixture shows the appearance of two new AA'XX' spin systems ($2 \times$ eight lines) at -17.7 and 15.2 ppm ($^2J_{\text{PP}'} = 28$ Hz, $^4J_{\text{PP}'} = 4$ Hz) and at -4.0 and 22.3 ($^2J_{\text{PP}'} = 34$ Hz, $^4J_{\text{PP}'} = 3$ Hz), respectively, reflecting the formation of two dinuclear intermediates **2** in a ratio of ca. 1:1. Complexes **2** are accompanied by remaining traces of the starting material **1** as well as already formed *syn*- and *anti*-**3**, the latter being both the only hydride species observed and the final products of the reaction (syn and anti refer to the relative positions of apical ligands, whereas cis and trans indicate the complex configuration with respect to the diphosphines). Although the exact nature of the intermediates is unknown, we tentatively assign them the structure of simple water addition products, as shown in Scheme 1. The typical butterfly-shaped nature of **1**,⁸ combined with the bulkiness of the diphosphine ligand, directs entering donors to the exo side of the complex, thus leading to *syn* bis-adducts. The latter could constitute the precursors to mononuclear $[\text{IrCl}(\text{H}_2\text{O})(\text{diphosphine})]$ complexes, as observed for the corresponding reaction with amines (vide infra). However, we did not succeed in identifying such mononuclear water adducts. Further stirring for ca. 1 h at room temperature causes precipitation of a bright yellow solid. This can be isolated in excellent yields and is an analytically pure mixture (ca. 50:50 *syn*-trans/*anti*-cis) of the μ -hydroxo–hydrido dinuclear complexes **3**. (For NMR characteristics, see the Experimental Section.) The *anti*-cis (and not, e.g., *anti*-trans) configuration of the second isomer is inferred from the endo orientation of the halide ligand with respect to the ferrocene core observed with no exceptions in Ir(III) systems of this type.¹⁰ Isomerization to the pure *syn*-*trans*-**3** takes place upon dissolution in THF.

Scheme 1



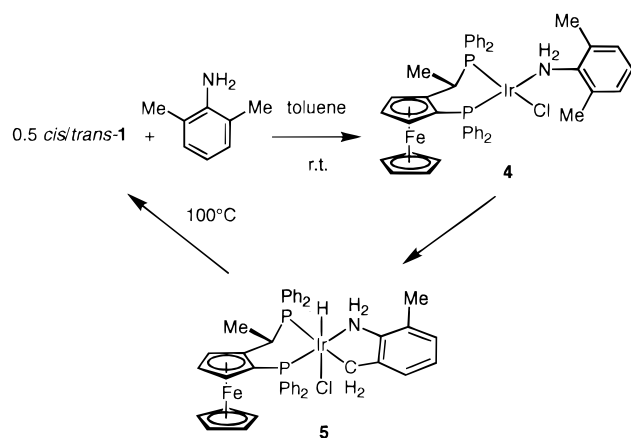
When a bright yellow solution of *syn*-*trans*-**3** in THF- d_8 is heated to 100 °C in a sealed NMR tube for several hours, reappearance of **1** can be observed in the ^{31}P NMR spectrum, this process being accompanied by a darkening of the solution. Although the ^{31}P NMR spectrum showed large amounts of **1** formed, the elimination is not a clean reaction. This is due to the fact that water addition is clean in toluene but not so in THF. Unfortunately the Ir(III) species **3** is almost insoluble in toluene, thus precluding a kinetic study of this reductive elimination.^{2b}

Compound **1** is thermally robust in C_6D_6 , toluene- d_8 , and THF- d_8 . Prolonged heating at 100 °C in these solvents does not alter the cis:trans ratio, nor can any C–H activation be detected. In view of catalytic asymmetric hydroamination involving N–H activation of an aromatic amine,^{8,9} it was of interest to assess the reactivity of complexes of type **1** with 2,6-dimethylaniline. The two methyl groups of this amine are potentially accessible to sp^3 C–H activation via coordination of the nitrogen atom. Alternatively simple N–H oxidative addition could occur.

Reaction of 2.2 equiv of 2,6-dimethylaniline with **1** leads immediately to the monomeric dimethylaniline adduct **4** (Scheme 2), as indicated by ^{31}P NMR spectroscopy. A pair of doublets at 28.8 and -2.2 ppm ($^2J_{\text{PP}'} = 34$ Hz), respectively, void of further splitting patterns due to long-range (4J) couplings, characteristic of dinuclear derivatives, is assigned to **4**. The reaction mixture contains some starting material, along with already formed **5**. Attempts to isolate **4** in pure form failed. We suggest that in **4** dimethylaniline coordinates trans to the less basic phosphine, as indicated in Scheme 2, and as one would expect on the basis of trans-influence arguments. When a large excess of the reagent is used, the reaction goes to completion within

(10) Dorta, R.; Togni, A. Unpublished results.

Scheme 2



ca. 30 min and affords the Ir(III) complex **5**. The somewhat surprising fact that the alkyl ligand in **5** is located *trans* to the more basic of the two phosphines (vide infra) also supports the proposed structure of adduct **4**. The potentially accessible isomer of **5** having the CH₂ group located *trans* to CpPPh₂ phosphorus could not be obtained. Indeed, attempts to force isomerization of **5** at 100 °C in toluene-*d*₈ led, after ca. 3 h of reaction time, to the clean formation of significant amounts of **1** (ratio 1:5 = 1:2.4) and free dimethylaniline instead, thus showing that the reaction is reversible. C–H reductive elimination from a similar Ir(III) hydrido–aminoalkyl species, although irreversible, has been observed in the context of catalytic olefin hydroamination.⁹

Finally, *syn-trans-3* may be used as a catalyst precursor for the addition of aniline to norbornene, in the presence of fluoride. The observed catalytic activity (TOF = 0.62 h⁻¹ at 75 °C) and selectivity (12% ee) is comparable to that of the parent complex **1**.⁸ This implies that the same catalytically active species is formed from both **1** and *syn-trans-3*.¹¹ On the other hand, **5** does not show any significant catalytic activity under the same conditions. This indicates that catalyst formation must take place via reductive elimination, a process too slow at 75 °C.

Solid State Structure of *syn-trans-3* and **5.** In order to unambiguously ascertain the exact configuration of complexes *syn-trans-3* and **5**, X-ray crystal structural studies have been carried out. Table 1 gives crystal and data collection parameters, and selected interatomic distances and angles are provided in Table 2.

As shown in the ORTEP representation of Figure 1, compound *syn-trans-3* displays a distorted octahedral geometry at the Ir(III) centers, with two bridging hydroxo ligands and terminal hydrido and chloro donors. Thus, the molecule has an approximate C₂ symmetry with the 2-fold axis going through the center of the Ir₂O₂ core. Whereas the combination of hydroxo and

Table 1. Experimental Data for the X-ray Diffraction Study of *syn-trans-3* and **5**

compd	<i>syn-trans-3</i> ·4THF	5 ·toluene
formula	C ₈₈ H ₁₀₀ Cl ₂ Fe ₂ Ir ₂ O ₆ P ₄	C ₅₁ H ₅₀ ClFeIrNP ₂
mol wt	1882.7	1022.4
cryst dimens (mm)	0.2 × 0.4 × 0.4	0.35 × 0.3 × 0.25
cryst syst	orthorhombic	orthorhombic
space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁
data collection T (°C)	20	-40
a (Å)	16.468(5)	11.4289(7)
b (Å)	20.684(8)	20.024(1)
c (Å)	25.552(9)	39.216(2)
V (Å ³)	8704(5)	8974.5(9)
Z	4	8
ρ (calcd) (g·cm ⁻³)	1.484	1.513
F(000)	3904	4104
diffractometer	Syntex P21	Siemens Platform CCD
radiation	Mo Kα, λ = 0.710 73 Å	Mo Kα, λ = 0.717 03 Å
measd rflns	0 ≤ h ≤ 13, 0 ≤ k ≤ 17, 0 ≤ l ≤ 21	-11 ≤ h ≤ 13, -23 ≤ k ≤ 9, -29 ≤ l ≤ 44
2θ range (deg)	3.0–40.0	2.0–50.0
scan type	ω	ω
no. of indep rflns	3129 [R(int) = 0.00]	13 808 [R(int) = 0.0579]
abs corr	n/a	n/a
no. of params refined (n _r)	399	958
final R indices (I > 2.0σ(I))	R1 = 0.0440, wR2 = 0.0945	R1 = 0.0518, wR2 = 0.0957
R indices (all data)	R1 = 0.0589, wR2 = 0.0984	R1 = 0.0843, wR2 = 0.1127
GOF on F ²	0.850	0.997

Table 2. Selected Bond Distances (Å)^a and Angles (deg)^a for *syn-trans-3* and **5**

<i>syn-trans-3</i>		5 ^b	
Bond Distances			
Ir(1)–O(1)	2.13(2)	Ir(1)–P(1)	2.224(3)
Ir(1)–O(2)	2.05(2)		[2.225(3)]
Ir(1)–Cl(1)	2.492(7)	Ir(1)–P(2)	2.325(3)
Ir(1)–P(1)	2.209(9)		[2.326(3)]
Ir(1)–P(2)	2.234(7)	Ir(1)–Cl(1)	2.543(3)
Ir(2)–O(1)	2.167(15)		[2.539(3)]
Ir(2)–O(2)	2.146(14)	Ir(1)–N(61)	2.110(10)
Ir(2)–Cl(2)	2.499(7)		[2.136(10)]
Ir(2)–P(3)	2.196(8)	Ir(1)–C(68)	2.108(12)
Ir(2)–P(4)	2.227(7)		[2.115(12)]
Bond Angles			
O(2)–Ir(1)–O(1)	78.1(6)	P(1)–Ir(1)–P(2)	90.18(12)
O(1)–Ir(1)–P(1)	95.1(5)		[91.09(12)]
O(2)–Ir(1)–P(2)	96.0(5)	P(2)–Ir(1)–N(61)	93.1(3)
P(1)–Ir(1)–P(2)	90.4(3)		[94.4(3)]
O(2)–Ir(2)–O(1)	75.5(6)	P(1)–Ir(1)–Cl(1)	98.74(11)
O(1)–Ir(2)–P(4)	96.8(5)		[100.45(19)]
O(2)–Ir(2)–P(3)	96.0(5)	P(2)–Ir(1)–Cl(1)	91.52(11)
P(3)–Ir(2)–P(4)	91.2(3)		[91.67(11)]
Ir(1)–O(1)–Ir(2)	96.5(6)	P(1)–Ir(1)–C(68)	96.1(3)
Ir(1)–O(2)–Ir(2)	99.7(6)		[93.1(3)]
		N(61)–Ir(1)–C(68)	80.6(4)
			[81.1(4)]
		C(68)–Ir(1)–Cl(1)	88.9(3)
			[90.9(3)]
		N(61)–Ir(1)–Cl(1)	85.2(3)
			[82.6(3)]

^a Numbers in parentheses are esd's in the least significant digits. ^b Figures in square brackets indicate corresponding bonding parameters for the second independent molecule.

hydrido ligands both in bridging positions has been observed in a variety of di- and polynuclear transition-metal complexes, *syn-trans-3* appears to be the first compound of this type having only the OH⁻ fragments acting as bridges. Closely related derivatives are the

(11) Driver and Hartwig have lately shown that a bridged Pd–hydroxo complex is more basic than the corresponding amido species in organic solvents. This stands in marked contrast with the relative basicities of alkali-metal hydroxides and amides, respectively. Thus, by analogy, catalyst formation might occur via amine deprotonation by *syn-trans-3*, and not via reductive elimination of water. See: (a) Driver, M. S.; Hartwig, J. F. *Organometallics* **1997**, *16*, 5706. (b) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 4206. (c) Hartwig, J. F. *Synlett* **1997**, 329.

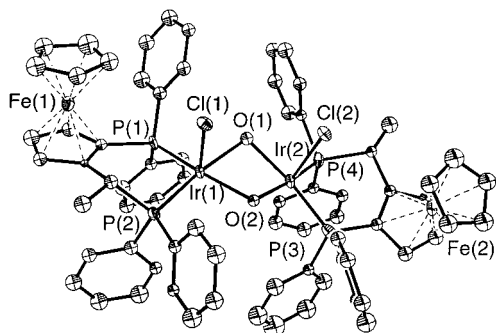


Figure 1. ORTEP view of the dinuclear complex *syn-trans-3* (ellipsoids at the 30% probability level).

triply bridged derivatives [(Et₃P)₂Hr(μ-OH)(μ-Cl)(μ-NHPh)IrH(PET₃)₂]Cl⁹ and [(BINAP)Hr(μ-OMe)₂(μ-Cl)-IrH(BINAP)]Cl, the latter very recently reported by Tani and co-workers, as the product of oxidative addition of MeOH to [Ir₂(BINAP)₂(μ-Cl)₂].^{1f} In view of these two examples and of the general tendency observed for dinuclear Ir(III) complexes to prefer triply bridged structures with anionic ligands,¹² the structure of *syn-trans-3* is quite uncommon and is paralleled only by the structure of *anti*-[(Et₃P)₂Ir(H)Cl(μ-NH₂)₂Ir(H)Cl(PET₃)₂], where two bridging amido groups replace the hydroxides.¹³ However, for the central core of the complex, interatomic distances reflect expected routine values.¹⁴ The chlorides occupy apical positions with respect to the two main Ir coordination planes defined by the oxygen and phosphorus atoms, these two planes spanning an interplanar angle of 142.2°. The hydride ligands were not located, and their position is inferred to be *trans* to the respective chlorides. They occupy the concave side of the molecule, i.e., they reside in the region between the four pseudoaxially arranged phenyl groups constituting the "lower" hydrophobic side of the molecule. The other four phenyl substituents form an equatorial array, thus rendering the "upper" convex side of the molecule more open, as shown in the schematic representation of Figure 2. Each of the two ferrocenyl ligands shows a conformation slightly deviating from the one usually observed for Josiphos-type derivatives.¹⁵ This is best reflected by the relative positions of the methyl groups, not being located in an endo position with respect to the ferrocene as usual, but lying slightly above (exo) their respective Cp rings. The Ir–Ir distance of 3.209–(2) Å does not imply a metal–metal interaction. Finally, the angles around the Ir atoms cover the range between 76.2° and 101.6°, the more acute one involving the two

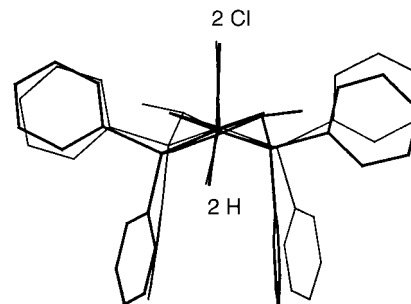


Figure 2. Schematic projection of *syn-trans-3* along the Ir–Ir axis, showing the relative positions of the hydrido and chloro ligands with respect to the axially and equatorially oriented phenyl groups, respectively (ferrocene fragments omitted for clarity).

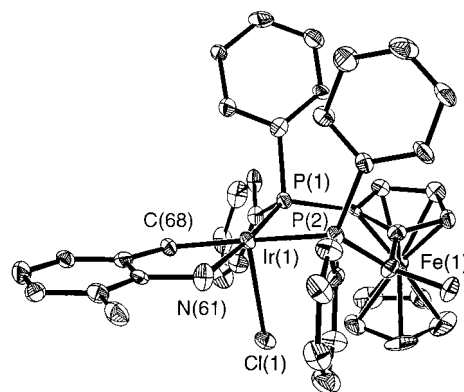


Figure 3. ORTEP view of complex **5** (ellipsoids at the 30% probability level).

oxygen atoms, and the bite angle of each diphosphine is very close to the ideal 90°.

An ORTEP view of one of the two crystallographically independent molecules of **5** is depicted in Figure 3. No significant or noteworthy differences in bonding parameters between these two molecules have been observed, and the discussion, therefore, will be restricted to only one of them. As expected, the geometry of the Ir(III) center is distorted octahedral, with the two phosphorus, nitrogen, and carbon atoms forming the equatorial plane, and the hydrido (not localized) and chloro ligands occupying apical positions.¹⁶ The largest deviation from the least-squares plane defined by Ir, P(1), P(2), N(61), and C(68) is, with 0.06 Å for Ir, relatively small. The chlorine atom is endo oriented with respect to the ferrocene (as indicated above, this appears to be a peculiarity of this system¹⁰), at 4.84 Å from the iron atom. The conformation of the ferrocenyl ligand in **5** is very similar to the one found for both diphosphines in *syn-trans-3*, as shown by the superposition depicted in Figure 4.

Conclusions

We have shown that chloro-bridged diphosphine complexes of type **1** display a pronounced reactivity toward a number of X–H bonds of very different polarities, such as O–H, N–H,^{8a} and C–H bonds. In all of these systems it seems that Lewis-base precoordination

(12) For examples, see: (a) Nolte, M. J.; Van der Stock, E.; Singleton, E. *Inorg. Chim. Acta* **1976**, *19*, L51. (b) Nolte, M. J.; Singleton, E.; Van der Stock, E. *Acta Crystallogr., Sect. B* **1978**, *34*, 1684. (c) Roberts, P. J.; Ferguson, G. *Acta Crystallogr., Sect. B* **1976**, *32*, 1513. (d) Muetting, A. M.; Boyle, P. D.; Wagner, R.; Pignolet, L. H. *Inorg. Chem.* **1988**, *27*, 271. (e) Crabtree, R. H.; Felkin, H.; Morris, G. E.; King, T. J.; Richards, J. A. *J. Organomet. Chem.* **1976**, *113*, C7.

(13) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *Inorg. Chem.* **1987**, *26*, 971.

(14) (a) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, Suppl., S1–S83. (b) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, Suppl., S1–S19.

(15) For a discussion of structural aspects of Josiphos-type ligands, see: (a) Togni, A. In *Organic Synthesis via Organometallics (OSM5)*; Helmchen, G., Dibo, J., Flubacher, D., Wiese, B., Eds.; Vieweg: Braunschweig, 1997; pp 185–208. (b) Togni, A.; Spindler, F.; Rihs, G.; Zanetti, N.; Soares, M. C.; Gerfin, T.; Gramlich, V. *Inorg. Chim. Acta* **1994**, *222*, 213.

(16) For a very similar coordination environment around Ir(III) (X-ray) due to intramolecular sp³ C–H activation, see: Farnetti, E.; Nardin, G.; Graziani, M. *J. Chem. Soc., Chem. Commun.* **1988**, 1264.

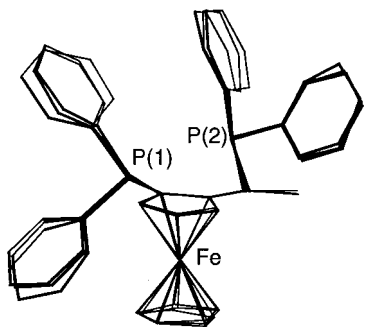


Figure 4. Schematic superposition of the ferrocenyl ligand fragments of *syn-trans*-**3** and **5** showing the optimal fit of conformations.

dination to **1** is necessary to trigger the activation process by (1) breaking the chloro bridges and (2) augmenting the electron density at the iridium center, before oxidative addition can take place. *syn-trans*-**3** is a rare example of a dinuclear hydrido–hydroxo Ir(III) system supported by two hydroxo bridging ligands only.¹⁷ The catalytic potential of complexes such as **1** involving O–H and C–H bond activation is the object of current studies. These will be reported in due course.

Experimental Section

General Considerations. All reactions with air- or moisture-sensitive materials were carried out under an argon or nitrogen atmosphere using standard Schlenk and glovebox techniques. Freshly distilled, dry, and oxygen-free solvents were used throughout. 1D-Routine ¹H (250.133 MHz), ¹³C (62.90 MHz), and ³¹P NMR (101.26 MHz) spectra were recorded using different deuterated solvents. Elemental analyses were performed by the “Mikroelementar-analytisches Laboratorium der ETH”.

cis- and trans-[Ir₂(μ-Cl)₂((R)-(S)-PPFPPPh₂)₂] (1**).** A red benzene (20 mL) solution of (R)-(S)-PPFPPPh₂ (3.27 g, 5.62 mmol) was added dropwise over 20 min to a bright orange benzene (20 mL) suspension of [Ir₂Cl₂(COE)₄] (2.54 g, 2.81 mmol, COE = cyclooctene), affording a deep red limpid solution. After the Schlenk tube had been left at 4 °C overnight, large amounts of an orange microcrystalline precipitate had formed. The solid was then filtered off and dried in vacuo for 24 h. This treatment is usually quite efficient in removing residual COE. Alternatively the solid may be washed with pentane and then dried. Yield: 3.95 g, 85%. ¹H NMR (THF-*d*₆): δ 0.60–0.85 (m, 6 H), 3.43 and 3.50 (2 singlets, Cp-*H*, isomers A and B, 10 H taken together), 3.50–3.90 (m, 4 H), 4.10 (m, 2 H), 4.19 (m, 2 H), 6.85–7.65 (m, 28 H), 8.00–8.35 (m, 10 H), 8.50–8.65 (m, 2 H), the spectrum indicates 1.5 equiv of benzene. ³¹P{¹H} NMR (THF-*d*₆), AA'XX' spin system, two isomers: δ -2.82 (²J_{PP'} + ⁴J_{PP'} = 38.5 Hz) (isomer A), -1.98 (²J_{PP'} + ⁴J_{PP'} = 30.7 Hz) (isomer B), 23.35 (²J_{PP'} + ⁴J_{PP'} = 38.5 Hz) (isomer A), 24.34 (²J_{PP'} + ⁴J_{PP'} = 30.7 Hz) (isomer B). Anal. Calcd for C₇₂H₆₄Cl₂Fe₂Ir₂P₄·1.5C₆H₆: C, 56.00; H, 4.24. Found: C, 56.03; H, 4.33.

syn-trans- and anti-cis-(((R)-(S)-PPFPPPh₂)₂Ir₂Cl₂(H)₂(μ-OH)₂) (3**).** To a yellow toluene (20 mL) slurry of [(R)-(S)-PPFPPPh₂]₂Ir₂(μ-Cl)₂·1.5C₆H₆ (333 mg, 0.191 mmol) was added H₂O (8.6 μL, 0.48 mmol) via syringe. The solution was stirred for 24 h at room temperature. This caused the precipitation of an orange solid. The solid was separated from the red supernatant by filtration and washed with pentane (10 mL). Drying in vacuo yielded 275 mg (82%). The NMR spectra show

a syn:anti ratio of about 50:50, although this varies from batch to batch. ³¹P{¹H} NMR (C₆D₆, only ²J_{PP'} could be resolved): δ -19.4 (²J_{PP'} = 28 Hz, syn isomer), -7.2 (²J_{PP'} = 25 Hz, anti isomer), 9.4 (²J_{PP'} = 25 Hz, anti), 15.1 (²J_{PP'} = 28 Hz, syn). ¹H NMR (C₆D₆): δ -20.6 (dd, J_{HP} ≈ J_{HP'} = 20.2 Hz, 2 H, anti), -19.5 (dd, J_{HP} ≈ J_{HP'} = 19.5 Hz, 2 H, syn), 1.33 (m, 6 H + 2 underlying H, anti), 1.54 (m, 6 H, syn), 1.69 (m, 2 OH, syn), 3.73 (s, 10 H, anti), 3.90–4.15 (m, 6 H, syn and trans), 4.08 (s, 10 H, syn), 4.31 (m, 2 H, anti), 4.36 (m, 2 H, anti), 4.46 (m, 2 H, syn), 5.52 (m, br, 2 H, anti), 5.98 (m, 2 H, syn), 6.60–7.30 (m, 52 H, syn and anti), 7.43 (m, 4 H, anti), 7.66 (m, 4 H, syn), 7.79 (m, 4 H, anti), 8.13 (m, 8 H, syn and anti), 8.43 (m, 8 H, syn and anti). The ¹H NMR spectrum indicates 1 equiv of toluene per dimer. Anal. Calcd for C₇₂H₆₈Cl₂Fe₂Ir₂O₂P₄·C₇H₈: C, 54.27; H, 4.38. Found: C, 54.05; H, 4.43.

syn-trans-(((R)-(S)-PPFPPPh₂)₂Ir₂Cl₂(H)₂(μ-OH)₂) (3**).** To a yellow toluene (20 mL) slurry of **1** (2.06 g, 1.26 mmol) was added H₂O (50 μL, 2.78 mmol) via syringe. The solution was stirred for 48 h at room temperature. Then the volatiles were removed in vacuo, THF (10 mL) was added, and the mixture was stirred overnight. The yellow microcrystalline product thus formed was filtered off and dried in vacuo. Yield: 2.04 g, 94%. IR (Nujol): 2263 cm⁻¹ (ν Ir–H). ³¹P{¹H} NMR (THF-*d*₆): δ -20.1 (d, ²J_{PP'} = 28.4 Hz), 14.4 (d, ²J_{PP'} = 28.4 Hz). ¹H NMR (C₆D₆/CD₂Cl₂): δ -19.5 (dd, J_{HP} ≈ J_{HP'} = 19.5 Hz, 2 H), 1.25 (m, 2 OH),¹⁸ 1.44 (m, 6 H), 3.97 (s, 10 H), 4.05 (m, 2 H), 4.45 (m, 2 H), 5.69 (m, 2 H), 6.50–7.25 (m, 30 H), 7.51 (m, 4 H), 7.87 (m, 4 H), 8.24 (m, 4 H). The ¹H NMR spectrum indicates 1 equiv of THF per dinuclear complex. Anal. Calcd for C₇₂H₆₈Cl₂Fe₂Ir₂O₂P₄·C₄H₈O: C, 52.82; H, 4.43; Cl, 4.10. Found: C, 52.81; H, 4.66; Cl, 4.22. Single crystals suitable for an X-ray diffraction analysis were grown from a saturated THF solution.

Preparation of Complex 5. 2,6-Dimethylaniline (31 μL, 0.25 mmol) was added to a toluene (1 mL) slurry of **1** (185 mg, 0.113 mmol). The mixture was stirred at room temperature for 96 h. Addition of diethyl ether (2 mL) and stirring for another 2 h caused precipitation of a yellow microcrystalline solid. The solid was filtered off and dried in vacuo. Yield: 165 mg (75%). From the mother liquor could be obtained another crop of crystals (12 mg, 11%) at 0 °C. ¹H NMR (C₆D₆): δ -21.42 (dd, J = 19.7 Hz, J = 9.4 Hz), 1.36 (s, 3 H), 1.79 (m, 3 H), 3.92 (m, 1 H), 3.99 (m, 1 H), 4.03 (m, 1 H), 4.11 (s, 5 H), 4.45 (br s, 1 H), 4.70–4.90 (m, 2 H), 6.34 (m, 1 H), 6.58 (m, 1 H), 6.90–7.50 (m, 19 H), 7.65 (m, 2 H), 8.72 (m, 2 H). The spectrum indicates 0.5 equiv of toluene. ³¹P{¹H} NMR (C₆D₆): δ -14.6 (d, J_{PP'} = 19 Hz), 15.3 (d, J_{PP'} = 19 Hz). Anal. Calcd for C₄₄H₄₃NP₂ClFeIr·0.5C₇H₈: C, 58.37; H, 4.85; N, 1.43; Cl, 3.63. Found: C, 58.13; H, 4.97; N, 1.27; Cl, 3.90. Crystals suitable for an X-ray diffraction analysis were grown by vapor diffusion of diethyl ether into a saturated toluene solution.

X-ray Structure Analysis of syn-trans-3a. Data were measured on a Syntex P21 diffractometer with variable scan speed to ensure constant statistical precision on the collected intensities. One standard reflection was measured every 120 reflections; no significant variation was detected. The structure was solved by Patterson methods and refined by full-matrix least squares using anisotropic displacement parameters only for non-hydrogen and non-carbon atoms. Due to the relatively poor quality of the data, the Cp and phenyl rings were refined as rigid bodies. There were four THF molecules per complex molecule in the asymmetric unit. Hydrogen atoms (not localized) were refined in idealized positions (riding model

(17) For a recent example of a mononuclear hydrido–hydroxo complex, see: Kaplan, A. W.; Bergman, R. G. *Organometallics* **1997**, *16*, 1106 and references therein.

(18) Assignment of the OH resonance was verified in a ³¹P–¹H-correlation study, utilizing standard pulse sequences (see: Sklenar, V.; Miyashiro, H.; Zon, G.; Miles, H. T.; Bax, A. *FEBS Lett.* **1986**, *208*, 94). Furthermore, the OH and hydride signals were absent in the spectrum of the corresponding compound prepared under the same conditions with D₂O.

with fixed isotropic $U = 0.080 \text{ \AA}^2$). All calculations were carried out using the SHELXTL Plus (VMS) and SHELXL93 systems.

X-ray Structure Analysis of 5. Intensity data were collected at $-40 \text{ }^\circ\text{C}$ on a Siemens Platform CCD (charge-coupled device) diffractometer. The program SMART (Siemens Analytical X-Ray Systems Inc.; Madison, WI) was used for the determination of the unit cell and for data collection. The data reduction was performed using SAINT (Siemens Analytical X-Ray Systems Inc.; Madison, WI). An empirical correction of the absorption was performed with SADABS (G. M. Sheldrick; University of Göttingen, Germany). The structure was solved and refined using the program SHELXS-96 (Sheldrick, G. M.; *SHELXS-96. Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1996) by direct methods. There were two complex and two toluene molecules in the asymmetric unit. Least-squares methods with anisotropic displacement parameters for all non-hydrogen atoms were used in the refinement of the complex molecules. However, the displacement parameters of the atoms in the solvent molecules were left isotropic. All hydro-

gen atom positions were placed in calculated positions (riding model) with isotropic parameters, fixed at $1.5 \times U(\text{eq})$ of the carbon atom for the methyl groups and $1.2 \times U(\text{eq})$ of the carbon atom for all of the other groups. The two hydrides were neither refined nor calculated.

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Supporting Information Available: Tables of crystallographic parameters, atomic coordinates, all bond distances and angles, anisotropic displacement coefficients, and coordinates of hydrogen atoms and ORTEP representations with complete atom-numbering schemes for *syn-trans*-**3** and **5** (39 pages). Ordering information is given on any current masthead page.

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