Iridium Complexes with Chiral and Achiral β-Aminophosphane Ligands: Catalysts for >C=O Hydrogenation and H/D Exchange Involving both Homo- and Heterolytic H_2 Activation[‡]

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Dedicated to the memory of Professor Dieter Sellmann, who has shed much light!

Keywords: Chirality / Hydrogenations / Isotopic exchange / Iridium

Chiral and achiral *P,N*-chelated Ir^I complexes of the general type $[(COD)Ir(P\cap NR^1R^2)]BF_4$, where COD = η^4-1,5-C_8H_{12} and $P\cap NR^1R^2$ = (1*R*,2*R*)-, (1*S*,2*S*)-, or (1*R*,2*S*)-$Ph_2PC^1H(Ph)C^2H(Me)NR^1R^2$ (NR^1R^2 = NH_2, NHMe, $NHCH_2Ph$, $NHCHMe_2$, NMe_2), $Ph_2PCH_2CR_2NH_2$ (R = H, Me), or 2-$Ph_2PC_6H_4NHMe$, have been prepared by treating $[Ir(COD)_2]BF_4$ with the required β-aminophosphane in THF. The monolithiated ligands $Ph_2PCH_2CMe_2N(Li)H$ and 2-$Ph_2PC_6H_4N(Li)Me$ interacted with $[\{(COD)Ir(\mu\text{-}Cl)\}_2]$ to give the neutral alkyl- and arylamido compounds [(COD)-$Ir(Ph_2PCH_2CMe_2NH)$] and [(COD)Ir(2-$Ph_2PC_6H_4NMe$)]. All Ir^I complexes $[(COD)Ir(P\cap NR^1R^2)]BF_4$ acted as catalysts for the direct hydrogenation of alkyl aryl ketones to the corresponding 1-phenylalkanols, if combined with an alkaline or amine base in methanol under H_2 (10–50 bar) between 25 and 50 °C. The reaction occurred with modest to moderate enantioselectivity (ca. 20–75% *ee*) if chelate complexes bearing the various optically active β-aminophosphanes were used as catalysts. The base-free amido complexes [(COD)-$Ir(P\cap NR)$] displayed similar catalytic activity to the combined systems $[(COD)Ir(P\cap NHR)]BF_4$–KOH ($P\cap NHR$ = $Ph_2PCH_2CMe_2NH_2$, 2-$Ph_2PC_6H_4NHMe$). The ability of both the cationic β-amino- and the neutral β-amidophosphane Ir^I complexes to undergo oxidative H_2 addition and the observation of H_2/D^+ as well as H_2/D_2 exchange processes during catalysis provided evidence for a mechanism involving reversible "$[Ir^{III}(H)_2\text{–}P\cap NHR]^+ \rightleftarrows [(\eta^2\text{-}H_2)\text{–}Ir^{III}(H)\text{–}P\cap NR]^+$" proton-to-hydride transfer and heterolytic H_2 cleavage on amino–dihydride and amido–dihydrogen–monohydride tautomers. The crystal structures of [(COD)Ir{(1*S*,2*S*)-$Ph_2PCH(Ph)CH(Me)NHCH_2Ph$}]$BF_4$·2THF, [(COD)Ir{1*R*,2*S*-$Ph_2PCH(Ph)CH(Me)NHMe$}]BF_4·THF, and the orthometalated 18e Ir^I complex [(COD)Ir{(1*R*,2*S*)-$Ph_2PCH(C_6H_4\text{-}o)$-$CH(Me)NHCHMe_2$}], which resulted from treatment of [(COD)Ir{(1*R*,2*S*)-$Ph_2PCH(Ph)CH(Me)NHCHMe_2$}]$BF_4$ with excess KOH, have been determined by single crystal X-ray diffraction studies.

Introduction

Metal complexes containing both *P* and *N* donor ligands have been dominating the field of homogeneous catalytic hydrogenation of organic carbonyl compounds for several years. In particular, Noyori's ruthenium complexes $[RuCl_2\{bis(phosphane)\}(1,2\text{-diamine})]$ have been found to be excellent catalysts for the enantioselective reduction, by H_2, of simple ketones if activated by an excess of strong base.[1] Intramolecular heterolytic H_2 splitting across the polar metal−amide bond of initially formed amine-amido hydrido complexes, $[RuH(P\cap P)(HN\cap NH_2)]$, to reversibly give diamine dihydrides, $[RuH_2(P\cap P)(H_2N\cap NH_2)]$, has been shown to be a key step involved in the catalytic cycle. From the latter, $H^{\delta-}/H^{\delta+}$ equivalents are transferred simultaneously to the ketonic substrate once the carbonyl group has come into close contact with the second coordination sphere of the catalyst through an unconventional $Ru-H^{\delta-}\cdots>C^{\delta+}=O^{\delta-}\cdots H^{\delta+}-N$ "metal−ligand bifunctional" interaction.[2,3,4]

A different type of a highly enantioselective >C=O hydrogenation catalyst is exemplified by Zhang's Rh−PennPhos system, made up from in situ generated [(COD)Rh{(*R*,*S*,*R*,*S*)-Me-PennPhos}]Cl and a weakly coordinating base of moderate strength, such as 2,6-lutidine ["(*R*,*S*,*R*,*S*)-Me-PennPhos" denotes *P*,*P*′-1,2-phenylene-bis{(1*R*,2*S*,4*R*,5*S*)-2,5-dimethyl-7-phosphabicyclo[2.2.1]-heptane}].[5] Zhang's catalyst is believed to support the homogeneous hydrogenation of ketones following the classic Schrock−Osborn pathway,[6] i.e., homolytic scission of the H_2 molecule by oxidative addition with subsequent

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>C=O/Rh−H insertion to produce an alkoxo hydrido rhodium(III) complex, in which the remaining hydride is *trans* to the alkoxo ligand so that reductive elimination of the product alcohol cannot easily occur. The authors speculated that the key function of the basic additive is to deprotonate the Rh−H bond forming baseH$^+$ as the conjugate acid, which in turn cleaves the Rh−alkoxo function by protonation.[5]

Based on this background, our recent activities have focussed on the catalytic potential in asymmetric >C=O hydrogenation of a class of optically active β-aminophosphane complexes of Ir^I and Rh^I, [(COD)M{Ph_2PCH-(Ph)CH(Me)NHR}]BF_4 (COD = η^4-1,5-C_8H_{12}; R = H, alkyl), having a chelated d^8 metal center (as found in Zhang's catalyst) embedded in a *P*,*N*-dominated coordination environment (which is an important characteristic of the Noyori systems).[7a,7b] An important further aspect of our work with these complexes arose from our interest in establishing whether the dihydrogen molecule is activated during catalysis by homolytic or heterolytic H−H bond breaking.[7b] Since it is well known that M−H derivatives of iridium, especially of Ir^{III}, are generally more stable and, hence, more readily accessible than those of rhodium, it has primarily been the family of iridium complexes that has been studied in detail up to now, notwithstanding a single observation that the Rh-based catalysts could be somewhat more selective than their iridium homologues (see below). Additional justification for the choice of aminophosphane-coordinated iridium complexes as potential >C=O hydrogenation catalysts arises from the observation that in situ systems composed of [{(COD)Ir(μ-Cl)}$_2$] or [Ir(COD)$_2$]BF_4 and 1,2-diphenylethylene-based chiral diamines can indeed catalyze the asymmetric reduction of ketones and α-keto esters with reasonable enantioselectivities.[8]

Results

Synthesis and Characterization of Ligands and Complexes

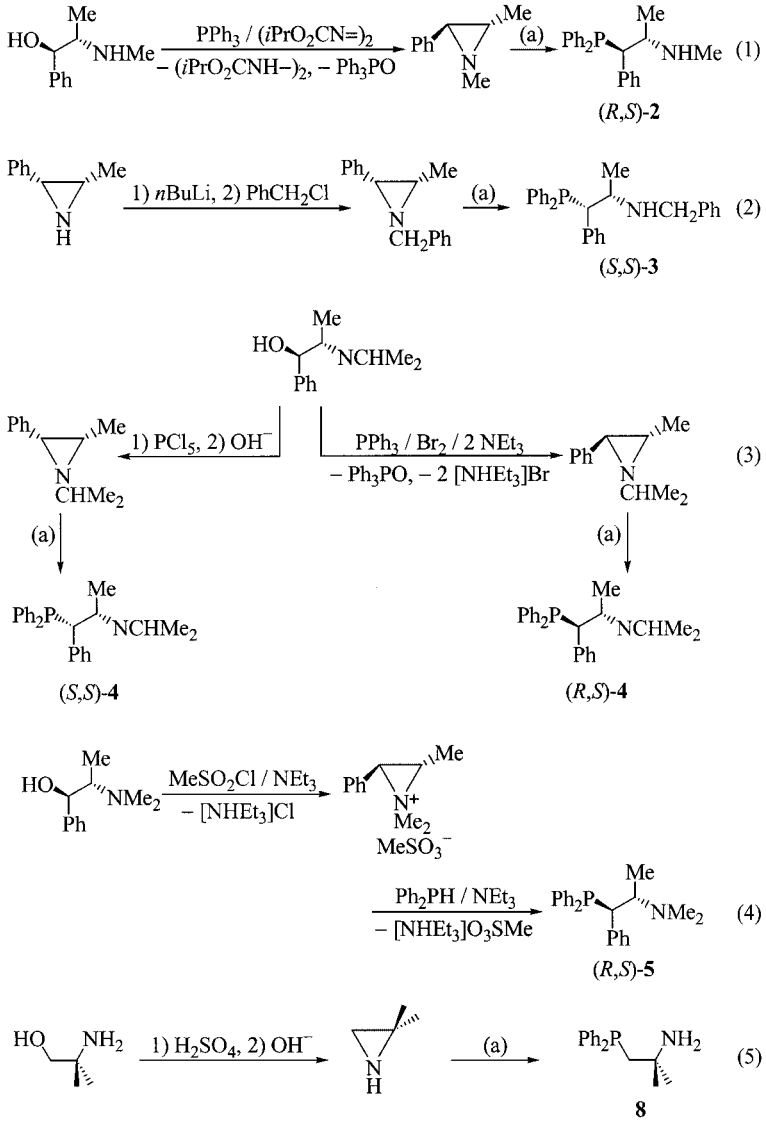
In earlier work[7a] we have worked out several useful procedures for the preparation of various optically active bidentate β-aminophosphanes, starting from commercially available (nor)ephedrine and pseudoephedrine diastereomers. In the first step of the syntheses, the different β-amino alcohols were stereospecifically converted into *cis* or *trans* aziridines using established synthetic organic methods.[9,10,11,12] Transformation of the aziridines into the desired *P*,*N* ligands was subsequently accomplished by regio- and stereospecific ring-opening with Ph_2PH in the presence of BF_3 as an activating additive. Enantiopure *P*,*N* ligands thus prepared included (+)-(1*S*,2*S*)-$Ph_2PCH(Ph)CH(Me)NH_2$ [(*S*,*S*)-**1**] hereafter, (−)-(1*R*,2*S*)-$Ph_2PCH(Ph)CH(Me)NH_2$ [(*R*,*S*)-**1**], and (−)-(1*R*,2*R*)-$Ph_2PCH(Ph)CH(Me)NHMe$ [(*R*,*R*)-**2**].[7a]

In a similar manner, (+)-(2*S*,3*S*)-*trans*-1,2-dimethyl-3-phenylaziridine[12] was used as a source of (−)-(1*R*,2*S*)-$Ph_2PCH(Ph)CH(Me)NHMe$ [(*R*,*S*)-**2**] for which a less direct four-step sequence had previously been described by Beck and Nagel[13] [Scheme 1, reaction (1)]. (−)-(2*S*,3*R*)-*cis*-1-benzyl-2-methyl-3-phenylaziridine analogously afforded (+)-(1*S*,2*S*)-$Ph_2PCH(Ph)CH(Me)NHCH_2Ph$ [(*S*,*S*)-**3**]. The required *N*-benzylaziridine had earlier been synthesized from (−)-norephedrine by consecutive reactions with PCl_5, benzaldehyde, and sodium borohydride[14] but was also readily accessible by alkylating the corresponding *N*-unsubstituted aziridine with *n*BuLi/benzyl chloride [Scheme 1, reaction (2)]. The (−)-(2*S*,3*R*)-*cis*- and (+)-(2*S*,3*S*)-*trans*-1-isopropyl-2-methyl-3-phenylaziridine isomers were obtained from (−)-*N*-isopropylnorephedrine[15] by the Gabriel method[9] or by reaction with the Horner reagent PPh_3/Br_2[11a] and nucleophilically opened with $Ph_2PH/F_3B{\cdot}OEt_2$ to furnish (+)-(1*S*,2*S*)-$Ph_2PCH(Ph)CH(Me)NHCHMe_2$ [(*S*,*S*)-**4**] and the corresponding (−)-(1*R*,2*S*) diastereomer (*R*,*S*)-**4** [Scheme 1, reaction (3)]. Conversion of (−)-*N*-methylephedrine with methanesulfonyl chloride to the *N*,*N*-dimethylaziridinium salt,[16] followed by treatment of the latter with Ph_2PH/NEt_3, cleanly afforded the *N*,*N*-dialkylated *P*,*N* ligand (−)-(1*R*,2*S*)-$Ph_2PCH(Ph)CH(Me)NMe_2$ [(*R*,*S*)-**5** Scheme 1, reaction (4)]. Additional β-aminophosphanes used in this study included the known achiral compounds $Ph_2PCH_2CH_2NH_2$ (**6**),[17] and 2-$Ph_2PC_6H_4NHMe$ (**7**)[18] and, as a new member of this family of ligands, $Ph_2PCH_2CMe_2NH_2$ (**8**) which resulted in the usual fashion from ring-opening of 2,2-dimethylaziridine, itself made from 2-amino-2-methylpropanol by the Wenker method[10,19] [Scheme 1, reaction (5)].

Similar to the procedures previously employed for the preparation of (−)-[(COD)Ir{(1*S*,2*S*)-$Ph_2PCH(Ph)$-$CH(Me)NH_2$}]BF_4 [**Ir**$^+$-(*S*,*S*)-**1**] and [(COD)M{(1*R*,2*R*)-$Ph_2PCH(Ph)CH(Me)NHMe$}]BF_4 [M = Rh: **Rh**$^+$-(*R*,*R*)-**2**; M = Ir: **Ir**$^+$-(*R*,*R*)-**2**],[7a] the new optically active chelate complexes [(COD)Ir{(1*S*,2*S*)-$Ph_2PCH(Ph)CH(Me)$-NHR}]BF_4 [R = CH_2Ph: **Ir**$^+$-(*S*,*S*)-**3**; R = $CHMe_2$: **Ir**$^+$-(*S*,*S*)-**4**] and [(COD)Ir{(1*R*,2*S*)-$Ph_2PCH(Ph)CH(Me)$-NR^1R^2}]BF_4 [R^1 = H, R^2 = Me: **Ir**$^+$-(*R*,*S*)-**2**; R^1 = H, R^2 = $CHMe_2$: **Ir**$^+$-(*R*,*S*)-**4**; R^1 = R^2 = Me: **Ir**$^+$-(*R*,*S*)-**5**] as well as their achiral analogues [(COD)Ir-($Ph_2PCH_2CR_2NH_2$)]BF_4 (R = H: **Ir**$^+$-**6**, R = Me: **Ir**$^+$-**8**) and [(COD)Ir(2-$Ph_2PC_6H_4NHMe$)]BF_4 (**Ir**$^+$-**7**) were isolated in high yield (>80%) from ligand exchange reactions between [Ir(COD)$_2$]BF_4 and equimolar quantities of the corresponding β-aminophosphane in THF (Scheme 2).

The monolithiated ligands 2-$Ph_2PC_6H_4N(Li)Me$ and $Ph_2PCH_2CMe_2N(Li)H$ interacted with [{(COD)Ir(μ-Cl)}$_2$] in hydrocarbon solution to give the neutral aryl- and alkylamido complexes [(COD)Ir(2-$Ph_2PC_6H_4NMe$)] [**Ir-7a**] and [(COD)Ir($Ph_2PCH_2CMe_2NH$)] [**Ir-8a**] as conjugate bases of their parent **Ir**$^+$-**7** and **Ir**$^+$-**8** cations (Scheme 3).

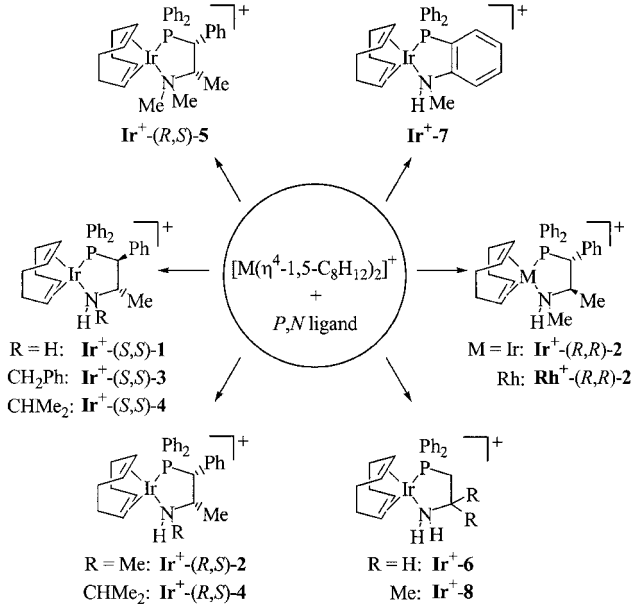
Crystallization of **Ir**$^+$-(*S*,*S*)-**3** and **Ir**$^+$-(*R*,*S*)-**2** from THF/pentane solvent mixtures afforded the two complexes as single-crystalline addition compounds, [(COD)Ir{(1*S*,2*S*)-$Ph_2PCH(Ph)CH(Me)NHCH_2Ph$}]$BF_4{\cdot}2$THF and [(COD)-Ir{(1*R*,2*S*)-$Ph_2PCH(Ph)CH(Me)NHMe$}]$BF_4{\cdot}$THF, respectively. The X-ray structural analyses of the two adduct complexes showed the presence of discrete ion pairs with the tetrafluoroborate anion hydrogen-bonded to the coordi-



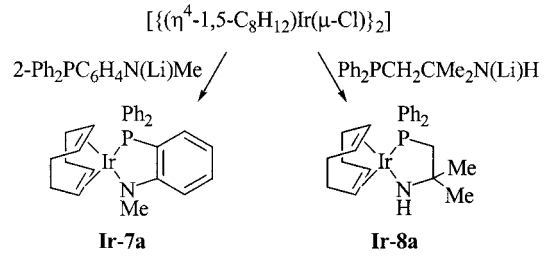
Scheme 1. Syntheses of new chiral and achiral β-aminophosphane ligands used in this work; step (a): 1. $F_3B{\cdot}OEt_2$, 2. Ph_2PH

nated amino functions (Figures 1 and 2). The Ir−P bond lengths of 2.279(7) and 2.298(4) Å, measured for the two compounds respectively, differ only slightly, if at all, and the same applies to the Ir−N distances which are 2.14 Å in both complexes. The chelate bite angles P−Ir−N are 83.0(6) and 83.7(3)° and thus compare well with the value of 82.3(2)° previously measured for the related rhodium cation $\mathbf{Rh}^+$-(*R*,*R*)-**2**.[7a] A common structural feature of the three complexes in the solid state is the equatorial alignment of the phenyl ring bonded to C-1 with respect to the five-membered chelate ring, causing the puckered metallacycle to adopt the δ conformation if the configuration at C-1 is *S* and, vice versa, to exist as a λ conformer if C-1 is in the *R* configuration. As a further consequence, the adjacent methyl group attached to C-2 is oriented equatorially if the two carbon atoms have like configuration (Figure 3; see also Figure 4 of ref.[7a]) but points to an axial direction if the configuration at C-2 is opposite to that at C-1 (Figure 4). Taking the surrounding of the coordinated nitrogen atom also into account, crystals of $\mathbf{Ir}^+$-(*S*,*S*)-**3**·2THF are seen to contain the chelate complex as a $\delta(S_{C\text{-}1},S_{C\text{-}2},S_N)$ diastereomer, the $\lambda(R_{C\text{-}1},S_{C\text{-}2},R_N)$ form being present in the solid state of $\mathbf{Ir}^+$-(*R*,*S*)-**2**·THF.

For $\mathbf{Rh}^+$-(*R*,*R*)-**2**, single crystals of which have been shown to be composed of the $\lambda(R_{C\text{-}1},R_{C\text{-}2},S_N)$ stereoisomer,[7a] and for its iridium homologue $\mathbf{Ir}^+$-(*R*,*R*)-**2** as well, ^{31}P NMR spectroscopic data indicated the presence in solution of three diastereomers in a roughly 10:3:1 distribution. Assuming that steric hindrance between the substituents attached to the chelate ring increases in the series $\lambda(R_{C\text{-}1},R_{C\text{-}2},S_N)$ (*C*-Ph, *C*-Me, and *N*-Me groups *all-trans-eq* aligned) < $\delta(R_{C\text{-}1},R_{C\text{-}2},S_N)$ (*all-trans-ax* conformer) ≈ $\lambda(R_{C\text{-}1},R_{C\text{-}2},R_N)$ (*C*-Ph/*C*-Me *trans-eq* oriented, *C*-Me/*N*-Me *cis-eq-ax* positioned) < $\delta(R_{C\text{-}1},R_{C\text{-}2},R_N)$ (*C*-Ph/*C*-Me in *trans-ax*, *C*-Me/*N*-Me in *cis-ax-eq* orientation), the observed isomers were previously assigned as sterically locked conformers $\lambda(R_{C\text{-}1},R_{C\text{-}2},S_N)$ (major), $\delta(R_{C\text{-}1},R_{C\text{-}2},S_N)$ (intermediate), and $\lambda(R_{C\text{-}1},R_{C\text{-}2},R_N)$ (minor).[7a] We have now ob-



Scheme 2. Collection of cationic β-aminophosphane Ir^{I} complexes (all BF_4^- salts) and abbreviations



Scheme 3. Synthesis of β-amidophosphane Ir^{I} complexes

served that acetone solutions of the *N*-benzyl complex **Ir**$^+$-(*S*,*S*)-**3** exhibit NMR spectra (^{1}H, ^{13}C, ^{31}P) consistent with the existence of the cation in the dissolved state existing as only two ring conformers in an approximately 2:3 molar ratio (from ^{31}P{^{1}H} NMR; cf. Table 1). Assuming that the crystallographically established δ($S_{C\text{-}1}$,$S_{C\text{-}2}$,S_N) form contributes significantly to the isomeric distribution formed in solution, we can assign the NMR spectra displaying 40% relative intensity to that (*C*-Ph/*C*-Me)-*trans-eq*/(*C*-Me/*N*-Me)-*cis-eq-ax* conformer and ascribe the resonances showing up with 60% relative intensity to the sterically more favorable *all-trans-eq* δ($S_{C\text{-}1}$,$S_{C\text{-}2}$,R_N) isomeric cation. By implication, it becomes necessary to re-assign the conformers previously observed for the two Rh and Ir complexes M$^+$−(*R*,*R*)-**2** at intermediate concentration (vide supra)[7a] as λ($R_{C\text{-}1}$,$R_{C\text{-}2}$,R_N), i.e. enantiomeric to δ($S_{C\text{-}1}$,$S_{C\text{-}2}$,S_N), rather than δ($R_{C\text{-}1}$,$R_{C\text{-}2}$,S_N), which accordingly can be attributed to the conformational isomers formed at minor concentration (Table 1 and Scheme 4). By similar reasoning the conformers of **Ir**$^+$-(*S*,*S*)-**4** in a 1:3 distribution in solution can be formulated as δ($S_{C\text{-}1}$,$S_{C\text{-}2}$,S_N) and δ($S_{C\text{-}1}$,$S_{C\text{-}2}$,R_N), respectively.

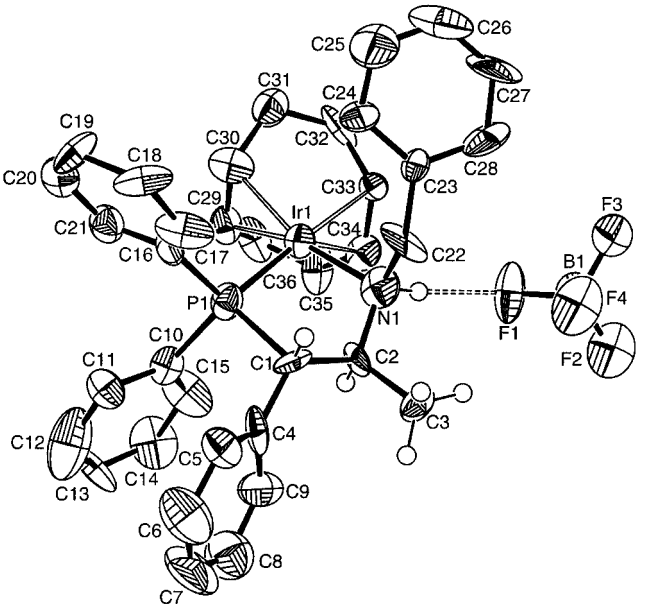


Figure 1. Perspective view of the [(COD)Ir{(1*S*,2*S*)-Ph_2PCH(Ph)CH(Me)NHCH$_2$Ph}]BF_4 ion pair; selected bond lengths [A] and angles [°]: Ir1−P1, 2.279(7); Ir1−N1, 2.14(2); Ir1−C29, 2.18(2); Ir1−C30, 2.13(2); Ir1−C33, 2.24(2); Ir1−C34, 2.24(2); N1−H···F1, 2.88(3). P1−Ir1−N1, 83.0(6); N1−H···F1, 166.7

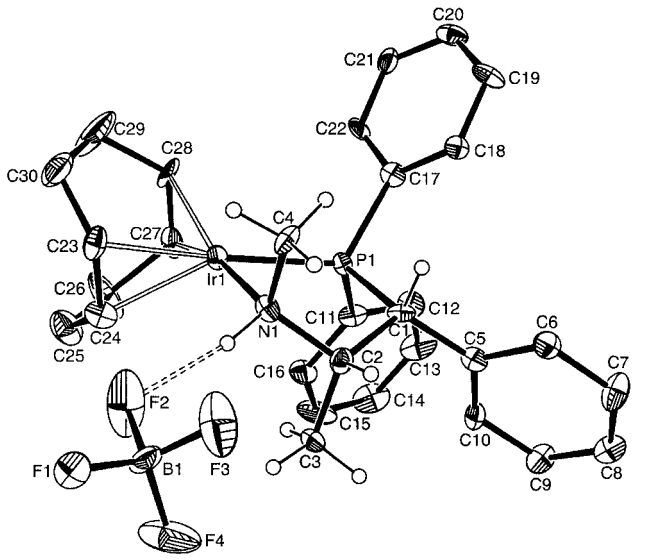


Figure 2. Perspective view of the [(COD)Ir{(1*R*,2*S*)-Ph_2PCH(Ph)CH(Me)NHMe}]BF_4 ion pair; selected bond lengths [A] and angles [°]: Ir1−P1, 2.298(4); Ir1−N1, 2.137(11); Ir1−C23, 2.224(14); Ir1−C24, 2.181(16); Ir1−C27, 2.165(16); Ir1−C28, 2.126(13); N1−H···F2, 2.925(16). P1−Ir1−N1, 83.7(3); N1−H···F2, 170.7

Solution ^{31}P NMR spectra of **Ir**$^+$-(*R*,*S*)-**2** and **Ir**$^+$-(*R*,*S*)-**4** indicate the presence of one exclusive [**Ir**$^+$-(*R*,*S*)-**4**] or at least one predominant [**Ir**$^+$-(*R*,*S*)-**2**] conformer. These can be assigned as λ($R_{C\text{-}1}$,$S_{C\text{-}2}$,R_N), i.e. identical with the isomeric form observed for **Ir**$^+$-(*R*,*S*)-**2** in the solid state. The favorable δ($S_{C\text{-}1}$,$S_{C\text{-}2}$) or λ($R_{C\text{-}1}$,$S_{C\text{-}2}$) foldings of the chelate rings with like or unlike configurations of the two bridging carbon atoms can also be ascribed to the single conformers

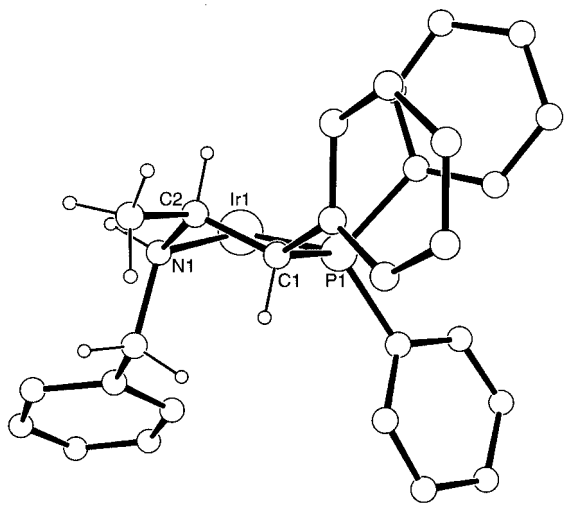


Figure 3. Schematic front view of the cation **Ir**$^+$-(*S*,*S*)-**3** emphasizing the $\delta(S_{C\text{-}1},S_{C\text{-}2},S_N)$ conformation of the chelate ring

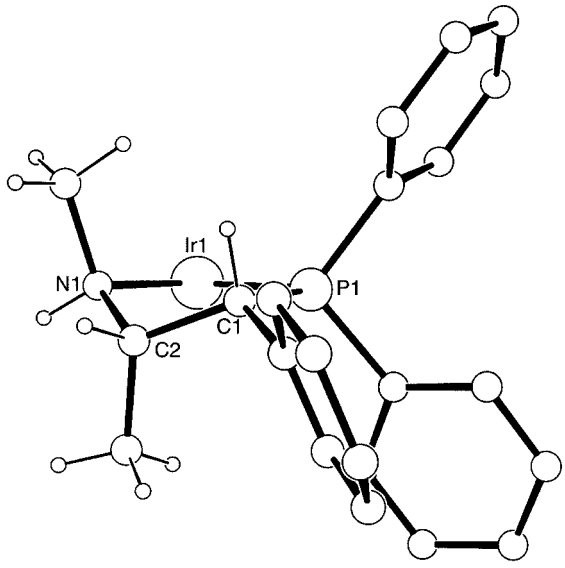


Figure 4. Schematic front view of the cation **Ir**$^+$-(*R*,*S*)-**2** emphasizing the $\lambda(R_{C\text{-}1},S_{C\text{-}2},R_N)$ conformation of the chelate ring

produced upon dissolution of the two complexes **Ir**$^+$-(*S*,*S*)-**1** and **Ir**$^+$-(*R*,*S*)-**5** possessing achiral amine functions (Table 1).

Catalytic >C=O Hydrogenation

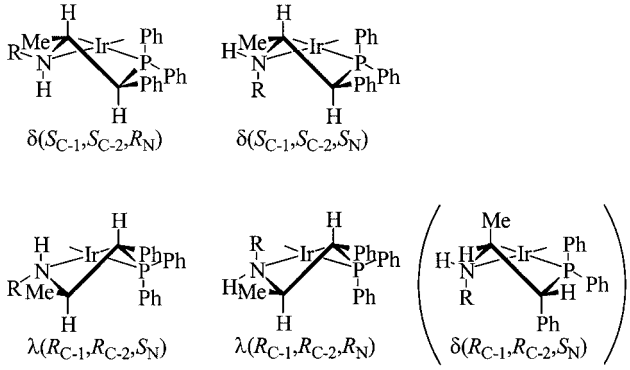
If combined with an alkaline or amine base (1−5 equiv.) in methanol under H_2 (10−50 bar) between 25 and 50 °C, all the complexes shown in Scheme 2 act as catalysts for the hydrogenation of alkyl aryl ketones to the corresponding 1-phenylalkanols (Tables 2−4). The homogeneous >C=O reduction occurs enantioselectively if chelate complexes bearing the various (pseudo)ephedrine-based β-aminophosphanes are used as catalysts (Scheme 5).

The success of the hydrogenation reaction depends on the presence of an extra base in the catalytic system and the use of a protic reaction medium. Thus, virtually no catalytic

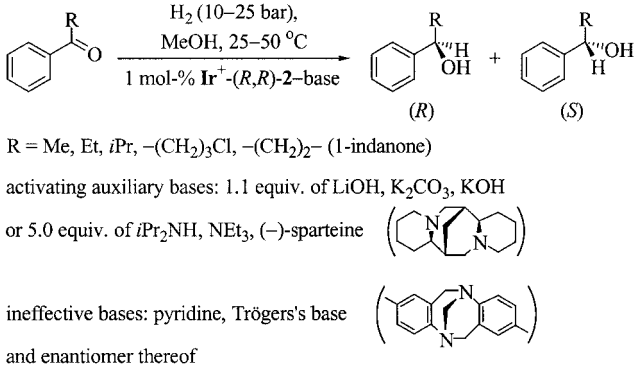
Table 1. ^{31}P NMR spectroscopic data of complex conformers observed in [D_6]acetone solution

Conformer[a]	δ(^{31}P)	Rel. conc. [%]
$\delta(S_{C\text{-}1},S_{C\text{-}2},R_N)$-**Ir**$^+$-(*S*,*S*)-**3**	46.65	60
$\delta(S_{C\text{-}1},S_{C\text{-}2},S_N)$-**Ir**$^+$-(*S*,*S*)-**3**	39.97	40
$\delta(S_{C\text{-}1},S_{C\text{-}2},R_N)$-**Ir**$^+$-(*S*,*S*)-**4**	45.44	75
$\delta(S_{C\text{-}1},S_{C\text{-}2},S_N)$-**Ir**$^+$-(*S*,*S*)-**4**	40.79	25
$\lambda(R_{C\text{-}1},R_{C\text{-}2},S_N)$-**Ir**$^+$-(*R*,*R*)-**2**	45.70[7a]	76
$\lambda(R_{C\text{-}1},R_{C\text{-}2},R_N)$-**Ir**$^+$-(*R*,*R*)-**2**	41.99[7a]	17
$\delta(R_{C\text{-}1},R_{C\text{-}2},S_N)$-**Ir**$^+$-(*R*,*R*)-**2**	38.07[7a]	7
$\lambda(R_{C\text{-}1},S_{C\text{-}2},R_N)$-**Ir**$^+$-(*R*,*S*)-**2**[b]	38.10	94
$\lambda(R_{C\text{-}1},S_{C\text{-}2},R_N)$-**Ir**$^+$-(*R*,*S*)-**4**	37.54	100
$\delta(S_{C\text{-}1},S_{C\text{-}2})$-**Ir**$^+$-(*S*,*S*)-**1**	46.44[7a]	100
$\lambda(R_{C\text{-}1},S_{C\text{-}2})$-**Ir**$^+$-(*R*,*S*)-**5**	35.70	100

[a] For stereochemical assignments, see text. [b] Low intensity singlets at δ = 38.01 and 41.27 are stereochemically unassigned.



Scheme 4. Drawings of preferred (less preferred) conformers observed in solution (cf. Table 1)



Scheme 5. Enantioselective hydrogenation of prochiral ketones using the **Ir**$^+$-(*R*,*R*)-**2** precatalyst in the presence of different bases

>C=O reduction occurred in methanol in the absence of an amine or an alkali metal hydroxide and, vice versa, in aprotic solvents, e.g. benzene, dichloromethane, or THF, containing such a basic additive. The likelihood of the ke-

Table 2. Enantioselective hydrogenation of acetophenone using the **Ir**$^+$-(*R*,*R*)-**2** catalyst modified by different bases

Auxiliary base (equiv. rel. to c_{Ir})[a]	$p(H_2)$ [bar]	T [°C]	t [h]	yield [%]	*ee* [%] (polar.)	*ee* [%] (HPLC)
iPr$_2$NH (5.0)	25	50	40	100	46 (*S*)	41 (*S*)
NEt$_3$ (5.0)	25	50	40	100	39 (*S*)	30 (*S*)
(−)-sparteine (5.0)	25	50	16	100	53 (*S*)	47 (*S*)
(+)-Tröger's base (5.0)	25	50	16	–		
(−)-Tröger's base (5.0)	25	50	16	–		
pyridine (5.0)	25	50	40	–		
(*S*)-PhCH$_2$CH(NH$_2$)CH$_2$OH (5.0)	25	50	80	55	53 (*S*)	48 (*S*)
(*R*)-PhCH$_2$CH(NH$_2$)CH$_2$OH (5.0)	25	50	80	56	60 (*S*)	54 (*S*)
(1*R*,2*R*)-Ph$_2$PCH(Ph)CH(Me)NHMe (5.0)	25	50	80	69	48 (*S*)	41 (*S*)
LiOH (1.1)	10	25	22	100	58 (*S*)	52 (*S*)
K$_2$CO$_3$ (1.1)	10	25	16	100	43 (*S*)	40 (*S*)
KOH (1.1)	10	25	7	100	62 (*S*)	55 (*S*)

[a] 0.02 mmol of metal complex plus added base together with 2.0 mmol of acetophenone in 3 mL of methanol.

Table 3. Homogeneous hydrogenation of acetophenone using different KOH- and (−)-sparteine-activated [(COD)M(P∩NR^{1}R^2)]$^+$ catalyst complexes; M = Ir (Rh)

Complex	Base[a]	t [h]	yield [%]	*ee* [%] (polar.)	*ee* [%] (HPLC)
Ir$^+$-(*S*,*S*)-**1**	KOH[b]	7	100	42 (*R*)	38 (*R*)
	(−)-sparteine[c]	16	100	19 (*R*)	15 (*R*)
Ir$^+$-(*S*,*S*)-**3**	KOH	32	100	27 (*R*)	26 (*R*)
	(−)-sparteine	70	51	33 (*R*)	31 (*R*)
Ir$^+$-(*S*,*S*)-**4**	KOH	12	100	51 (*R*)	51 (*R*)
	(−)-sparteine	16	100	44 (*R*)	44 (*R*)
Rh$^+$-(*R*,*R*)-**2**	KOH	6	100	77 (*S*)	71 (*S*)
	(−)-sparteine	28	100	39 (*S*)	34 (*S*)
Ir$^+$-(*R*,*R*)-**2**	KOH	7	100	62 (*S*)	55 (*S*)
	(−)-sparteine	16	100	53 (*S*)	47 (*S*)
Ir$^+$-(*R*,*S*)-**2**	KOH	32	100	45 (*S*)	38 (*S*)
	(−)-sparteine	43	100	5 (*S*)	4 (*S*)
Ir$^+$-(*R*,*S*)-**4**	KOH	50	100	21 (*S*)	19 (*S*)
	(−)-sparteine	55	100	9 (*S*)	7 (*S*)
Ir$^+$-(*R*,*S*)-**5**	KOH	58	100	36 (*S*)	36 (*S*)
	(−)-sparteine	70	25	10 (*S*)	9 (*S*)
Ir$^+$-**6**	KOH	4	100		
	(−)-sparteine	40	92		
Ir$^+$-**7**	KOH[d]	65	100		
	(−)-sparteine[d]	65	82		
Ir$^+$-**8**	KOH	3	100		
	(−)-sparteine	35	92		

[a] 0.02 mmol of [(COD)M(P∩NR^{1}R^2)]$^+$−KOH or [(COD)M(P∩NR^{1}R^2)]$^+$−(−)sparteine (M/KOH = 1:1.1; M/(−)-sparteine = 1:5.0), and 2.0 mmol of acetophenone in 3 mL of methanol. [b] KOH-activated precatalysts: $p(H_2)$ = 10 bar, T = 25 °C. [c] (−)-Sparteine-modified complexes: $p(H_2)$ = 25 bar, T = 50 °C. [d] $p(H_2)$ = 50 bar, T = 50 °C.

tone reduction proceeding by metal-assisted direct transfer of $H^{\delta-}/H^{\delta+}$ equivalents from the H_2 molecule to the carbonyl function was substantiated by ruling out the alternative pathway involving $H^{\delta-}/H^{\delta+}$ transfer from the primary alcohol. No transformation of acetophenone to 1-phenylethanol was observed when the ketone and a catalytic system composed of **Ir**$^+$-(*R*,*R*)-**2** and (−)-sparteine in a 1:5 molar ratio (vide infra) were kept in a catalyst-to-substrate ratio of 1:100 in methanol at 50 °C for 40 h in the absence of hydrogen gas, although quantitative >C=O hydrogenation did occur if the same catalyst was combined with the ketone in a 1:100 stoichiometry under 25 bar of H_2 at 50 °C for 40 h in Me$_3$COH which, as a tertiary alcohol, cannot serve as a proton/hydride source.

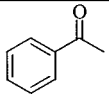
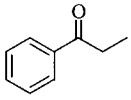
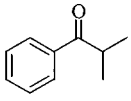
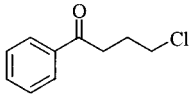
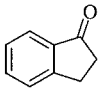
The influence on the catalytic activity of the different oxygen and nitrogen bases depicted in Scheme 5 was qualitatively studied for a standard system composed of the acetophenone substrate and the **Ir**$^+$-(*R*,*R*)-**2**−base catalyst in question (Table 2). While pyridine and the two enantiomers of Tröger's base did not support the hydrogenation reaction, tertiary and secondary alkylamines such as NEt$_3$, (−)-sparteine, and iPr$_2$NH performed reasonably if added in fivefold excess relative to the **Ir**$^+$-(*R*,*R*)-**2** concentration. Reaction times required for complete transformation of the

ketone at 50 °C under a pressure of 25 bar of H_2 were ≈ 40 h with triethyl and isopropylamine and only ca. 16 h with (−)-sparteine as auxiliary bases. It can therefore be concluded that the strength of the base which, compared with alkylamines, is low for heteroaromatic and arylamines,[20] exerts the important influence. In full agreement with this reasoning, strong oxygen bases such as LiOH, K_2CO_3, and particularly KOH were found to further decrease the times needed for quantitative hydrogenation, even if employed in a near equimolar **Ir**$^+$-(*R*,*R*)-**2**/base ratio at reduced temperature (25 °C) and H_2 pressure (10 bar). The addition of optically active chelating β-amino alcohols or -phosphanes had no significant influence on the selectivity of the catalysts but exerted a detrimental effect on their activity in that only reduced yields of the alcohol products were obtained after prolonged periods of time. Hence, for the catalytic runs described in the next section, potassium hydroxide or (−)-sparteine were employed as the "optimized" alkaline and amine bases.

The enantiomeric excesses of (*R*)- or (*S*)-PhCH(OH)Me that could be achieved in the hydrogenation of the standard acetophenone substrate in the presence of KOH-activated complexes ranged from 19−21% (*S*) for the iridium (pre)-catalyst **Ir**$^+$-(*R*,*S*)-**4** to 71−77% (*S*) for the rhodium system **Rh**$^+$-(*R*,*R*)-**2** (Table 3). Although the iridium homologue of the latter, **Ir**$^+$-(*R*,*R*)-**2**, was comparable in activity (≈ 7 vs. ≈ 6 h for quantitative >C=O reduction) it afforded a decidedly lower *ee* of only 55−62%. In the series of iridium complexes bearing chiral β-aminophosphanes with like configuration of their chelate backbone carbon atoms, viz. **Ir**$^+$-(*R*,*R*)-**2** and **Ir**$^+$-(*S*,*S*)-**1**,-**3**,-**4**, the *ee*'s were observed to increase in the order of their nitrogen substituents i.e. R = CH_2Ph < H < $CHMe_2$ < Me, suggesting that substitution by a medium sized methyl group is sufficient to afford the maximum enantioselectivity that can be achieved with these systems. Catalyst complexes bearing chiral *P*,*N* ligands with unlike stereochemistry of their backbone carbon atoms, i.e. **Ir**$^+$-(*R*,*S*)-**2**, **Ir**$^+$-(*R*,*S*)-**4**, and **Ir**$^+$-(*R*,*S*)-**5**, required much longer times for complete >C=O hydrogenation and also showed lower selectivities than their diastereomers with like carbon configurations in the C_2 linkages, viz. **Ir**$^+$-(*R*,*R*)-**2** and **Ir**$^+$-(*S*,*S*)-**4**. Furthermore, catalytically sluggish as *N*,*N*-dialkylated **Ir**$^+$-(*R*,*S*)-**5** proved to be, its mere ability to act as a catalyst gives unequivocal evidence that the presence of at least one NH function (which is met in all other complexes) is *not* a prerequisite for the particular compound to exhibit catalytic behavior. Nevertheless there exist major differences between the two classes of complexes with respect to their reactivity towards the dihydrogen molecule as will be shown below. Finally, the preferential formation of the product alcohol in the (*R*) configuration induced by complexes with δ($S_{C\text{-}1}$) stereochemistry of their chelate rings and, correspondingly, the predominance of the (*S*) enantiomer in the isomeric mixtures resulting from reactions promoted by all λ($R_{C\text{-}1}$) conformers shows that the hydrogenation catalysts described herein follow a λ/δ rule which predicts that λ chelates will give the (*S*) enantiomeric alcohol while δ chelates will produce the (*R*) enantiomer. Similar stereoselection has previously been documented for Ru^{II}-catalyzed >C=O hydrogenations.[3c][3d] The somewhat disappointing result that the product alcohols are generally formed, at best, in moderate optical yields either indicates an inherently low enantioselectivity of the systems or points to side reactions overriding the true selectivity of the complexes; e.g. the mixture of diastereomeric ring conformers detected in solution (Table 1) might act as interfering catalysts involved in competitive hydrogenation reactions.

Prochiral alkyl aryl ketones other than acetophenone which could be enantioselectively hydrogenated included propio- and isobutyrophenone, 3-chlorobutyrophenone, as well as 1-indanone (Table 4). Using the **Ir**$^+$-(*R*,*R*)-**2**-(−)-sparteine catalytic system, the product alcohols were formed as (*S*) enantiomers with optical yields between 29 and 68%, in full agreement with the empirical λ/δ rule formulated before. Attempts at the metal-assisted hydrogenation of dialkyl ketones such as 2-butanone, isopropyl methyl ketone, or pinacolone failed. Due to the basic conditions, these substrates underwent aldol reactions rather than reduction to give solids that were also isolated if the ketones were allowed to react in the presence of base but the absence of any added metal complex.

Table 4. Enantioselective hydrogenation of alkyl aryl ketones using the **Ir**$^+$-(*R*,*R*)-**2**−(−)-sparteine catalytic system[a]

Ketone	*t* [h]	yield [%]	*ee* [%] (polar.)
	16	100	53 (*S*)
	16	100	42 (*S*)
	23	100	48 (*S*)
	40	46[b]	68 (*S*)
	20	100	29 (*S*)

[a] 0.02 mmol of **Ir**$^+$-(*R*,*R*)-**2**, 0.1 mmol of (−)-sparteine, and 2.0 mmol of the ketonic substrate in 3 mL of methanol; $p(H_2)$ = 25 bar, *T* = 50 °C. [b] As a result of base-induced HCl elimination, the formation of 2-phenyltetrahydrofuran in low yield (≈4%) was also observed.

The mandatory presence of base in the catalytic systems suggests the intermediacy of in situ generated species that have lost H^+. For all catalysts derived from precursor complexes possessing *P*,*N* ligands with primary or secondary amine functions these could conceivably be amidoiridium(I) or -rhodium(I) complexes. In fact, the amides **Ir-7a** and **Ir-8a** (which were intentionally prepared for this specific pur-

pose) did catalyze the hydrogenation of acetophenone to 1-phenylethanol without the addition of base, quantitatively transforming the ketone to the alcohol under the usual conditions in approximately the same periods of time as the combined catalytic systems **Ir**$^+$**-7**−KOH and **Ir**$^+$**-8**−KOH, respectively. Thus, with 1 mol % of **Ir-7a** and **Ir**$^+$**-7**−KOH as catalysts, the reactions were complete after 2 and 3 h under 10 bar of H_2 at 25 °C, while 60−65 h at 50 °C under 50 bar of H_2 were needed for the quantitative formation of the alcohol in the presence of 1 mol % of **Ir-8a** or **Ir**$^+$**-8**−KOH. The ability of the two base-free β-amidophosphane iridium(I) complexes to catalyze the homogeneous >C=O reduction by molecular hydrogen likewise depends on the use of alcohols (MeOH, *t*BuOH) as reaction media, wherein the iridium−amide bond remains unprotonated. The obviously low amide basicity can be attributed to the involvement of the nitrogen lone-pair in π bonding to the central metal[21] with resultant $sp^3 \rightarrow sp^2$ rehybridization, similar to the situation that has previously been encountered for the closely related anilide [Ir(CO)(PPh_3)(2-$Ph_2PC_6H_4NMe$)], where the nitrogen atom features a trigonal-planar rather than a pyramidal surrounding and can be protonated only by very strong acids such as hydrochloric[22a] or tetrafluoroboric.[22b]

In view of the catalytic efficacy of **Ir-7a** and **Ir-8a**, numerous attempts were made to obtain similar amides also by deprotonation of the *chiral* [(COD)Ir(P∩NHR]$^+$ precatalysts but they remained unsuccessful. Either the amine function stayed unattacked, e.g. by amines or dilute KOH/methanol, or complex reaction mixtures containing ketonic and/or imine-type components [IR (KBr): $\tilde{\nu}$ = 1685 and 1715 cm^{-1}] were produced, if the cationic aminophosphane complexes were treated with very strong bases such as excess alkoxide or *n*BuLi. Obviously, those amine complexes which are different from **Ir**$^+$**-7** and **Ir**$^+$**-8** and possess CH units adjacent to the amino group tend to undergo degradation of their *P*,*N* ligands in the presence of strong base − most probably by >C=NR elimination from initially formed β-H containing amides which decompose easily due to their coordinative unsaturation.

Only in a single and probably serendipitous case we were able to isolate a well-defined product from such reactions. Combination of **Ir**$^+$-(*R*,*S*)-**4** with concentrated methanolic KOH and subsequent crystallization of the crude product from hot acetone gave cyclometalated [(COD)Ir{(1*R*,2*S*)-$Ph_2PCH(C_6H_4$-*o*)CH(Me)NHCHMe$_2$}] [**Ir**-(*R*,*S*)-**4a**] (Figure 5); i.e. deprotonation had occurred at one of the *ortho* C−H bonds of the phenyl ring attached to chelate backbone rather than at the amino function; Scheme 6. Presumably because of the hemilabile nature of the extraordinarily long Ir−N bond, measured as 2.448(6) and 2.514(6) Å for the two crystallographically independent molecules, this coordinatively saturated complex does exhibit some catalytic activity, slowly transforming acetophenone in methanol under 10 bar of H_2 to racemic 1-phenylethanol. The formation of the product alcohol without any notable stereodiscrimination strongly suggests that the orthometalated complex is not an actual intermediate maintaining the catalytic cycle

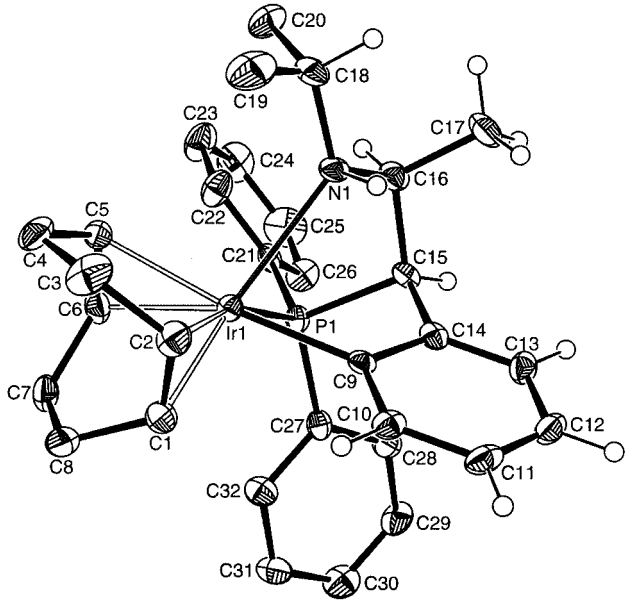
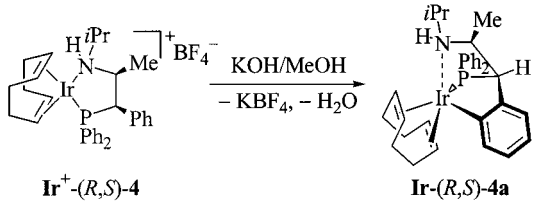


Figure 5. Perspective view of one of the two crystallographically independent molecules of orthometalated [(COD)Ir{(1*R*,2*S*)-$Ph_2PCH(C_6H_4$-*o*)CH(Me)NHCHMe$_2$] ("molecule 1"); selected bond lengths [Å] and angles [°]: Ir1−P1, 2.2917(18); Ir1−N1, 2.514(6); Ir1−C1, 2.099(7); Ir1−C2, 2.137(7); Ir1−C5, 2.183(7); Ir1−C6, 2.216(7); Ir1−C9, 2.104(7). P1−Ir1−N1, 78.86(14); P1−Ir1−C9, 77.13(19); N1−Ir1−C9, 75.3(2). Corresponding structural parameters for "molecule 2": Ir2−P2, 2.2942(18); Ir2−N2, 2.448(6); Ir2−C33, 2.213(7); Ir2−C34, 2.200(7); Ir2−C37, 2.119(7); Ir2−C38, 2.090(7); Ir2−C41, 2.119(7). P2−Ir2−N2, 80.50(14); P2−Ir2−C41, 77.11(19); N2−Ir2−C41, 75.3(2)



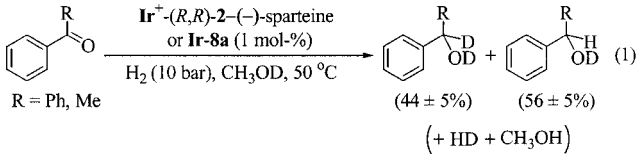
Scheme 6. KOH-assisted orthometalation

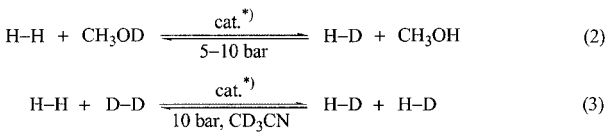
of enantioselective >C=O reduction but should rather be looked upon as a by-product resulting from a base-induced side reaction.

H/D Exchange Processes and H_2 Activation

When aceto- or benzophenone, dissolved in CH_3OD, were hydrogenated with H_2 employing either the base-free amide **Ir-8a** or the combined system **Ir**$^+$-(*R*,*R*)-**2**-(−)-sparteine as catalysts, the product alcohols were invariably characterized by NMR spectroscopy (^{1}H, ^{2}H, ^{13}C{^{1}H}; see Exp. Sect.) as mixtures containing the two isotopomers R^1R^2CHOD and R^1R^2CDOD in an almost 1:1 molar ratio. The evolution of *HD* gas was observed to be concomitant with the incorporation of solvent deuterons as $D^{\delta-}$ equivalents into the product carbinols [Scheme 7, reation (1)], as was the increasing formation of non-deuterated MeOH. No such uptake of D^+ as D^- by the ketonic substrate was noted if the hydrogenation was catalyzed by complex **Ir**$^+$-(*R*,*S*)-**5** possessing a tertiary amino donor group. Iridium-

catalyzed H_2/D^+ exchange with concomitant formation of HD was similarly observed when MeOD solutions of all base-free aminophosphane complexes containing at least one N−H bond were pressurized in the absence of any ketonic substrate in an NMR tube to 5−10 bar of H_2 [Scheme 7, reation (2)], but again did not take place on attempted catalysis by the *N*,*N*-dialkylated cation **Ir**$^+$-(*R*,*S*)-**5**. Hence, the exchange of isotopes between the protic solvent and the hydrogen atmosphere, which is typical of heterolytic H−H cleavage during reaction,[3,23−30] neither depends on the presence of base nor is contingent on simultaneous >C=O hydrogenation but requires at least one acidic N−H bond in the coordination sphere of the catalyst complex.



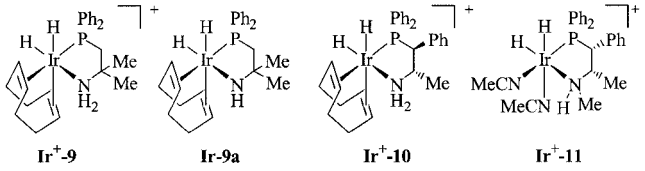


*) catalyzed by any NH-containing Ir^+ complex as well as by **Ir-7a** and **Ir-8a**

Scheme 7. Catalytic H_2/D^+ isotope exchange and H_2/D_2 scrambling in the presence [reation (1)] and absence of ketonic substrates [reations (2) and (3)]

Catalytic scrambling of isotopes with formation of HD was also detected when acetonitrile solutions of all NH-containing $[(COD)Ir(P\cap NHR)]^+$ complexes were exposed to 10 bar of an equimolar H_2/D_2 mixture [Scheme 7, reation (3)] but once more did not occur in the presence of the *N*,*N*-dialkylated derivative **Ir**$^+$-(*R*,*S*)-**5**. Control experiments in CD_3CN making use of a D_2-free hydrogen atmosphere ruled out the possibility that the observed HD did actually result from H_2/D^+ exchange between the H_2 component and the moderately acidic C−D bonds of the solvent molecules. The observed exchange of isotopes between the two gases implies the intermediate coordination of H_2 or D_2 to iridium, although the formation of any sufficiently long-lived Ir−H_2 adduct could not be traced by NMR spectroscopy down to −60 °C. Similar to the H_2/D^+ exchange described above, the observed H_2/D_2 scrambling process should involve heterolytic fission of the H−H and D−D bonds, respectively, since any isotope exchange brought about by homolytic cleavage of the two molecules would require simultaneous coordination of H_2 and D_2 to the same central metal, which is regarded as highly unlikely.[23c,23i,30]

Despite all failures to transform the iridium(I) amine complexes into their conjugate amides (vide supra), both the H_2/D_2 and the H_2/D^+ exchange processes were also catalyzed by the two amido complexes **Ir-7a** and **Ir-8a** [Scheme 7, reations (2) and (3)]. Furthermore, the initial product of the reaction between dihydrogen (5 bar) and **Ir-8a** in CD_3CN solution was unequivocally identified (see Exp. Sect.) as an *amido dihydride*, *cis*-[(CO-D)$IrH_2(Ph_2PCH_2CMe_2NH)$] (**Ir-9a**), originating from homolytic oxidative H_2 addition to the central metal (Scheme 8), rather than an *amino monohydride*, [(CO-D)$IrH(Ph_2PCH_2CMe_2NH_2)$] which would result from heterolytic H_2 addition to the N−H bond. The preference of **Ir-8a** to add the dihydrogen molecule by homolytic bond cleavage clearly contrasts with the heterolytic H−H fission concluded from the foregoing exchange experiments, notwithstanding that it corresponds to the low basicity of its amide function and also parallels the behavior of the related anilide $[Ir(CO)(PPh_3)(2\text{-}Ph_2PC_6H_4NMe)]$ described in previous work.[22a] As a further seemingly paradoxical result, the cationic aminophosphane complexes **Ir**$^+$**-8** and **Ir**$^+$-(*S*,*S*)-**1** were likewise seen to interact with molecular hydrogen by conventional oxidative addition, giving *cis*-[(CO-D)$IrH_2(Ph_2PCH_2CMe_2NH_2)]BF_4$ (**Ir**$^+$**-9**) and *cis*-$[(COD)IrH_2\{(1S,2S)\text{-}Ph_2PCH(Ph)CH(Me)NH_2\}]BF_4$ (**Ir**$^+$-**10**) as the first formed products (Scheme 8). Prolonged exposure of the iridium(I) precursors to H_2 at elevated pressures (> 10 bar) resulted in hydrogenic loss of the cyclooctadiene ligand with formation of solvate-stabilized adducts with *cis*,*cis*-$[(MeCN)_2IrH_2\{(1R,2S)\text{-}Ph_2PCH(Ph)CH(Me)NHMe\}]BF_4$ (**Ir**$^+$-**11**) being a representative example.

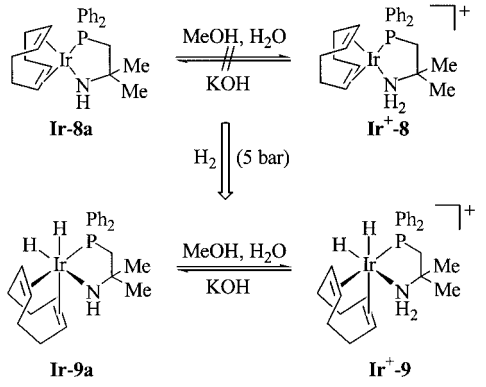


Scheme 8. Products of oxidative H_2 addition to β-amino- and β-amidophosphane iridium(I) precursors (cationic complexes: BF_4^- salts)

It was two important properties of the neutral amido and the cationic amino iridium(III) dihydrides that served to unravel the perplexing inconsistencies emerging, on the one hand, from the experimentally established homolytic H_2 addition by both the $[(COD)Ir(P\cap NHR)]^+$ and [(CO-D)$Ir(P\cap NR)$] complexes and, on the other hand, from the ability of the very same compounds to catalyze H_2/D_2 and H_2/D^+ scrambling processes.

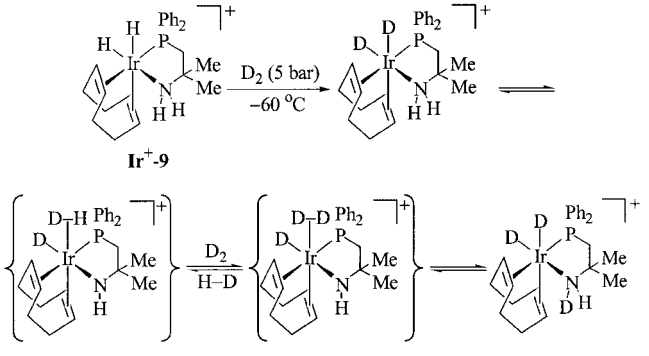
Firstly, while the *amino*phosphane iridium(I) complex **Ir**$^+$**-8** and its (formally) conjugate *amide* **Ir-8a** do not coexist in alcoholic media in an acid−base equilibrium, the products of oxidative H_2 addition to these two d^8 substrates, **Ir**$^+$**-9** and **Ir-9a**, do so (Scheme 9). Pressurizing a solution of **Ir-8a** in methanol to 5 bar of H_2 which, as mentioned above, does not lead to any detectable **Ir**$^+$**-8**, not only gave the amido dihydride **Ir-9a** but also produced the conjugate amino dihydro complex **Ir**$^+$**-9** at spectroscopically

detectable concentrations. The same result was obtained if a droplet of water was added to a solution of preformed **Ir-9a** in carefully dried CD_3CN. Vice versa, the latter amido dihydride was detected in addition to the predominantly formed amino dihydride $\mathbf{Ir^+}$**-9**, if a solution of $\mathbf{Ir^+}$**-8** in methanol containing dilute aqueous KOH at low concentration was pressurized with H_2 (Scheme 9). The basic properties of the amido function of the 18*e* complex **Ir-9a** can safely be attributed to its coordinative saturation which prevents the nitrogen lone-pair from engaging in π-bonding to the central metal. The reversible protonation of amido donor groups attached to an Ir^{III} center has some precedent in the literature: the amido-/aminophosphane complexes $[Ir(H)(Cl)(2\text{-}Ph_2PC_6H_4NR)(2\text{-}Ph_2PC_6H_4NHR)]$ (R = Et, CH_2Ph) react with protic acids HX (X = Cl, OH, O_2CMe) to yield cationic bis(aminophosphane) products, $[Ir(H)(Cl)(2\text{-}Ph_2PC_6H_4NHR)_2]^+$, from which the amido-/aminophosphane precursors can be restored by the addition of strong bases such as DABCO.[31]



Scheme 9. Reversible (*de*)protonation of coordinatively saturated amino and amido dihydro Ir^{III} complexes

Secondly, cationic amino dihydrido complexes of the type $[(COD)IrH_2(P\cap NHR)]^+$ will undergo substitution of their hydride ligands by deuteride forming $[(COD)IrD_2(P\cap NHR)]^+$ (and presumably $[(COD)IrD_2(P\cap NDR)]^+$ as well) if treated with D_2. This behavior has been verified for $\mathbf{Ir^+}$**-9**, which was generated in situ by exposing an acetonitrile solution of $\mathbf{Ir^+}$**-8** at −60 °C in a high-pressure NMR tube to 5 bar of H_2. The diagnostic NMR signals of the H_2 adduct [δ(IrH) = −15.78 (d, *cis*-$^2J_{P,H}$ = 10.95 Hz), −12.60 (d, *cis*-$^2J_{P,H}$ = 15.91 Hz); δ(^{31}P) = 31.87] persisted when the excess pressure was released from the tube showing that $\mathbf{Ir^+}$**-9**, which at ambient conditions under an inert atmosphere reductively eliminates dihydrogen, remains stable if kept under 1 bar of hydrogen at low temperature. With constant cooling to −60 °C, the H_2 atmosphere was then replaced by D_2 under normal pressure, which was subsequently raised again to 5 bar. As a result, the original dihydride $[(COD)IrH_2(Ph_2PCH_2CMe_2NH_2)]^+$ was converted into the dideuteride $[(COD)IrD_2(Ph_2PCH_2CMe_2NH_2)]^+$ manifesting itself by (i) the disappearance of the IrH doublets in the ^{1}H NMR spectrum, (ii) the persistence of the ^{31}P singlet (δ = 31.4 for the deuterated compound) and (iii) the appearance of two high-field ^{2}H peaks at δ = −15.7 and −12.7, indicating an IrD_2 substructure with non-equivalent Ir−D bonds. As a particularly illuminating feature, the ^{2}H NMR spectrum furthermore displayed an HD doublet at δ = 4.37 ($^1J_{H,D}$ = 42.6 Hz) in addition to the D_2 singlet at δ = 4.33, demonstrating that catalytic H_2/D_2 scrambling goes together with $IrH_2 \rightarrow IrD_2$ exchange (Scheme 10). A comparatively broad resonance centered at δ = 2.3 and partly overlapping the CDH_2CN triplet at δ = 1.98, could not be assigned with certainty It may originate from deuterated amino functions which would then be consistent with the presence in solution of $[(COD)IrD_2(Ph_2PCH_2CMe_2NHD)]^+$ and $[(COD)IrD_2(Ph_2PCH_2CMe_2ND_2)]^+$ isotopomers as required by the equilibria shown in Scheme 10. However, the assignment to C−D bonds resulting from deuteration and de-coordination of the cyclooctadiene ligand, could not be excluded.



Scheme 10. Intermolecular D_2/Ir−H exchange and intramolecular Ir−D/N−H scrambling involving reversible "$[Ir^{III}(H)_2-P\cap NH_2]^+$" ⇄ "$[(\eta^2\text{-}H_2)\text{-}Ir^{III}(H)-P\cap NH]^+$" tautomerization

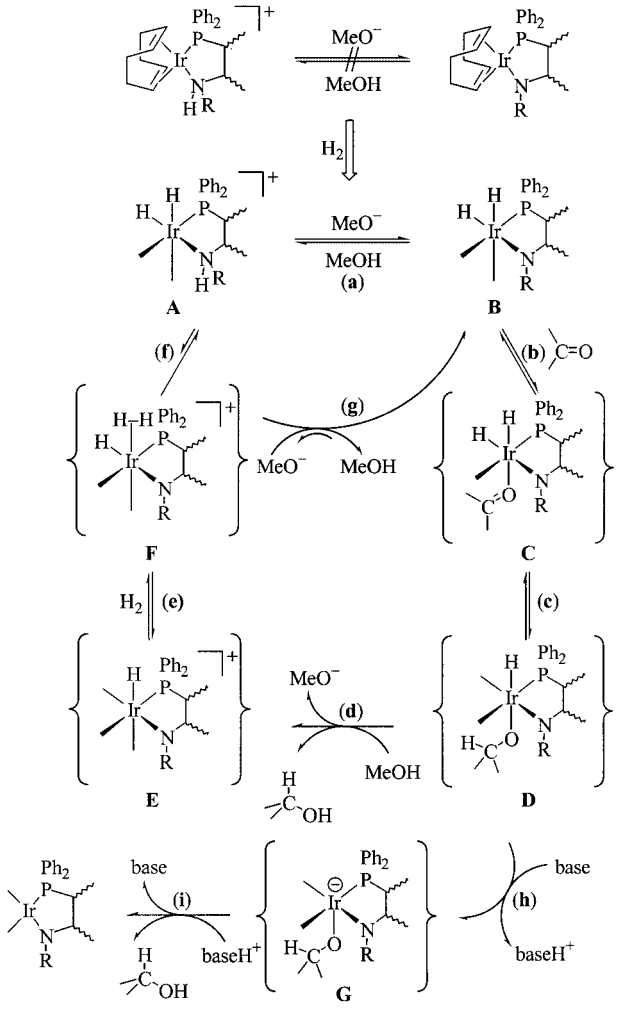
In an independent concluding experiment aiming at the unequivocal demonstration of the $[(COD)Ir(P\cap NHR)]^+$-catalyzed exchange of protons between the amino group and the gas, *N*-deuterated $[(COD)Ir\{(1R,2S)\text{-}Ph_2PCH(Ph)CH(Me)ND CHMe_2\}]^+$ [IR (KBr): $\tilde{\nu}$ = 2398 (ND) cm^{-1}] was first prepared from $\mathbf{Ir^+}$**-(*R*,*S*)-4** [IR (KBr): $\tilde{\nu}$ = 3209 (NH) cm^{-1}] and [D_1]methanol and then allowed to interact with H_2 under pressure in dry [D_8]THF. The solid that was recovered after removal of all volatile material displayed the characteristic N−H stretching vibration of the starting $\mathbf{Ir^+}$**-(*R*,*S*)-4**$^+$ complex, showing that an H_2/−NDR → HD/−NHR re-exchange of isotopes had occurred.

The formation of HD as a product obligatorily accompanying the hydride/deuteride exchange at the Ir^{III} center and the observation that both the catalyzed H_2/D_2 scrambling and the exchange of isotopes between dihydrogen molecules and solvent protons is only supported by complexes containing at least one N−H bond [Scheme 7, reactions (2) and (3)] are strongly suggestive of an equilibrium between two amino−dihydrido and amido−dihydrogen−monohydrido tautomers, "$[Ir^{III}(H)_2-$

P∩NH$_2$]$^+$" and "[(η^2-H$_2$)-Ir^{III}(H)−P∩NH]$^+$", even if the η^2-H$_2$ isomeric form, which maintains the exchange of isotopes by intramolecular H/D scrambling (cf. Scheme 10),[23c,23e,23i,25] remained undetected by NMR spectroscopy down to −60 °C. Related equilibria that have previously been established, generally in an indirect fashion by the observation of H$_2$/D$^+$ exchange processes and/or isotopic scrambling between metal−hydride and protonated ligand sites, include the pairs of tautomers "H−M^{II}−S(H)R ⇄ (η^2-H$_2$)−M^{II}−SR" (M = Ru,[23h,27c,27d] Os,[28b,28c], Ni[27e,27f]) and "H−M^{III}−LH ⇄ (η^2-H$_2$)−M^{III}−L" (M = Rh: LH = RSH;[27a,27b] M = Ir: LH = NH$_3$,[26] OH$_2$,[25a,25b] RSH[28a]) as well as a family of Ir^{III} complexes containing a pendant basic aniline (acidic anilinium) function in addition to an acidic η^2-bound H$_2$ ligand (basic hydride).[25c,25d] Only in favorable cases where the pK_a of the coordinated dihydrogen molecule and the protonated ancillary ligand were similar[23i] was it possible to directly observe the equilibrium between the two tautomers.[28c] For the most part however, either the η^2-H$_2$ complex[25c,25d,26,27b,28] or the metal hydride containing the protonated N,[25c,25d] O,[25a] or S[27c] ligand remained undetected transients in the isotopic scrambling, depending on whether the coordinated H$_2$ molecule or the ligand bearing the proton was the stronger Brønsted acid or, vice versa, whether the ancillary deprotonated ligand or the metal−hydride bond[32] was the stronger Brønsted base.[25c,25d] With regard to the "[IrH$_2$(Ph$_2$PCH$_2$-CMe$_2$NH$_2$)]$^+$" ⇄ "[(η^2-H$_2$)(H)(Ph$_2$PCH$_2$CMe$_2$NH)]$^+$" tautomerization, we conclude that the amido−dihydrogen−monohydrido complex cannot be seen but resembles the undetected dihydrogen amide forms "[Ir^{III}(η^2-H$_2$)NH$_2$]$^{n+}$" of the long known hydrido ammine complexes [Ir^{III}(H)(NH$_3$)$_2$(PEt$_3$)$_2$L]$^{n+}$ (n = 1; L = Cl; n = 2: L = NH$_3$, PEt$_3$)[26] in being a transient species immediately yielding the other tautomer because the basicity of the coordinated amide by far exceeds that of the metal−hydride bond in the adjacent *cis* position.

Concluding Discussion

Putting all evidence together, we propose that H$_2$ activation as well as H$_2$/D$^+$ and H$_2$/D$_2$ exchange follow the cycle outlined in Scheme 11, which rests on the formation of either COD-coordinated or solvated *amino* and *amido* dihydro iridium(III) complexes, A and B, as the first key intermediates. Because of their coordinative saturation, amides B can act as bases toward the protic solvent to generate the conjugate amino complexes A at equilibrium concentrations (step a) and, equally important, are inert towards elimination of imine fragments from *P*,*N* ligands possessing β-hydrogen atoms. The readily occurring H$_2$/D$_2$ exchange processes, which require the presence of at least one acidic N−H function, points to a tautomeric equilibrium between A and the dihydrogen−hydrido−amido form F. Even if the tautomerization step f yields F only at spectroscopically undetectable transitory concentrations, these are sufficient to



Scheme 11. Proposed catalytic cycle for >C=O hydrogenation and concomitant H$_2$/D$^+$ and H$_2$/D$_2$ exchange reactions (unlabeled coordination sites occupied by weakly bonded solvent molecules)

account for the observed H/D exchange processes since cationic Ir^{III}(μ-H$_2$)(H) complexes combine the possibility of facile *inter*molecular exchange between the bound H$_2$ ligand and free D$_2$ molecules (or molecules containing exchangeable protons) with low barriers to *intra*molecular exchange with the hydride ligand.[23c,23i]

The transient formation of tautomers F also explains the incorporation of solvent deuterons as D$^{\delta-}$ equivalents into the product alcohols that were obtained if the [(COD)Ir(P∩NHR)]$^+$−base-assisted hydrogenation of ketones was conducted in MeOD [Scheme 7, reaction (1)]. We propose that the catalysts described herein follow the classic Schrock−Osborn pathway[6] of >C=O/Ir−H insertion rather than the alternative Noyori−Morris mechanism of "metal−ligand bifunctional" interaction with the substrate,[2,3,4] mainly because the latter[5,6] does *not* depend on the use of protic reaction media but also occurs with comparable results in aprotic solvents such as benzene.[3] In the associated catalytic cycle the first formed amido dihydrides B are converted via ketone adducts C into alkoxo hydrides D, where the *trans* bond weakening H$^-$ ligand is expected

to be bonded opposite to the alkoxide so that release of the alcohol by reductive elimination is impeded (steps b and c).[5] Protonation of the alkoxide ligand by the solvent with subsequent release of the product from the metal (step d) is a more feasible option which would also explain why the use of protic reaction media is essential for the catalysis. Addition of H_2 to the vacant (or weakly solvated) coordination site of the remaining cationic Ir^{III} species E (step e) leads back to F as the key transient that is able to connect the cycle of catalytic >C=O hydrogenation with the pathway of H_2/D^+ scrambling. *Intra*molecular deprotonation of the acidic H_2 ligand by the amide site (step f) will restore the amino dihydrido species A, which in turn can be converted into the conjugate amides B by the added base. Alternatively, *inter*molecular deprotonation (g) by the methoxide released during product formation (or even by the solvent itself) will directly regenerate the starting amido dihydrides B and, hence, can likewise serve to close the two interlinked cycles. An additional function of the mandatory base may be to deprotonate the alkoxo hydride D at the Ir−H bond forming G as a transient anionic Ir^{III} species which then is re-protonated by the conjugate acid baseH^+ at the alkoxo site[5,6] to release the product and regenerate the starting Ir^I amido complex (steps h and i). In this context, we briefly note that the proposed >C=O/Ir−H pathway can also explain the finding that *N*,*N*-dialkylated $[(COD)Ir\{(1R,2S)\text{-}Ph_2PCH(Ph)CH(Me)NMe_2\}]^+$ [**Ir**$^+$-(*R*,*S*)-**5**] in the presence of base *does* exhibit some catalytic activity for homogeneous ketone hydrogenation *but does not* act as a catalyst for either the H_2/D_2 or H_2/D^+ exchange processes. Oxidative addition of H_2, followed by coordination and insertion of the ketone, will give a *cationic* alkoxo hydrido intermediate in place of the *neutral* species D proposed in Scheme 11. Removal of the alcohol from the coordination sphere on the MeO^-/MeOH-driven pathway h → i therefore leads back to $[L_2Ir\{(1R,2S)\text{-}Ph_2PCH(Ph)CH(Me)NMe_2\}]^+$ as a solvated analogue of the starting compound **Ir**$^+$-(*R*,*S*)-**5**, thus maintaining the cycle of >C=O hydrogenation but barring the way to concomitant isotopic scrambling.

In summary, evidence has been presented for a mechanism of >C=O hydrogenation and H/D exchange catalyzed by iridium β-aminophosphane complexes which involves both homo- and heterolytic H_2 activation at the same metal center.[33]

Experimental Section

General Remarks: All manipulations were performed under nitrogen using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents prior to use. IR: Mattson Polaris. NMR: Bruker DPX 300 (300.1 MHz for ^1H, 75.5 MHz for ^{13}C, 121.5 MHz for ^{31}P, and 46.1 MHz for ^2H) at 20±2 °C (if not stated otherwise) using $SiMe_4$ (or the solvent) or H_3PO_4 as internal or external standards, respectively (downfield positive; "m": deceptively simple multiplets); high-pressure experiments in Wilmad 528-PV-1 tubes (inner diameter: 2.2 mm). Polarimetry: Perkin−Elmer PE 241 (1 dm cells at room temperature). $[\alpha]_\lambda$ in 10 deg·cm^2·g^{-1} (estimated accuracy: ±3%), *c* in g 100 mL^{-1}. HPLC: Thermoquest P 4000 (UV detector).

(2-Aminoethyl)diphenylphosphane as well as the β-amino alcohols (−)-norephedrine, (−)-ephedrine, (−)-*N*-methylephedrine, (+)-pseudoephedrine, (−)-pseudoephedrine, and 2-amino-2-methylpropanol were used as obtained commercially (Fluka, Aldrich). Other starting materials, including (−)-*N*-isopropylnorephedrine,[15] diphenylphosphane,[34] the aziridines 2,2-dimethyl-,[19] (−)-(2*S*,3*R*)-*cis*-2-methyl-3-phenyl-,[7a][9b] (−)-(2*S*,3*S*)-*trans*-2-methyl-3-phenyl-,[7a][12c] (+)-(2*R*,3*S*)-*cis*-1,2-dimethyl-3-phenyl-,[7a] and (+)-(2*S*,3*S*)-*trans*-1,2-dimethyl-3-phenylaziridine,[12b][12c] the *P*,*N* ligands (2-diphenylphosphanyl)-*N*-methylaniline,[18] (+)-(1*S*,2*S*)-(2-amino-1-phenylpropyl)-, (−)-(1*R*,2*S*)-(2-amino-1-phenylpropyl)-, and (−)-(1*R*,2*R*)-(2-methylamino-1-phenylpropyl)diphenylphosphane[7a] as well as the iridium and rhodium complexes *trans*-$[IrCl(CO)PPh_3)_2]$,[35] $[\{(COD)Ir(\mu\text{-}Cl)\}_2]$,[36] $[Ir(COD)_2]BF_4$,[37] (−)-$[(COD)Ir\{(1S,2S)\text{-}Ph_2PCH(Ph)CH(Me)NH_2\}]BF_4$, and $[(COD)M\{(1R,2R)\text{-}Ph_2PCH(Ph)CH(Me)NHMe\}]BF_4$ (M = Rh, Ir)[7a] were prepared as described previously.

(−)-(2*S*,3*R*)-*cis*-1-Benzyl-2-methyl-3-phenylaziridine: A solution of (−)-(2*S*,3*R*)-*cis*-2-methyl-3-phenylaziridine (480 mg, 3.60 mmol) in THF (40 mL) was treated with *n*-butyllithium (2.25 mL of a 1.6 M solution in hexane) at 0 °C. After the addition of benzyl chloride (0.44 mL, 3.80 mmol) and stirring overnight, 2% aqueous citric acid (40 mL) and dichloromethane (50 mL) were added. The aqueous layer was saturated with NaCl and repeatedly extracted with CH_2Cl_2. The combined organic phases were thoroughly washed with $NaHCO_3$ and the solvents evaporated to dryness. The remaining colorless oil was purified by chromatography on a silica gel column with diethyl ether/*n*-pentane (1:8) as the eluent. Evaporation of the solvent from the eluate left the product as a colorless oil; yield 460 mg (57%). ^1H NMR ($CDCl_3$, ppm): δ = 0.87 (d, $^3J_{H,H}$ = 5.49 Hz, 3 H, CH_3), 1.82 ["qui", 1 H, C(2)-H)], 2.57 [d, $^3J_{H,H}$ = 6.57 Hz, 1 H, C(3)-H], 3.49, 3.66 (AB-dd, $^2J_{H,H}$ = 13.91 Hz, 2 H, CH_2), 7.1−7.5 (m, 10 H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): δ = 12.79 (CH_3), 41.72 (C-2), 46.18 (C-3), 64.42 (CH_2), 126.4−139.4 (C_6H_5). The NMR spectroscopic data corresponded to those reported in the literature in every respect.[14] $[\alpha]_{589}$ = −112.4 (*c* = 1.3, CH_2Cl_2).

(−)-(2*S*,3*R*)-*cis*-1-Isopropyl-2-methyl-3-phenylaziridine: (−)-(1*R*,2*S*)-*N*-Isopropylnorephedrine (830 mg, 3.97 mmol) was combined in chloroform (30 mL) at 0 °C with PCl_5 (1.10 g, 5.30 mmol). The mixture was heated to reflux for 1 h, then cooled in an ice bath and worked up by the cautions addition of methanol (15 mL). The residue remaining after evaporation to dryness, addition of ethanol (20 mL), and renewed removal of all volatile material was triturated with diethyl ether, separated by filtration and re-dissolved in chilled 5 M sodium hydroxide solution (40 mL). The resultant mixture was heated at 90 °C for 2 h, cooled to room temperature and extracted with diethyl ether. The combined organic layers were dried with Na_2SO_4, evaporated, and then distilled at 70 °C in the vacuum of an oil pump to give the product as a colorless liquid which solidified overnight forming tiny needle-shaped crystals; yield 375 mg (54%). ^1H NMR ($CDCl_3$, ppm): δ = 0.74 (d, $^3J_{H,H}$ = 5.67 Hz, 3 H, CH_3), 1.00, 1.02 [both d, $^3J_{H,H}$ = 5.85 Hz each, both 3 H, $CH(CH_3)_2$], 1.53 [sept, $CH(CH_3)_2$], 1.58 ["qui", 1 H, C(2)-H], 2.33 [d, $^3J_{H,H}$ = 6.75 Hz, 1 H, C(3)-H], 7.0−7.2 (m, 5 H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): δ = 13.70 (CH_3), 21.88, 22.08 [both $CH(CH_3)_2$], 40.51 (C-2), 45.87 (C-3), 61.34 [$NCH(CH_3)_2$], 125.4−138.0 (C_6H_5). $[\alpha]_{589}$ = −106.1 (*c* = 6.1, CH_2Cl_2).

(+)-(2*S*,3*S*)-*trans*-1-Isopropyl-2-methyl-3-phenylaziridine: A solution of bromine (255 μL, 4.95 mmol) in acetonitrile (5 mL) was

added dropwise at 0 °C to triphenylphosphane (1.30 g, 4.95 mmol) dissolved in MeCN (15 mL). The resultant mixture was stirred for 2 h at room temperature, cooled in an ice bath, and then treated with an acetonitrile solution (5 mL) containing (−)-(1*R*,2*S*)-*N*-isopropylnorephedrine (1.035 g, 4.95 mmol) together with triethylamine (1.38 mL, 9.89 mmol). Stirring overnight caused a precipitate of triethylammonium bromide to separate from the solution, which was filtered off. The filtrate was thoroughly extracted with *n*-pentane and the combined extracts were concentrated to a small residual volume to deposit a white precipitate of triphenylphosphane oxide which was removed by filtration. The filtrate was evaporated in vacuo and then distilled with an oil pump generated vacuum at 70 °C to give 317 mg (43%) of the aziridine as a colorless liquid. ^{1}H NMR ($CDCl_3$, ppm): δ = 1.07, 1.10 [both d, $^3J_{H,H}$ = 6.21 Hz each, both 3 H, CH(C*H*$_3$)$_2$], 1.33 (d, $^3J_{H,H}$ = 5.85 Hz, 3 H, CH_3), 2.06 [d, $^3J_{H,H}$ = 2.91 Hz, 1 H, C(3)-H], 2.11 [m, 1 H, C(2)−H], 2.36 [sept, 1 H, C*H*(CH$_3$)$_2$], 7.0−7.3 (m, 5 H, C_6H_5). ^{13}C{^{1}H} NMR ($CDCl_3$, ppm): δ = 11.14 (CH_3), 22.87, 22.94 [both CH(*C*H$_3$)$_2$], 42.45 (C-2), 46.94 (C-3), 51.70 [N*C*H(CH$_3$)$_2$], 126.1−141.1 (C_6H_5). [α]$_{589}$ = +64.8 (*c* = 4.7, CH_2Cl_2).

(−)-(1*R*,2*S*)-(2-Methylamino-1-phenylpropyl)diphenylphosphane [(*R*,*S*)-2]: Boron trifluoride−diethyl etherate (2.32 mL, 18.50 mmol) was added dropwise to a $CHCl_3$ solution of (+)-(2*S*,3*S*)-*trans*-1,2-dimethyl-3-phenylaziridine (2.717 g, 18.45 mmol) and diphenylphosphane (3.20 mL, 18.50 mmol). The mixture was heated to reflux overnight, then hydrolyzed and adjusted to pH 8 by addition of $NaHCO_3$. The organic phase was separated, washed with 5% aqueous sodium hydrogencarbonate, dried over Na_2SO_4, and the solvents evaporated to leave a yellowish oily residue. The oil was re-dissolved in diethyl ether, filtered, evaporated again, and heated at 100 °C under a dynamic vacuum in order to remove any remaining diphenylphosphane; yield 289 mg (47%) of (*R*,*S*)-**2** as a colorless wax. ^{1}H NMR ($CDCl_3$, ppm): δ = 0.98 (d, $^3J_{H,H}$ = 6.39 Hz, 3 H, CCH_3), 1.83 [s (br), 1 H, NH], 2.30 (s, 3 H, NCH_3), 2.80 [m, 1 H, C(2)-H], 3.62 ["t", Σ|$^2J_{P,H}$ + $^3J_{H,H}$| = 11.70 Hz, 1 H, C(1)-H], 7.0−7.7 (m, 15 H, C_6H_5). ^{13}C{^{1}H} NMR ($CDCl_3$, ppm): δ = 18.60 (d, $^3J_{P,C}$ = 4.36 Hz, C*C*H$_3$), 34.11 (s, NCH_3), 51.89, 56.52 (both d, $J_{P,C}$ = 13.08, 16.72 Hz, C-1/*C*-2), 126.5−138.6 (C_6H_5). ^{31}P{^{1}H} NMR ($CDCl_3$, ppm): δ = −7.00. [α]$_{589}$ = −218 (*c* = 0.9, THF). $C_{22}H_{24}NP$ (333.4): calcd. C 79.25, H 7.26, N 4.20; found C 79.47, H 7.43, N 4.11.

(+)-(1*S*,2*S*)-(2-Benzylamino-1-phenylpropyl)diphenylphosphane [(*S*,*S*)-3]: The preparation was carried out as described for (*R*,*S*)-**2** by reacting BF_3-activated (−)-(2*S*,3*R*)-*cis*-1-benzyl-2-methyl-3-phenylaziridine (367 mg, 1.65 mmol) with diphenylphosphane (0.29 mL, 1.65 mmol); yield 325 mg (48%) of (*S*,*S*)-**3** as a white powder. ^{1}H NMR ($CDCl_3$, ppm): δ = 1.04 (d, $^3J_{H,H}$ = 6.57 Hz, 3 H, CCH_3), 1.41 [s (br), 1 H, NH], 2.81 [m, 1 H, C(2)-H], 3.64, 3.66 (AB-dd, $^2J_{H,H}$ = 13.45 Hz, 2 H, CH_2), 3.83 [dd, $^2J_{P,H}$/$^3J_{H,H}$ = 5.49/5.67 Hz, 1 H, C(1)-H], 6.9−7.5 (m, 20 H, C_6H_5). ^{13}C{^{1}H} NMR ($CDCl_3$, ppm): δ = 17.90 (d, $^3J_{P,C}$ = 9.45 Hz, C*C*H$_3$), 50.63 (s, NCH_2), 48.98, 53.54 (both d, $J_{P,C}$ = 14.53, 17.43 Hz, C-1/C-2), 119.5−140.2 (C_6H_5). ^{31}P{^{1}H} NMR ($CDCl_3$, ppm): δ = −8.05. [α]$_{589}$ = +64.5 (*c* = 6.7, CH_2Cl_2). $C_{28}H_{28}NP$ (409.5): calcd. C 82.12, H 6.89, N 3.42; found C 81.95, H 7.01, N 3.31.

(+)-(1*S*,2*S*)-(2-Isopropylamino-1-phenylpropyl)diphenylphosphane [(*S*,*S*)-4]: This material was obtained as outlined before by treating (−)-(2*S*,3*R*)-*cis*-1-isopropyl-2-methyl-3-phenylaziridine (263 mg, 1.50 mmol) in the presence of $F_3B{\cdot}OEt_2$ with diphenylphosphane (0.26 mL, 1.50 mmol); yield 421 mg (78%) of a colorless waxy solid. ^{1}H NMR ($CDCl_3$, ppm): δ = 0.63 (d, $^3J_{H,H}$ = 6.03 Hz, 3 H, CCH_3), 0.83, 1.00 [both d, $^3J_{H,H}$ = 6.21, 6.60 Hz, both 3 H, CH(C*H*$_3$)$_2$], 2.74 [m, 1 H, C(2)-H], 2.91 [sept, 1 H, C*H*(CH$_3$)$_2$], 3.81 [dd, $^2J_{P,H}$/$^3J_{H,H}$ = 3.84/6.60 Hz, 1 H, C(1)-H], 6.9−7.7 (m, 15 H, C_6H_5); NH not observed. ^{13}C{^{1}H} NMR ($CDCl_3$, ppm): δ = 18.20 (d, $^3J_{P,C}$ = 8.72 Hz, C*C*H$_3$), 22.24, 23.04 [both s, both CH(*C*H$_3$)$_2$], 43.94 [s, N*C*H(CH$_3$)$_2$], 47.70, 50.00 (both d, $J_{P,C}$ = 14.53, 16.71 Hz, C-1/C-2), 126.4−137.7 (C_6H_5). ^{31}P{^{1}H} NMR ($CDCl_3$, ppm): δ = −9.04. [α]$_{589}$ = +37.1 (*c* = 2.4, CH_2Cl_2). $C_{24}H_{28}NP$ (361.5): calcd. C 79.75, H 7.81, N 3.87; found C 79.63, H 7.99, N 3.79.

(−)-(1*R*,2*S*)-(2-Isopropylamino-1-phenylpropyl)diphenylphosphane [(*R*,*S*)-4]: The compound was prepared in a similar way to its (1*S*,2*S*) diastereomer above using BF_3-activated (+)-(2*S*,3*S*)-*trans*-1-isopropyl-2-methyl-3-phenylaziridine (371 mg, 2.12 mmol) together with an equimolar quantity of diphenylphosphane (0.37 mL) in $CHCl_3$; yield 669 mg (87%) of a colorless sticky solid. ^{1}H NMR ($CDCl_3$, ppm): δ = 0.64 (d, $^3J_{H,H}$ = 6.24 Hz, 3 H, CCH_3), 0.86, 0.88 (both d, $^3J_{H,H}$ = 6.39 Hz each, both 3 H, CH(C*H*$_3$)$_2$], 2.70 [sept, 1 H, C*H*(CH$_3$)$_2$], 2.99 [m, 1 H, C(2)-H], 3.52 [dd, $^2J_{P,H}$/$^3J_{H,H}$ = 4.84/6.60 Hz, 1 H, C(1)-H], 6.9−7.6 (m, 15 H, C_6H_5); NH not observed. ^{13}C{^{1}H} NMR ($CDCl_3$, ppm): δ = 20.32 (d, $^3J_{P,C}$ = 5.08 Hz, C*C*H$_3$), 22.01, 24.22 [both s, both CH(*C*H$_3$)$_2$], 45.34 [s, N*C*H(CH$_3$)$_2$], 51.41, 51.90 (both d, $J_{P,C}$ = 15.26, 12.35 Hz, C-1/C-2), 126.4−130.5 (C_6H_5). ^{31}P{^{1}H} NMR ($CDCl_3$, ppm): δ = −7.68. [α]$_{589}$ = −205 (*c* = 1.1, CH_2Cl_2). $C_{24}H_{28}NP$ (361.5): calcd. C 79.75, H 7.81, N 3.87; found C 79.52, H 8.02, N 3.73.

(−)-(1*R*,2*S*)-(2-Dimethylamino-1-phenylpropyl)diphenylphosphane [(*R*,*S*)-5]: Methanesulfonyl chloride (1.27 mL, 16.35 mmol) and triethylamine (3.50 mL, 24.52 mmol) were sequentially added to a chilled THF solution (40 mL) of (−)-*N*-methylephedrine (1.465 g, 8.17 mmol). The aziridinium methanesulfonate which was formed after stirring the mixture for 1 h at room temperature was further reacted by heating to reflux a toluene solution (50 mL) containing diphenylphosphane (1.42 mL, 8.17 mmol) and an additional amount of NEt_3 (2.30 mL, 16.35 mmol). After hydrolysis the product was isolated following the workup procedure described above for (*R*,*S*)-**2**; yield 1.11 g (39%) of the aminophosphane as a colorless wax. ^{1}H NMR ($CDCl_3$, ppm): δ = 0.87 (d, $^3J_{H,H}$ = 6.75 Hz, 3 H, CCH_3), 1.96 [s, 6 H, N(CH$_3$)$_2$], 3.04 [m, 1 H, C(2)-H], 3.55 [dd, $^2J_{P,H}$/$^3J_{H,H}$ = 6.03/7.68 Hz, 1 H, C(1)-H], 6.9−7.7 (m, 15 H, C_6H_5). ^{13}C{^{1}H} NMR ($CDCl_3$, ppm): δ = 18.60 (d, $^3J_{P,C}$ = 4.36 Hz, C*C*H$_3$), 34.11 [s, N(CH$_3$)$_2$], 51.89, 56.52 (both d, $J_{P,C}$ = 13.08, 16.72 Hz, C-1/C-2), 126.5−138.6 (C_6H_5). ^{31}P{^{1}H} NMR ($CDCl_3$, ppm): δ = −4.24. [α]$_{589}$ = −318 (*c* = 3.1, THF). $C_{23}H_{26}NP$ (347.4): calcd. C 79.51, H 7.54, N 4.03; found C 79.84, H 7.88, N 3.92.

(2-Amino-2-methylpropyl)diphenylphosphane (8): A mixture composed of 9.96 mmol in each case of 2,2-dimethylaziridine (708 mg), boron trifluoride diethyl etherate (1.26 mL), and diphenylphosphane (1.73 mL) in $CHCl_3$ (50 mL) was heated to reflux for 3 h. An oily precipitate resulting from polymerization of the aziridine was removed by decanting the supernatant liquid, which was worked up by hydrolysis as outlined before for (*R*,*S*)-**2** to give 870 mg (34%) of the *P*,*N* ligand as a clear colorless oil. ^{1}H NMR ($CDCl_3$, ppm): δ = 1.21 (s, 6 H, CH_3), 1.36 [s (br), 2 H, NH_2], 2.36 (d, $^2J_{P,H}$ = 3.66 Hz, CH_2), 7.2−7.6 (m, 10 H, C_6H_5). ^{13}C{^{1}H} NMR ($CDCl_3$, ppm): δ = 32.01 (d, $^3J_{P,C}$ = 7.99 Hz, CH_3), 45.83, 50.00 (both d, $J_{P,C}$ = 15.25, 15.26 Hz, C-1/C-2), 128.3−139.5 (C_6H_5). ^{31}P{^{1}H} NMR ($CDCl_3$, ppm): δ = −23.09. $C_{16}H_{20}NP$ (257.3): calcd. C 74.69, H 7.83, N 5.44; found C 74.79, H 7.98, N 5.21.

[(COD)Ir(Ph$_2$PCH$_2$CH$_2$NH$_2$)]BF$_4$ [Ir$^+$-6]: To [Ir(COD)$_2$]BF$_4$ (472 mg, 0.95 mmol) suspended in THF (10 mL) was added dropwise a solution of **6** (220 mg, 0.96 mmol) in THF (15 mL). The dark red solution which formed on stirring overnight was reduced in vacuo to a small residual volume. Dilution with diethyl ether and *n*-pentane (20 mL each) caused the product to separate from solution as an orange microcrystalline precipitate which was collected by filtration, thoroughly washed with diethyl ether, and dried under a dynamic vacuum; yield 540 mg (91%). ^{1}H NMR (CDCl$_3$, ppm): δ = 1.7−2.3 (m, 8 H, diene CH$_2$), 2.85, 2.95 (both m, 2 H each, PCH$_2$/NCH$_2$), 3.36 [s (br), 2 H, NH$_2$], 4.7, 5.1 (both m, 2 H each, both diene CH), 7.1−7.7 (m, 10 H, C$_6$H$_5$). ^{13}C{^{1}H} NMR (CDCl$_3$, ppm): δ = 29.30 (s, 2 diene CH$_2$), 31.56 (d, $^1J_{P,C}$ = 32.69 Hz, PCH$_2$), 32.41 (s, 2 diene CH$_2$), 44.69 (d, $^2J_{P,C}$ = 5.09 Hz, NCH$_2$), 61.64 (s, CH=CH *trans* N), 93.33 (d, $^2J_{P,C}$ = 11.62 Hz, CH=CH *trans* P), 128.8−133.2 (C$_6$H$_5$). ^{31}P{^{1}H} NMR (CDCl$_3$, ppm): δ = 38.61. C$_{22}$H$_{28}$BF$_4$IrNP (616.5): calcd. C 42.86, H 4.58, N 2.27; found C 43.02, H 4.67, N 2.09.

The following complexes were prepared by a procedure analogous to that detailed before.

[(COD)Ir(2-Ph$_2$PC$_6$H$_4$NHMe)]BF$_4$ [Ir$^+$-7]: Yield, from [Ir(COD)$_2$]BF$_4$ (574 mg, 1.16 mmol) and the chelate ligand (338 mg, 1.16 mmol), 630 mg (80%) of **Ir$^+$-7** as a reddish brown solid. ^{1}H NMR (CDCl$_3$, ppm): δ = 1.6−2.5 (m, 8 H, diene CH$_2$), 2.85 (d, $^3J_{H,H}$ = 6.03 Hz, 3 H, CH$_3$), 3.1, 4.0, 5.2, 5.75 (all m, 1 H each, all diene CH), 7.2−8.0 (m, 14 H, C$_6$H$_5$ and C$_6$H$_4$); NH not observed. ^{13}C{^{1}H} NMR (CDCl$_3$, ppm): δ = 28.94, 31.13, 31.48, 34.77 (all s, all diene CH$_2$), 48.28 (s, CH$_3$), 61.92, 65.92 (both s, CH=CH *trans* N), 94.81, 98.99 (both d, $^2J_{P,C}$ = 13.08, 10.17 Hz, CH=CH *trans* P), 123.3−135.5 (C$_6$H$_5$ and C$_6$H$_4$), 157.83 (d, $^2J_{P,C}$ = 18.17 Hz, phenylene C-1). ^{31}P{^{1}H} NMR (CDCl$_3$, ppm): δ = 30.39. C$_{27}$H$_{30}$BF$_4$IrNP (678.6): calcd. C 47.79, H 4.46, N 2.06; found C 47.62, H 4.67, N 1.94.

[(COD)Ir(Ph$_2$PCH$_2$CMe$_2$NH$_2$)]BF$_4$ [Ir$^+$-8]: Yield, from [Ir(COD)$_2$]BF$_4$ (131 mg, 0.26 mmol) and the β-aminophosphane (68 mg, 0.26 mmol), 151 mg (88%) of **Ir$^+$-8** as a dark reddish brown solid. ^{1}H NMR (CDCl$_3$, ppm): δ = 1.40 (s, 6 H, CH$_3$), 1.7−2.4 (m, 8 H, diene CH$_2$), 2.51 (d, $^2J_{P,H}$ = 9.51 Hz, 2 H, PCH$_2$), 3.41 [s (br), 2 H, NH$_2$], 4.8, 5.3 (both m, 2 H each, both diene CH), 7.3−7.8 (m, 10 H, C$_6$H$_5$). ^{13}C{^{1}H} NMR (CDCl$_3$, ppm): δ = 28.88, 28.98, 29.28, 31.72 (all s, all diene CH$_2$), 32.31 (d, $^3J_{P,C}$ = 2.91 Hz, CH$_3$), 43.61 (d, $^1J_{P,C}$ = 30.52 Hz, PCH$_2$), 61.77 (d, $^2J_{P,C}$ = 5.09 Hz, NCH$_2$), 61.86 (s, CH=CH *trans* N), 93.73 (d, $^2J_{P,C}$ = 12.35 Hz, CH=CH *trans* P), 129.0−133.4 (C$_6$H$_5$). ^{31}P{^{1}H} NMR (CDCl$_3$, ppm): δ = 29.14. C$_{24}$H$_{32}$BF$_4$IrNP (644.6): calcd. C 44.73, H 5.00, N 2.17; found C 44.42, H 5.09, N 2.09.

[(COD)Ir{(1*S*,2*S*)-Ph$_2$PCH(Ph)CH(Me)NHCH$_2$Ph}]BF$_4$ [Ir$^+$-(*S*,*S*)-3]: Yield, from [Ir(COD)$_2$]BF$_4$ (235 mg, 0.48 mmol) and (*S*,*S*)-**3** (195 mg, 0.48 mmol), 314 mg (82%) of the complex as an orange solid containing the δ($S_{C\text{-}1}$,$S_{C\text{-}2}$,S_N) conformer (≈ 40%) together with the δ($S_{C\text{-}1}$,$S_{C\text{-}2}$,R_N) form (≈ 60%) as sterically locked ring conformers (isomeric distribution estimated from ^{1}H and ^{31}P{^{1}H} NMR). ^{1}H NMR ([D$_6$]acetone, ppm): δ[δ($S_{C\text{-}1}$,$S_{C\text{-}2}$,S_N)] = 1.32 (d, $^3J_{H,H}$ = 6.39 Hz, 3 H, CCH$_3$), 1.4−2.5 (m, 8 H, diene CH$_2$), 2.92 [m, 1 H, MeC(2)-H], 3.20, 3.39 (both m, 1 H each, both diene CH), 4.20, 4.22 (AB-dd, $^2J_{H,H}$ = 6.93 Hz, 2 H, CH$_2$), 4.58 [dd, $^2J_{P,H}$/$^3J_{H,H}$ = 6.39/3.63 Hz, 1 H, PhC(1)-H], 5.63 (m, 2 H, diene CH), 6.3 [s (br), 1 H, NH], 6.8−8.1 (m, 20 H, C$_6$H$_5$); δ[δ($S_{C\text{-}1}$,$S_{C\text{-}2}$,R_N)] = 1.19 (d, $^3J_{H,H}$ = 6.03 Hz, 3 H, CCH$_3$), 1.4−2.5 (m, 8 H, diene CH$_2$), 2.65 [m, 1 H, MeC(2)-H], 3.61, 3.67 (both m, 1 H each, both diene CH), 4.57 [dd, $^2J_{P,H}$/$^3J_{H,H}$ = 6.75/4.41 Hz, 1 H, PhC(1)-H], 4.71, 4.75 (AB-dd, $^2J_{H,H}$ = 6.48 Hz, 2 H, CH$_2$), 5.51 (m, 2 H, diene CH), 5.9 [s (br), 1 H, NH], 6.8−8.1 (m, 20 H, C$_6$H$_5$). ^{13}C{^{1}H} NMR ([D$_6$]acetone, ppm): δ[δ($S_{C\text{-}1}$,$S_{C\text{-}2}$,S_N)] = 17.37 (d, $^3J_{P,C}$ = 13.80 Hz, C*C*H$_3$), 26.1−37.6 (diene CH$_2$; partially obscured by solvent), 47.09 (d, $^1J_{P,C}$ = 24.71 Hz, PCH), 51.23 (s, CH$_2$), 64.40 (d, $^2J_{P,C}$ = 9.45 Hz, NCH), 64.52, 69.12 (both s, CH=CH *trans* N), 82.35, 94.20 (both d, $^2J_{P,C}$ = 16.72, 7.99 Hz, CH=CH *trans* P), 125.0−138.5 (C$_6$H$_5$); δ[δ($S_{C\text{-}1}$,$S_{C\text{-}2}$,R_N)] = 16.50 (d, $^3J_{P,C}$ = 13.80 Hz, C*C*H$_3$), 26.1−37.6 (diene CH$_2$; partially obscured by solvent), 53.45 (s, CH$_2$), 54.18 (d, $^1J_{P,C}$ = 25.43 Hz, PCH), 60.02 (d, $^2J_{P,C}$ = 9.45 Hz, NCH), 60.79, 65.65 (both s, CH=CH *trans* N), 92.89, 98.31 (both d, $^2J_{P,C}$ = 14.54, 8.72 Hz, CH=CH *trans* P), 125.0−138.5 (C$_6$H$_5$). ^{31}P{^{1}H} NMR ([D$_6$]acetone, ppm): δ = 39.97 [δ($S_{C\text{-}1}$,$S_{C\text{-}2}$,S_N) conformer], 46.65 [δ($S_{C\text{-}1}$,$S_{C\text{-}2}$,R_N) conformer]. C$_{36}$H$_{40}$BF$_4$IrNP (796.8): calcd. C 54.27, H 5.06, N 1.76; found C 54.52, H 5.21, N, 1.62.

[(COD)Ir{(1*S*,2*S*)-Ph$_2$PCH(Ph)CH(Me)NHCHMe$_2$}]BF$_4$ [Ir$^+$-(*S*,*S*)-4]: Yield, from [Ir(COD)$_2$]BF$_4$ (347 mg, 0.70 mmol) and (*S*,*S*)-**4** (300 mg, 0.76 mmol), 456 mg (87%) of the product as an orange solid composed of the two ring conformers δ($S_{C\text{-}1}$,$S_{C\text{-}2}$,S_N), ≈ 25%, and δ($S_{C\text{-}1}$,$S_{C\text{-}2}$,R_N), ≈ 75% (isomeric distribution estimated from the relative intensities of the ^{31}P resonances). ^{1}H NMR (CDCl$_3$, ppm): δ[δ($S_{C\text{-}1}$,$S_{C\text{-}2}$,R_N)] = 1.37 ["t", Σ|$^3J_{H,H}$ +$^5J_{H,H}$| = 13.14 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.50 (d, $^3J_{H,H}$ = 6.78 Hz, 3 H, CCH$_3$), 1.5−2.4 (m, 8 H, diene CH$_2$), 3.22 [m, 1 H, MeC(2)-H], 3.34 [s (br), 1 H, NH], 3.63 (sept, $^3J_{H,H}$ = 6.57 Hz, 1 H, C*H*(CH$_3$)$_2$], 4.29 [dd, $^2J_{P,H}$ = 12.17, $^3J_{H,H}$ = 7.04 Hz, 1 H, PhC(1)-H], 4.87, 5.15, 5.37, 5.75 (all m, 1 H each, all diene CH), 6.8−7.6 (m, 15 H, C$_6$H$_5$). ^{13}C{^{1}H} NMR (CDCl$_3$, ppm): δ[δ($S_{C\text{-}1}$,$S_{C\text{-}2}$,R_N)] = 19.83 (d, $^3J_{P,C}$ = 13.08 Hz, C*C*H$_3$), 21.98, 24.23 [both s, CH(*C*H$_3$)$_2$], 26.10, 27.18, 31.81, 36.78 (all s, all diene CH$_2$), 54.71 (d, $^1J_{P,C}$ = 25.43 Hz, PCH), 55.03 [s, *C*H(CH$_3$)$_2$], 56.31, 62.88 (both s, CH=CH *trans* N), 60.75 (d, $^2J_{P,C}$ = 7.99 Hz, NCH), 93.90, 97.87 (both d, $^2J_{P,C}$ = 13.80, 9.44 Hz, CH=CH *trans* P), 124.5−136.9 (C$_6$H$_5$); ^{1}H and ^{13}C{^{1}H} spectra of the minor δ[δ($S_{C\text{-}1}$,$S_{C\text{-}2}$,S_N)] conformer not assigned. ^{31}P{^{1}H} NMR ([D$_6$]acetone, ppm): δ = 40.79 [δ($S_{C\text{-}1}$,$S_{C\text{-}2}$,S_N) conformer], 45.44 [δ($S_{C\text{-}1}$,$S_{C\text{-}2}$,R_N) conformer]. C$_{32}$H$_{40}$BF$_4$IrNP (748.7): calcd. C 51.34, H 5.39, N 1.87; found C 51.83, H 5.77, N 1.73.

[(COD)Ir{(1*R*,2*S*)-Ph$_2$PCH(Ph)CH(Me)NHMe}]BF$_4$ [Ir$^+$-(*R*,*S*)-2]: Yield, from [Ir(COD)$_2$]BF$_4$ (206 mg, 0.42 mmol) and the *P*,*N* ligand (153 mg, 0.46 mmol), 243 mg (81%) of **Ir$^+$**-(*R*,*S*)-**2** as a dark red precipitate containing the λ($R_{C\text{-}1}$,$S_{C\text{-}2}$,R_N) conformer (94%) in addition to two further sterically locked isomers of unassigned stereochemistry. ^{1}H NMR ([D$_6$]acetone, ppm): δ[λ($R_{C\text{-}1}$,$S_{C\text{-}2}$,R_N)] = 1.14 (d, $^3J_{H,H}$ = 6.54 Hz, 3 H, CCH$_3$), 1.4−2.6 (m, 8 H, diene CH$_2$), 2.67 (d, $^3J_{H,H}$ = 5.85 Hz, 3 H, NCH$_3$), 2.88 [m, 1 H, MeC(2)-H], 3.11 (m, 1 H, diene CH), 3.22 [s (br), 1 H, NH], 3.71 (m, 1 H, diene CH), 4.31 [dd, $^2J_{P,H}$ = 14.26, $^3J_{H,H}$ = 4.20 Hz, 1 H, PhC(1)-H], 5.27, 5.61 (both m, 1 H each, both diene CH), 6.7−8.2 (m, 15 H, C$_6$H$_5$). ^{13}C{^{1}H} NMR ([D$_6$]acetone, ppm): δ[λ($R_{C\text{-}1}$,$S_{C\text{-}2}$,R_N)] = 15.17 (d, $^3J_{P,C}$ = 11.62 Hz, C*C*H$_3$), 27.4−36.6 (diene CH$_2$; partially obscured by solvent), 40.13 (s, NCH$_3$), 56.76 (d, $^1J_{P,C}$ = 29.79 Hz, PCH), 60.07, 62.61 (both s, CH=CH *trans* N), 66.49 (d, $^2J_{P,C}$ = 9.45 Hz, NCH), 93.59, 96.20 (both d, $^2J_{P,C}$ = 10.17, 13.08 Hz, CH=CH *trans* P), 126.0−136.4 (C$_6$H$_5$). ^{31}P{^{1}H} NMR ([D$_6$]acetone, ppm): δ = 38.10 [94%; λ($R_{C\text{-}1}$,$S_{C\text{-}2}$,R_N)], 38.01 (≈ 4%), 41.27 (≈ 2%); both unassigned. C$_{30}$H$_{36}$BF$_4$IrNP (760.6): calcd. C 50.00, H 5.04, N 1.94; found C 50.24, H 5.32, N 2.01.

(−)-[(COD)Ir{(1*R*,2*S*)-Ph$_2$PCH(Ph)CH(Me)NHCHMe$_2$}]BF$_4$ [Ir$^+$-(*R*,*S*)-4]: Yield, from [Ir(COD)$_2$]BF$_4$ (863 mg, 1.74 mmol) and the β-aminophosphane (634 mg, 1.75 mmol), 1.070 g (82%) of the

complex as an orange solid. ^{1}H NMR ([D$_6$]acetone, ppm): δ = 1.24, 1.32 [both d, $^3J_{H,H}$ = 6.78 Hz each, both 3 H, CH(CH_3)$_2$], 1.39 (d, $^3J_{H,H}$ = 6.57 Hz, 3 H, CCH$_3$), 1.7 (m, 1 H, diene CH$_2$), 1.9−2.3 (m, 5 H, diene CH$_2$), 2.3−2.6 (m, 2 H, diene CH$_2$), 3.12 [m, 1 H, MeC(2)-H], 3.4−3.6 (m, 2 H, diene CH), 3.65 [s (br), 1 H, NH], 4.51 [dd, $^2J_{P,H}$ = 12.99, $^3J_{H,H}$ = 4.95 Hz, 1 H, PhC(1)-H], 4.80 (sept, 1 H, CH(CH$_3$)$_2$], 5.41, 5.87 (both m, 1 H each, both diene CH), 6.8−7.9 (m, 15 H, C$_6$H$_5$). ^{13}C{^{1}H} NMR ([D$_6$]acetone, ppm): δ = 18.47 (d, $^3J_{P,C}$ = 7.99 Hz, CCH$_3$), 22.46, 23.71 [both s, CH(CH_3)$_2$], 26.37−35.90 (diene CH$_2$; partially obscured by solvent), 53.98 (d, $^1J_{P,C}$ = 27.61 Hz, PCH), 55.80 [s, CH(CH$_3$)$_2$], 61.67, 62.10 (both s, CH=CH *trans* N), 62.37 (d, $^2J_{P,C}$ = 7.99 Hz, NCH), 90.25, 93.91 (both d, $^2J_{P,C}$ = 14.54, 8.72 Hz, CH=CH *trans* P), 128.4−135.3 (C$_6$H$_5$). ^{31}P{^{1}H} NMR ([D$_6$]acetone, ppm): δ = 37.54. [α]$_{589}$ = −295 (*c* = 0.7, MeOH). C$_{32}$H$_{40}$BF$_4$IrNP (748.7): calcd. C 51.34, H 5.39, N 1.87; found C 51.65, H 5.30, N 2.00.

(−)-[(COD)Ir{(1*R*,2*S*)-Ph$_2$PCH(Ph)CH(Me)NMe$_2$}]BF$_4$ [Ir$^+$-(*R*,*S*)-5]: Yield, from [Ir(COD)$_2$]BF$_4$ (104 mg, 0.21 mmol) and the *P*,*N* ligand (80 mg, 0.23 mmol), 140 mg (83%) of **Ir$^+$-(*R*,*S*)-5** as an orange solid. ^{1}H NMR (CDCl$_3$, ppm): δ = 1.40 (d, $^3J_{H,H}$ = 6.60 Hz, 3 H, CCH$_3$), 1.5−2.4 (m, 8 H, diene CH$_2$), 2.90, 3.13 (both s, both NCH$_3$), 3.15 [m, 1 H, MeC(2)-H], 3.27, 3.37 (both m, 1 H each, both diene CH), 4.53 [dd, $^2J_{P,H}$ = 9.78, $^3J_{H,H}$ = 4.65 Hz, 1 H, PhC(1)-H], 4.71, 5.26 (both m, 1 H each, both diene CH), 6.8−7.6 (m, 15 H, C$_6$H$_5$). ^{13}C{^{1}H} NMR (CDCl$_3$, ppm): δ = 15.97 (d, $^3J_{P,C}$ = 6.54 Hz, CCH$_3$), 29.36, 29.69, 30.74, 32.63 (all s, all diene CH$_2$), 47.41 (d, $^1J_{P,C}$ = 23.25 Hz, PCH), 48.75, 50.15 (both s, both NCH$_3$), 59.00, 65.56 (both s, CH=CH *trans* N), 76.07 (d, $^2J_{P,C}$ = 7.26 Hz, NCH), 93.34, 97.34 (both d, $^2J_{P,C}$ = 12.35, 10.90 Hz, CH=CH *trans* P), 127.1−137.5 (C$_6$H$_5$). ^{31}P{^{1}H} NMR (CDCl$_3$, ppm): δ = 35.70. [α]$_{589}$ = −95.4, [α]$_{578}$ = −112 (both *c* = 0.3, MeOH). C$_{31}$H$_{38}$BF$_4$IrNP (734.7): calcd. C 50.68, H 5.21, N 1.91; found C 50.65, H 5.30, N 2.00.

[(COD)Ir(2-Ph$_2$PC$_6$H$_4$NMe)] (Ir-7a): A solution of **7** (318 mg, 1.09 mmol) in *n*-pentane (10 mL) was cooled to −70 °C and treated with *n*-butyllithium (0.44 mL, 1.10 mmol of a 2.5 M hexane solution). The resultant suspension of the monolithiated *P*,*N* ligand was allowed to warm to ambient temperature and then added to a stirred suspension of [{(COD)Ir(μ-Cl)}$_2$] (366 mg, 0.54 mmol) in benzene. Stirring for 3 h at ambient conditions caused the precipitation of lithium chloride which was separated by filtration. The filtrate was reduced in volume in vacuo to give 558 mg (87%) of a bright red solid retaining some residual solvent even after prolonged drying under a dynamic vacuum. ^{1}H NMR (CDCl$_3$, ppm): δ = 1.82, 2.18 (both m, 4 H each, both diene CH$_2$), 2.81 (m, 2 H, diene CH), 3.05 (s, 3 H, CH$_3$), 4.96 (m, 2 H, diene CH), 6.26, 6.53, 6.96, 7.08 (all m, 1 H each, all C$_6$H$_4$), 7.2−7.7 (m, 10 H, C$_6$H$_5$). ^{13}C{^{1}H} NMR (CDCl$_3$, ppm): δ = 30.47, 32.77 (both s, both diene CH$_2$), 39.24 (s, CH$_3$), 52.98 (s, CH=CH *trans* N), 91.62 (d, $^2J_{P,C}$ = 13.08 Hz, CH=CH *trans* P), 110.70, 114.29, (both d, $J_{P,C}$ = 12.82, 6.79 Hz, both phenylene C), 118.66 (d, $^1J_{P,C}$ = 54.34 Hz, phenylene C-2), 128.2−133.2 (C$_6$H$_5$ and 2 phenylene C), 171.84 (d, $^2J_{P,C}$ = 24.71 Hz, phenylene C-1). ^{31}P{^{1}H} NMR (C$_6$D$_6$, ppm): δ = 42.61. C$_{27}$H$_{29}$IrNP (590.7): calcd. C 54.90, H 4.95, N 2.73. C$_{27}$H$_{30}$IrNP·1/2C$_6$H$_6$ (629.8): calcd. C 57.21, H 5.12, N 2.22; found C 57.98, H 5.17, N 2.22.

[(COD)Ir(Ph$_2$PCH$_2$CMe$_2$NH)] (Ir-8a): The complex was prepared by analogy to the procedure outlined before employing ligand **8** (218 mg, 0.85 mmol), an equimolar portion of *n*BuLi in hexane, and [{(COD)Ir(μ-Cl)}$_2$](284 mg, 0.42 mmol); yield 385 mg (82%) of the amido complex as a dark red solid. ^{1}H NMR (C$_6$D$_6$, ppm): δ = 1.36 (s, 6 H, CH$_3$), 2.03, 2.24 (both m, 2 H each, both diene CH$_2$), 2.28 (d, $^2J_{P,C}$ = 10.23 Hz, 2 H, PCH$_2$), 2.40, 2.59 (both m, 2 H each, both diene CH$_2$), 2.99 (m, 2 H, diene CH), 4.5 [s (br), 1 H, NH], 4.90 (m, 2 H, diene CH), 7.15 (m, 6 H, C$_6$H$_5$), 7.74 (m, 4 H, C$_6$H$_5$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, ppm): δ = 31.14, 35.60 (both s, both diene CH$_2$), 36.09 (d, $^3J_{P,C}$ = 7.99 Hz, CH$_3$), 46.89 (d, $^1J_{P,C}$ = 31.24 Hz, PCH$_2$), 47.62 (s, CH=CH *trans* N), 67.30 (d, $^2J_{P,C}$ = 9.45 Hz, NCH$_2$), 84.33 (d, $^2J_{P,C}$ = 14.54 Hz, CH=CH *trans* P), 128.7−134.1 (C$_6$H$_5$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, ppm): δ = 49.85. C$_{24}$H$_{31}$IrNP (556.7): calcd. C 51.78, H 5.61, N 2.52; found C 52.55, H 5.97, N 2.12.

[(COD)Ir{(1*R*,2*S*)-Ph$_2$PCH(C$_6$H$_4$-*o*)CH(Me)NHCHMe$_2$] [Ir-(*R*,*S*)-4a]: A solution of potassium hydroxide (400 mg, 7.13 mmol) in methanol (10 mL) was combined with **Ir$^+$-(*R*,*S*)-4** (103 mg, 0.14 mmol) dissolved in MeOH (10 mL) to give an orange precipitate which was collected by filtration and washed with a few milliliters of methanol. Re-dissolution of the solid in hot acetone, followed by cooling to room temperature afforded the orthometalated complex as orange crystals which tenaciously retained some residual acetone solvent. ^{1}H NMR ([D$_6$]acetone, ppm): δ = 0.95, 1.08 [both d, $^3J_{H,H}$ = 6.24 each, both 3 H, CH(CH_3)$_2$], 1.20 (d, $^3J_{H,H}$ = 6.42 Hz, 3 H, CCH$_3$), 1.4−2.6 (m, 8 H, diene CH$_2$), 2.65 [m, 2 H, MeC(2)-H and CH(CH$_3$)$_2$], 3.95 [s (br), 1 H, NH], 4.05, 4.22 (both m, 1 H each, both diene CH), 4.39 [m, 1 H, PhC(1)-H], 5.21, 5.47 (both m, 1 H each, both diene CH), 6.81 (m, 2 H, C$_6$H$_4$), 7.08 (m, 1 H, C$_6$H$_4$), 7.26 (m, 3 H, C$_6$H$_5$), 7.29 (m, 1 H, C$_6$H$_4$), 7.44, 7.67 (both m, 7 H each, C$_6$H$_5$). ^{31}P{^{1}H} NMR ([D$_6$]acetone, ppm): δ = 44.99. C$_{32}$H$_{39}$IrNP (660.9): calcd. C 58.16, H 5.95, N 2.12. C$_{32}$H$_{39}$IrNP·C$_3$H$_6$O (718.9) calcd. C 58.47, H 6.31, N 1.95; found C 58.67, H 6.33, N 1.91.

***cis*-[(COD)IrH$_2$(Ph$_2$PCH$_2$CMe$_2$NH$_2$)]BF$_4$, (Ir$^+$-9):** A sample of **Ir$^+$-8** (20 mg) was dissolved in CD$_3$CN (2 mL), transferred into a high-pressure NMR tube and treated with 5 bar of H$_2$. ^{1}H NMR (CD$_3$CN, ppm): δ = −15.78 (d, *cis*-$^2J_{P,H}$ = 10.95 Hz, 1 H, IrH *trans* N), −12.60 (d, *cis*-$^2J_{P,H}$ = 15.91 Hz, 1 H, IrH *trans* >C=C<), 1.17 (s, 6 H, CH$_3$), 1.6−2.9 (m, 8 H, diene CH$_2$), 3.00 (d, $^2J_{P,H}$ = 9.33 Hz, 2 H, PCH$_2$), 3.89, 4.67 (both m, 1 H each, both diene CH), 4.93 [s (br), 2 H, NH$_2$], 5.58, 5.71 (both m, 1 H each, both diene CH), 7.1−8.2 (m, 10 H, C$_6$H$_5$). ^{31}P{^{1}H} NMR (CD$_3$CN, ppm): δ = 31.87.

***cis*-[(COD)IrH$_2$(Ph$_2$PCH$_2$CMe$_2$NH)] (Ir-9a):** A CD$_3$CN solution of **Ir-8a** was pressurized, in an NMR tube, to 5 bar of H$_2$. ^{1}H NMR (CD$_3$CN, ppm): δ = −18.13 (d, *cis*-$^2J_{P,H}$ = 8.79 Hz, 1 H, IrH *trans* N), −7.09 (d, *cis*-$^2J_{P,H}$ = 13.18 Hz, 1 H, IrH *trans* >C=C<), 1.13 (s, 6 H, CH$_3$), 1.5−2.7 (m, 10 H, diene CH$_2$ overlapping with PCH$_2$), 3.17 (m, 2 H, diene CH), 3.85 [s (br), 1 H, NH], 4.17 (m, 2 H, diene CH), 7.1−8.0 (m, 10 H, C$_6$H$_5$). ^{31}P{^{1}H} NMR (CD$_3$CN, ppm): δ = 17.68.

***cis*-[(COD)IrH$_2${(1*S*,2*S*)-Ph$_2$PCH(Ph)CH(Me)NH$_2$]BF$_4$ (Ir$^+$-10):** A sample of **Ir$^+$-(*S*,*S*)-1** (≈ 20 mg) in [D$_8$]THF (2 mL) was exposed to 1 bar of H$_2$ and immediately characterized by NMR spectroscopy. ^{1}H NMR ([D$_8$]THF, ppm): δ = −16.31 (d, *cis*-$^2J_{P,H}$ = 11.52 Hz, 1 H, IrH *trans* N), −12.44 (d, *cis*-$^2J_{P,H}$ = 14.82 Hz, 1 H, IrH *trans* >C=C<), 0.89 (d, $^3J_{H,H}$ = 6.03 Hz, 3 H, CH$_3$), 1.5−2.9 (m, 8 H, diene CH$_2$), 2.74 [m, 1 H, MeC(2)-H], 4.01 [dd, $^2J_{P,H}$ = 12.63, $^3J_{H,H}$ = 4.95 Hz, 1 H, PhC(1)-H], 4.16, 4.56, 4.77, 4.96, 5.27, 5.45 (all m, 1 H each, diene CH overlapping with NH$_2$), 6.9−7.7 (m, 15 H, C$_6$H$_5$). ^{31}P{^{1}H} NMR ([D$_8$]THF, ppm): δ = 46.03.

***cis*,*cis*-[(MeCN)$_2$IrH$_2${(1*R*,2*S*)-Ph$_2$PCH(Ph)CH(Me)NHMe]BF$_4$ (Ir$^+$-11):** A solution of **Ir$^+$-(*R*,*S*)-2** (90 mg, 0.12 mmol) in acetonitrile (2 mL) was stirred under 25 bar of H$_2$ for 2 h in an autoclave. The solid residue remaining after removal of all volatiles in vacuo

was re-dissolved in CD_2Cl_2 and immediately characterized by NMR spectroscopy. ^1H NMR (CD_2Cl_2, ppm): δ = −21.20, −21.14 (*AB*X m, *cis*-$^2J_{P,H}$ = 17.22, 22.11, *cis*-$^2J_{H,H}$ = 7.13 Hz, 1 H each, IrH_2), 1.09 (d, $^3J_{H,H}$ = 6.06 Hz, 3 H, $CHCH_3$), 1.73, 2.37 (both s, 3 H each, both CH_3CN), 2.87 (d, $^3J_{H,H}$ = 6.06 Hz, 3 H, NCH_3), 3.19 [m, 1 H, MeC(2)-H], 3.42 [s (br), 1 H, NH)], 4.01 [dd, $^2J_{P,H}$ = 13.71, $^3J_{H,H}$ = 4.38 Hz, 1 H, PhC(1)-H], 6.9−7.7 (m, 15 H, C_6H_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, ppm): δ = 1.70, 2.97 (both s, CH_3CN), 15.27 (d, $^3J_{P,C}$ = 10.90 Hz, $CHCH_3$), 37.04 (s, NCH_3), 51.62, (d, $^1J_{P,C}$ = 34.15 Hz, PCH), 64.40 (d, $^2J_{P,C}$ = 5.81 Hz, NCH), 115.99 [s (br), CH_3CN *trans* H], 119.63 (d, $^3J_{P,C}$ = 18.90 Hz, CH_3CN *trans* P), 123.0−134.4 (C_6H_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, ppm): δ = 32.27.

X-ray Structure Determinations: Single crystals of **Ir**$^+$-(*S*,*S*)-**3**·2THF (size 0.33 × 0.10 × 0.08 mm), **Ir**$^+$-(*R*,*S*)-**2**·THF (size 0.38 × 0.33 × 0.28 mm), and **Ir**-(*R*,*S*)-**4a** (size 0.50 × 0.45 × 0.23 mm) were grown from THF/*n*-pentane [**Ir**$^+$-(*S*,*S*)-**3**·2THF and **Ir**$^+$-(*R*,*S*)-**2**·THF] or acetone [**Ir**-(*R*,*S*)-**4a**]. Diffraction measurements were made at −90±2 °C [**Ir**$^+$-(*R*,*S*)-**2**·THF] and at −80±2 °C [**Ir**$^+$-(*S*,*S*)-**3**·2THF and **Ir**-(*R*,*S*)-**4a**] on an Enraf−Nonius CAD-4 MACH 3 diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å); orientation matrices and unit cell parameters from the setting angles of 25 centered medium-angle reflections; collection of the diffraction intensities by ω scans (data corrected for absorption either empirically by ψ scans[38] [**Ir**$^+$-(*S*,*S*)-**3**·2THF: T_{min} = 0.406, T_{max} = 0.777; **Ir**$^+$-(*R*,*S*)-**2**·THF: T_{min} = 0.217, T_{max} = 0.316] or by refined absorption methods[39] [**Ir**-(*R*,*S*)-**4a**: T_{min} = 0.087, T_{max} = 0.318]. The structures were solved by direct methods and subsequently refined by full-matrix least-squares procedures on F^2 allowing for anisotropic thermal motion of all non-hydrogen atoms employing the WinGX package[40a] with the relevant programs (SIR-97,[41] SHELXL-97,[42] ORTEP-3[40b]) implemented therein. **Ir**$^+$-(*S*,*S*)-**3**·2THF: $C_{36}H_{40}IrNP$, BF_4, $2(C_4H_8O)$ (940.9); monoclinic, $P2_1$, a = 14.8593(15), b = 9.215(2), c = 15.108(2) Å, β = 93.506(9)°, V = 2064.8(5) Å^3, Z = 2, $d_{calcd.}$ = 1.513 g·cm^{-3}, μ(Mo-K_α) = 3.327 mm^{-1}; 2.59° ≤ Θ ≤ 22.48°, 6018 reflections collected (−15 ≤ h ≤ +15, −9 ≤ k ≤ +9, −16 ≤ l ≤ +16, including Friedel pairs), 5363 unique; wR = 0.1824 for all data and 488 parameters, R = 0.0835 for 3495 structure factors F_o > 4σ(F_o), absolute structure parameter[43] x = 0.00(3). **Ir**$^+$-(*R*,*S*)-**2**·THF: $C_{30}H_{36}IrNP$, BF_4, C_4H_8O (792.7); orthorhombic, $P2_12_12_1$, a = 9.268(2), b = 12.889(1), c = 27.147(6) Å, V = 3243(1) Å^3, Z = 4, $d_{calcd.}$ = 1.642 g·cm^{-3}, μ(Mo-K_α) = 4.218 mm^{-1}; 2.18° ≤ Θ ≤ 25.17°, 6122 reflections collected (−11 ≤ h ≤ +11, −15 ≤ k ≤ +15, −25 ≤ l ≤ +25, including Friedel pairs), 5418 unique; wR = 0.1328 for all data and 390 parameters, R = 0.0633 for 3963 structure factors F_o > 4σ(F_o), x = 0.02(2). **Ir**-(*R*,*S*)-**4a**: $C_{32}H_{39}IrNP$ (660.8); monoclinic, $P2_1$, a = 9.097(2), b = 19.312(4), c = 15.709(6) Å, β = 98.99(2)°, V = 2726(1) Å^3, Z = 4, $d_{calcd.}$ = 1.610 g·cm^{-3}, μ(Mo-K_α) = 4.978 mm^{-1}; 2.11° ≤ Θ ≤ 26.56°, 12154 reflections collected (−11 ≤ h ≤ +11, −24 ≤ k ≤ +24, −19 ≤ l ≤ +19, including Friedel pairs), 11382 unique; wR = 0.0734 for all data and 637 parameters, R = 0.0321 for 10345 structure factors F_o > 4σ(F_o), x = −0.012(6). CCDC-215609 [**Ir**$^+$-(*S*,*S*)-**3**·2THF], CCDC-215607 [**Ir**$^+$-(*R*,*S*)-**2**·THF], and CCDC-215608 [**Ir**-(*R*,*S*)-**4a**] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

General Procedure for Catalytic >C=O Hydrogenation: A 10 mL capacity Schlenk tube equipped with a small magnetic stirring bar was charged with the catalyst complex dissolved in methanol (typically 0.02 mmol in 3.0 mL). The required equivalent of activating nitrogen or alkaline base (cf. Tables 2−4) and 2.0 mmol of acetophenone were added, the mixture was stirred for 10 min at ambient conditions, and the tube was inserted into an argon-filled stainless steel autoclave. The autoclave was sealed, pressurized and vented several times with H_2 (Messer-Griesheim; 99.999%), and subsequently pressurized (usually to 10−25 bar) and maintained with stirring at 25 or 50 °C. At the end of the reaction, the pressure was released, the solvent removed in vacuo, and the residue diluted with *n*-pentane to precipitate the catalyst as a red oil. The pentane solution was decanted and chromatographed on a silica gel column using diethyl ether/*n*-pentane (1:1) as the eluent. Volatiles were distilled off and the mixture of products was analyzed by ^1H NMR spectroscopy. Conversions and product compositions were determined on the basis of the integrations of the $PhC(O)CH_3$ and $PhCH(OH)CH_3$ signals. Enantiomeric excesses were measured either by HPLC using a Daicel Chiralcel OD column or by polarimetry as detailed elsewhere.[7a] Optical rotations were referenced to the following $[\alpha]_D$ values of the pure enantiomers taken from the literature: (*R*)-1-phenylethanol, +48.6 (*c* = 1, CH_2Cl_2);[44a] (*S*)-1-phenylpropanol, −47.7 (*c* = 6.8, Et_2O);[44b] (*S*)-2-methyl-1-phenylpropanol, +5.3 (*c* = 1.1, EtOH);[44c] (*S*)-1-indanol, +31.7 (*c* = 1, $CHCl_3$);[44d] (*S*)-4-chloro-1-phenylbutanol, −33 (*c* = 1, $CHCl_3$).[44e]

Representative Catalytic >C=O Hydrogenations and H_2/D^+ Exchange Experiments in CH_3OD: (a) A solution of of **Ir**$^+$-(*R*,*R*)-**2** (9.5 mg, 0.013 mmol), (−)-sparteine (14 μL, 0.065 mmol) and benzophenone (150 mg, 1.25 mmol) in CH_3OD (3 mL) was kept, in an autoclave, under 10 bar of H_2 at 50 °C for 10 h. The residue remaining after removal of the solvent was analyzed by NMR spectroscopy. ^1H NMR (CD_2Cl_2, ppm): δ = 5.76 (s with half intensity relative to 10 phenyl H, Ph_2CHOD), 7.2−7.5 (m, 10 H, C_6H_5). ^2H NMR (CH_2Cl_2, ppm): δ = 2.42 (br., OD), 5.78 (s, Ph_2CDOD). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, ppm): δ = 76.52 (1:1:1 t, $^1J_{C,D}$ = 22.16 Hz, Ph_2CDOD), 76.93 (s, Ph_2CHOD). (b) The solution of catalyst complex, auxiliary base, and ketone in [D_1]methanol was prepared as before, transferred into a high-pressure NMR tube, exposed to 10 bar of H_2 at ambient conditions overnight, and then examined by ^1H NMR (ppm): δ = 4.37 (1:1:1 t, $^1J_{H,D}$ = 42.63 Hz, *H*D), 4.42 (s, H_2), 4.46 (s, OH), 5.92 (s, ≈ 0.6 H relative to 10 phenyl H, CH), 7.2−7.5 (m, 10 H, C_6H_5). (c) Experiment (b) was repeated in the absence of the base and the ketone. ^1H NMR: δ = 4.39 (1:1:1 t, $^1J_{H,D}$ = 42.63 Hz, *H*D), 4.42 (s, H_2), 4.46 (s with increasing intensity, OH).

General Procedure for H_2/D_2 Exchange Experiments: A high pressure NMR tube was charged with a solution of ≈0.01 mmol of any [(COD)Ir(P∩NHR]BF_4 complex in CD_3CN or CH_3CN. The solution was exposed to 10 bar of a 1:1 H_2/D_2 mixture and immediately analyzed by NMR spectroscopy. ^1H NMR (CD_3CN, ppm): δ = 4.37 (1:1:1 t, $^1J_{H,D}$ = 42.63 Hz, *H*D), 4.41 (s, H_2). ^2H NMR (CH_3CN, ppm): δ = 4.33 (s, D_2), 4.37 (d, $^1J_{H,D}$ = 42.5 Hz, H*D*).

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[33] In the reviewing process, an alternate mechanism based on the intermediacy of [Ir(P∩NR)] and [IrH(P∩NHR)] as spectroscopically undetected but kinetically relevant transients was proposed for isotopic scrambling and >C=O reduction: [Ir(P∩NR)] + H_2 = [IrH(P∩NHR)]; [IrH(P∩NHR] + H_2 = [IrH_3(P∩NHR)]; [IrH_3(P∩NHR)] + MeOD = [IrH_3(P∩NDR)] + MeOH; [IrH_3(P∩NDR)] = [IrH(P∩NDR)] + H_2; [IrH(P∩NDR)] = [Ir(P∩NR)] + HD etc.; [IrH_3(P∩NHR)] + R_2CO = [IrH_2(P∩NR)] + R_2CHOH. This sequence does not, however, fit the experimental evidence in that it involves IrH_3 intermediates which should be quite stable and inert but were never met in the chemistry described in this communication. Furthermore, in order to make the suggested >C=O reduction step catalytic, the resulting amido dihydrides [IrH_2(P∩NR)] must regenerate the postulated [IrH_3(P∩NHR)] amino trihydrides either by hydrogen transfer

from the solvent or by H_2 addition across the Ir−N bond. Again, no such chemistry was observed for amido dihydro complex **Ir-9a** reacting with MeOH under H_2 to reversibly produce $[IrH_2(P\cap NHR)]^+$ (**Ir**$^+$**-9**; Scheme 9) rather than H_2CO and/or $[IrH_3(P\cap NHR)]$.

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