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Hybrid P–N phosphines as participative ligands in iridium hydrogenation catalysts *

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Abstract

Iridium complexes formed *in situ* from $[Ir(cod)(OMe)]_2$ and a potentially bidentate ligand such as $P(o\text{-}C_6H_4NH_2)\ Ph_2$ (= P–NH$_2$) or $P(o\text{-}C_6H_4NMe_2)Ph_2$ (= P–NMe$_2$) catalyze the chemoselective hydrogenation of benzylideneacetone. In the presence of $HIr(P\text{-}NH)_2(P\text{-}NH_2)$ the substituted allylic alcohol is obtained in 92% yield, whereas in the presence of $H_2Ir(P\text{-}NMeCH_2)(P\text{-}NMe_2)$ there is a much poorer selectivity. The features of the catalysis are discussed in relation to the nature of the iridium species formed; steric factors appear to play a crucial role in determining the selectivity. Monitoring of the progress of the reaction catalyzed by the Ir/P–NH$_2$ system by NMR spectroscopy has revealed the sequence of reactions, including ready intramolecular N–H activation. The crystal structure of Ir-$(P\text{-}NH_2)_3$ has been determined.

Introduction

Potentially bidentate phosphorous–nitrogen ligands have been studied by several research groups [1–12]. Such ligands are expected to be useful in homogeneous catalysis, since the nitrogen can usually be displaced by π-acceptor ligands such as CO and olefins, thus making a coordination site readily available, for example for coordination of the substrate. Moreover, the use of ligands containing an NH group has particular potential for the catalytic amination of olefins to give amides. Some attempts have been made to carry out insertion of a transition metal into an N–H bond, which is a key step in such catalytic reactions, but only a few have been successful. Roundhill et al. reported on the oxidative addition to an iridium(I) centre of the N–H bond of the ligands $P(o\text{-}C_6H_4NHCOMe)Ph_2$ [13] and $P(o\text{-}C_6H_4NHR)Ph_2$ ($R = CH_2Ph$, Et) [14]. Such a reaction has not been observed with the analogous Pd and Pt complexes [13,15]. Recently the first example of catalytic amination of olefins involving N–H activation was reported by Milstein et al. [16], who employed an iridium(I) complex as catalyst.

During our studies of the use of iridium–phosphine catalysts for the chemoselective hydrogenation of conjugated unsaturated carbonyl compounds, we obtained

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* Dedicated to the memory of Professor Piero Pino.

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evidence for some links between the steric properties of the catalyst and the observed selectivity. Complexes possessing two monodentate phosphines (or one bidentate phosphine) in the coordination sphere of iridium promote the reduction of the C=C bond of the substrate. In contrast, trisphosphino complexes of the type H_3IrP_3 (P = $PEtPh_2$, PEt_2Ph, $PMePh_2$) catalyze the selective reduction of the carbonyl group of α,β-unsaturated ketones [17,18]. This behaviour is also observed with complexes of the type $[H_2Ir(P-P)_2]^+$ if one of the coordinated diphosphines can behave as a monodentate ligand [19], which is the case when a large chelate ring is formed on coordination to the metal. These latter systems however display a rather low catalytic activity, and this is probably related to the difficulty of dissociation of only one phosphorus atom of the chelated ligand from the metal. The selectivity observed with trisphosphino complexes appears to be related to steric control of the coordination mode of the substrate, which can only coordinate to the metal via the less sterically demanding carbonyl group. We expected that the use of potentially bidentate P–N ligands might lead to steric control (and therefore to a chemoselectivity) similar to that observed with diphosphines, but at the same time such hybrid ligands were likely to undergo easier dissociation of the nitrogen function from the metal, leading to higher catalytic activity.

We report below the results of a study of chemoselective hydrogenation of α,β-unsaturated ketones catalyzed by iridium complexes containing the ligands $P(o\text{-}C_6H_4NH_2)Ph_2$ (= $P-NH_2$) and $P(o\text{-}C_6H_4NMe_2)Ph_2$ (= $P-NMe_2$). The selectivity of the reaction is discussed in relation to the nature of the iridium species formed in solution.

Experimental section

General

All the reactions were performed under argon by Schlenk-tube techniques. The complex $[Ir(cod)(OMe)]_2$ was prepared as described previously [18]. The ligands $P(o\text{-}C_6H_4NH_2)Ph_2$ (= $P-NH_2$) [20] and $P(o\text{-}C_6H_4NMe_2)Ph_2$ (= $P-NMe_2$) [21] were prepared by published methods, except for one modification, namely that in the synthesis of $P-NH_2$ the reduction of the phosphinoxide was carried out by use of $LiAlH_4$ in the place of methylpolysiloxane, thereby giving better yields. Benzylideneacetone was recrystallized three times before use. Toluene was distilled over sodium under an inert atmosphere.

Infrared spectra were recorded on a Perkin–Elmer 983 B spectrophotometer interfaced to a Perkin–Elmer 3600 data station. The ^1H and ^{31}P NMR spectra were recorded on a Bruker WP80 or on a Bruker WM250 instrument; the ^1H chemical shifts are reported relative to external tetramethylsilane, and ^{31}P chemical shifts relative to external H_3PO_4 85%, with downfield shifts positive.

Conductivities were measured with a Beckman RC-18A conductivity bridge. The conductivity data were obtained for sample concentrations of ca. 1×10^{-3} *M* in nitrobenzene solutions.

Preparation of $HIr(P-NH)_2(P-NH_2)$ (IV)

A solution of $[Ir(cod)(OMe)]_2$ (66 mg, 0.1 mmol) in 3 ml of benzene was treated under argon with an excess of $P-NH_2$ (277 mg, 1.0 mmol). The bright orange solution obtained was kept at room temperature under a flow of hydrogen, for 2 h and the product was then precipitated by addition of 6 ml of hexane. The yellow solid was washed with ether and hexane and dried under vacuum. Yield 76%. IR (Nujol mull): ν(N–H) 3410, 3386, 3360 and 3315 cm^{-1}; ν(Ir–H) 2092 cm^{-1}. ^1H NMR (250.13 MHz, C_6D_6): δ 8.2–6.0 (m, 42 H, Ar), 3.82 (bs, 2 H, P–NH_2), 3.45 (s, 1 H, P–NH), 3.14 (s, 1 H, P–NH), −15.15 (doublet of pseudotriplets, 1 H, Ir–H, J(P–H) 10.8 and 20.4 Hz). ^{31}P NMR (101.26 MHz, C_6D_6) AMX spin system: δ_A +24.6 dd, δ_M + 7.2 pseudotriplet, δ_X −3.8 dd, J(A–M) 18 Hz, J(M–X) 21 Hz, J(A–X) 365 Hz. Λ_M 4.5 Ω^{-1} cm^2 mol^{-1} in nitrobenzene.

Catalytic experiments

Catalytic reactions were performed in a stainless steel autoclave with a Teflon lining, as follows. The appropriate amount of the phosphine was added under argon to a solution of $[Ir(cod)(OMe)]_2$ (6.6 mg, 0.01 mmol) in 50 ml toluene. Hydrogen was then bubbled into the resulting solution for 15 min, and after addition of the substrate the mixture was transferred into the autoclave, which was charged with 20 atm H_2 and then heated to 100 °C.

The catalytic reactions were monitored by glc on a Perkin–Elmer Sigma 3B chromatograph fitted with a Supelcowax 10 wide-bore capillary column (30 m × 0.75 mm i.d.).

Structure determination of V

Small crystals of V suitable for the X-ray diffraction study were obtained by slow diffusion of n-pentane into a solution of IV in CH_2Cl_2 at room temperature. A plate of 0.05 × 0.05 × 0.2 mm was used for intensity collection on an Enraf–Nonius CAD-4 four-circle diffractometer. Cell constants were obtained by least squares fit of the 2θ values of 20 reflections ($10° \leqslant \theta \leqslant 16°$) by use of the centering routines

Table 1

Crystallographic data collection for $Ir(P–NH)_3$

Formula	$C_{54}H_{45}IrN_3P_3$
Mol. wt.	1021.0
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	14.363(2)
b (Å)	14.575(3)
c (Å)	22.627(3)
β (°)	105.13(1)
V (Å^3)	4572.6(9)
ρ (calc., g cm^{-3})	1.45
μ (cm^{-1})	15.63
Radiation	Mo-K_α (λ 0.71069 Å)
2θ range (°)	5.0: 48.0
Scan type	$\omega/2\theta$
Nr. of independent data	1531
R (obs. reflections)	0.096
R_w	0.125

Table 2

Positional parameters and their estimated standard deviations

Atom	x	y	z	B (Å^2) [a]	Atom	x	y	z	B (Å^2)
Ir	−0.0638(2)	0.1052(2)	0.0892(1)	1.53(3)	C25	−0.067(4)	−0.038(4)	0.220(2)	2(1) *
P1	0.053(1)	0.188(1)	0.1615(6)	2.1(3) *	C26	−0.100(4)	−0.041(4)	0.274(3)	3(1) *
P2	−0.137(1)	0.020(1)	0.1510(7)	2.4(3) *	C27	−0.050(4)	−0.086(4)	0.323(3)	4(1) *
P3	−0.181(1)	0.214(1)	0.0476(6)	1.8(3) *	C28	0.042(4)	−0.152(4)	0.324(3)	4(1) *
N1	0.044(4)	0.005(4)	0.101(2)	5(1) *	C29	0.071(5)	−0.135(5)	0.269(3)	5(2) *
N2	−0.136(3)	0.008(3)	0.025(2)	1.3(8) *	C30	0.016(4)	−0.098(6)	0.218(3)	6(2) *
N3	−0.011(3)	0.152(3)	0.017(2)	3(1) *	C31	−0.236(4)	0.071(4)	0.178(2)	3(1) *
C1	0.040(3)	0.196(4)	0.239(2)	2(1) *	C32	−0.336(5)	0.034(5)	0.152(3)	4(2) *
C2	0.067(4)	0.126(4)	0.280(2)	4(1) *	C33	−0.410(4)	0.070(4)	0.173(3)	4(1) *
C3	0.049(4)	0.138(5)	0.338(3)	5(2) *	C34	−0.376(4)	0.146(5)	0.219(3)	4(2) *
C4	0.010(4)	0.220(4)	0.348(2)	2(1) *	C35	−0.291(4)	0.180(5)	0.241(3)	4(2) *
C5	−0.014(4)	0.293(4)	0.315(3)	3(1) *	C36	−0.216(5)	0.142(6)	0.222(3)	7(2) *
C6	−0.001(4)	0.277(4)	0.253(2)	2(1) *	C37	−0.313(4)	0.176(4)	0.028(3)	3(1) *
C7	0.151(3)	0.120(4)	0.164(2)	1(1) *	C38	−0.339(4)	0.119(5)	−0.013(3)	4(1) *
C8	0.260(5)	0.126(5)	0.202(3)	6(2) *	C39	−0.440(3)	0.087(3)	−0.031(2)	0.8(9) *
C9	0.340(4)	0.079(5)	0.198(3)	5(2) *	C40	−0.509(4)	0.136(4)	−0.009(3)	3(1) *
C10	0.317(4)	−0.010(4)	0.179(2)	3(1) *	C41	−0.473(3)	0.206(3)	0.030(2)	1(1) *
C11	0.222(5)	−0.027(5)	0.140(3)	5(2) *	C42	−0.377(5)	0.243(5)	0.048(3)	5(2) *
C12	0.136(4)	0.035(4)	0.133(3)	3(1) *	C43	−0.154(3)	0.230(3)	−0.020(2)	1(1) *
C13	0.092(3)	0.299(4)	0.142(2)	2(1) *	C44	−0.062(3)	0.203(3)	−0.026(2)	0.7(9) *
C14	0.146(4)	0.350(5)	0.189(3)	4(2) *	C45	−0.037(4)	0.228(4)	−0.077(3)	4(1) *
C15	0.199(6)	0.435(6)	0.182(4)	8(2) *	C46	−0.094(4)	0.267(5)	−0.124(3)	4(2) *
C16	0.168(8)	0.464(8)	0.115(5)	13(4) *	C47	−0.195(3)	0.289(3)	−0.130(2)	1(1) *
C17	0.122(6)	0.422(6)	0.068(4)	9(2) *	C48	−0.219(4)	0.271(5)	−0.077(3)	4(2) *
C18	0.067(4)	0.326(5)	0.084(3)	4(2) *	C49	0.331(5)	0.162(5)	0.581(3)	6(2) *
C19	−0.189(4)	−0.080(5)	0.101(3)	5(2) *	C50	0.334(7)	0.09(1)	0.549(5)	14(3) *
C20	−0.181(3)	−0.061(3)	0.041(2)	2(1) *	C51	0.336(7)	0.007(8)	0.575(5)	12(3) *
C21	−0.218(3)	−0.128(4)	−0.002(2)	2(1) *	C52	0.338(7)	−0.004(8)	0.634(4)	10(3) *
C22	−0.247(5)	−0.216(5)	0.019(3)	6(2) *	C53	0.317(4)	0.068(4)	0.667(3)	4(2) *
C23	−0.257(4)	−0.224(4)	0.083(3)	4(1) *	C54	0.313(5)	0.169(6)	0.643(3)	6(2) *
C24	−0.226(3)	−0.156(4)	0.123(2)	2(1) *					

[a] Starred atoms were refined isotropically. Ir is given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)\times[a2\times B(1,1)+b2\times B(2,2)+c2\times B(3,3)+ab(\cos \text{gamma})\times B(1,2)+ac(\cos \text{beta})\times B(1,3)+bc(\cos \text{alpha})\times B(2,3)]$

of the diffractometer. Crystallographic data and details of the data collection are given in Table 1.

Three standard reflections, measured every 300 min, were used to check the stability of the crystal and no significant variations were detected. The orientation of the crystal was checked every 100 reflections. Intensity data were corrected for Lorentz and polarization effects. No correction for absorption was made in view of the small size of the crystal.

The intensities of 1531 independent reflections with $I > 3\sigma(I)$ were used in the solution and refinement of the structure. All calculations were carried out by use of the Enraf–Nonius SDP library [22]. Neutral atom scattering factors were those given by Cromer and Waber [23]. The structure was solved and refined by conventional three-dimensional Patterson, Fourier and full-matrix least-squares methods. The positions of the hydrogen atoms were calculated by the "Hydro" program of SDP.

Owing to the low number of the experimental intensities with $I > 3\sigma(I)$, only the Ir atom was refined anisotropically, and the other non-hydrogen atoms were refined with isotropic thermal parameters. During the last stage of the refinement, the hydrogen atoms were introduced at their calculated positions, with B 7.0 Å^2, but not refined. The final R value was 0.096 using unit weights. The final atomic coordinates for non-hydrogen atoms are listed in Table 2. A complete table of bond lengths and angles and lists of observed and calculated structure factors are available from the authors.

Results and discussion

The catalytic systems initially employed were prepared from $[Ir(cod)(OMe)]_2$ and an excess of the ligand by the procedure previously used to prepare the catalysts with mono- and di-phosphines. In Table 3 are reported the results in the hydrogenation of benzylideneacetone (PhCH=CHCOMe): the catalytic behaviour of the system employing the P–N ligands is compared with that of the system with a P–O type ligand (P–O = $P(o\text{-}C_6H_4OMe)_3$). When the latter is used, only C=C bond reduction takes place, to give the saturated ketone plus a small amount of the saturated alcohol. The same result is obtained when $P\text{–}NH_2$ is used as a [P]/[Ir] ratio of up to 2. However, when this ligand is employed in greater excess ([P]/[Ir] >

Table 3

Hydrogenation of PhCH=CHCOMe catalyzed by $[Ir(cod)(OMe)]_2 + P\text{–}X$ [a]

P–X	P/Ir	% conversion (hours)	% saturated ketone	% saturated alcohol	% unsaturated alcohol
$P\text{–}NH_2$	1	82 (7)	69	8	5
	2	95 (7)	67	21	7
	3	70 (7)	30	5	35
	5	95 (7)	8	11	76
$P\text{–}NMe_2$	5	93 (46)	21	23	49
P–OMe [b]	10	92 (5)	72	18	2

[a] Reaction conditions: $[Ir] = 4 \times 10^{-4}$ M; [sub]/[Ir] = 500; $P(H_2) = 20$ atm; $T = 100\,°C$; solvent: toluene. [b] P–OMe = $P(o\text{-}C_6H_4OMe)_3$.

3), the carbonyl group of the substrate is selectively hydrogenated, to give the corresponding allylic alcohol. Different behaviour is exhibited by the catalytic system involving P–NMe$_2$, which gives a mixture of the three reduction products, with a selectivity towards the unsaturated alcohol of about 50%.

Another marked difference between the two Ir/P–N systems appears in the reaction rate. The catalytic activity of the system involving P–NH$_2$ is at least one order of magnitude greater than that of the catalysts with bidentate phosphines; in contrast, the catalyst with P–NMe$_2$ is markedly less active.

Overall, the results suggest that with the ligands of the P–N type different iridium species are formed under the catalytic conditions. A more detailed study of the chemistry of these Ir/P–N systems was thus in order to allow rationalization of the catalytic results obtained.

NMR studies on the system [Ir(cod)(OMe)]$_2$ + P–NMe$_2$ ([P]/[Ir] = 2) revealed that under conditions similar to those employed in the hydrogenation reaction, the metallated species $H_2\overline{Ir(P\text{–}NMeCH_2})(P\text{–}NMe_2)$ (I) is formed. This complex had previously been isolated under different experimental conditions, and characterized by both NMR spectroscopy and an X-ray diffraction study [17]. When this metallated species is used as catalyst precursor the rate and the selectivity of the hydrogenation reaction are quite similar to those observed with the in situ system Ir/P–NMe$_2$, indicating that I is indeed formed under the catalytic conditions.

The situation is more complicated when the Ir/P–NH$_2$ system is used. When [Ir(cod)(OMe)]$_2$ is treated with P–NH$_2$ in toluene (or benzene) under an inert atmosphere a new species is readily formed, and this has been identified as Ir(cod)(P–NH) (II), in which the phosphine acts as a bidentate ligand (^{1}H NMR (C_6D_6) δ 7.8–6.4 (m, 14 H, Ar), 5.30 (s, 1 H, P–N*H*), 4.5 (bs, 2 H, CH=CH), 3.47 (s, 2 H, CH=CH), 2.2 (bm, 4 H, CH$_2$), 1.8 (bm, 4 H, CH$_2$); ^{31}P NMR (C_6D_6) δ +24.0 s [24*]). The reaction occurs by elimination of MeOH from the initially formed Ir(OMe)(cod)(P–NH$_2$); the presence of free methanol in the reaction mixture was confirmed by the NMR spectrum. If a benzene solution of II is treated with H$_2$ in the presence of an excess of ligand ($[P]_{tot}/[Ir] = 5$), cyclooctadiene is hydrogenated and leaves the coordination sphere of iridium, which is approached by a second phosphine to give species III. This complex has one hydride and two phosphines in the coordination sphere, as shown by spectroscopic data (^{1}H NMR (C_6D_6) δ −19.3 t, *J*(P–H) 15.5 Hz; ^{31}P NMR (C_6D_6) δ +32.3 s): we suggest that it is the Ir(I) species HIr(P–NH$_2$)$_2$ (III) (see Scheme 1), formed by oxidative addition of H$_2$ and subsequent migration of a hydride on the coordinated amido group. The identification of III is complicated by the fact that as soon as species II is transformed into species III the iridium centre readily picks up one more phosphine to give a new trisphosphino species IV. The latter complex, which appears to be the stable species under a hydrogen atmosphere at r.t., has three phosphines coordinated in a meridional configuration, as evidenced by the ^{31}P NMR spectrum which shows an AMX spin pattern (δ_A +24.6dd, δ_M +7.2 pseudotriplet, δ_X −3.8dd, J_{AM} 18 Hz, J_{MX} 21 Hz, J_{AX} 365 Hz). The high field ^{1}H NMR signals indicate that one hydride is present in a *cis* position with respect to the three phosphorous atoms (δ −15.15 doublet of pseudotriplets, *J*(P–H) 10.8 and 20.4 Hz)

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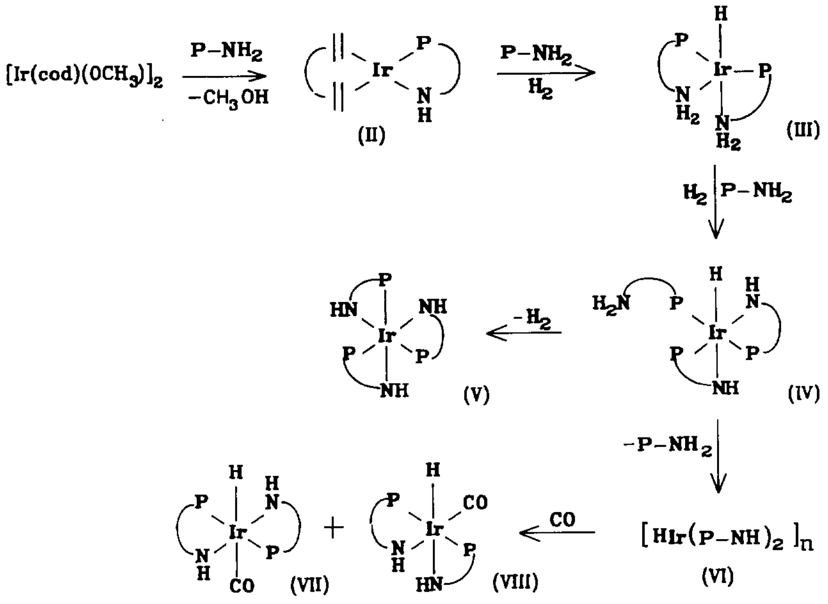
* Reference number with asterisk indicates a note in list of references.



Scheme 1

(see experimental section for complete spectral data). The infrared spectrum shows a band for ν(Ir–H) at 2092 cm^{-1}; moreover, conductivity data indicate that IV behaves as a non-electrolyte. The overall spectroscopic data are consistent with the formulation of species IV as $HIr(P\text{–}NH)_2(P\text{–}NH_2)$.

In order to provide unequivocal confirmation of the formulation of species IV, crystals suitable for an X-ray diffraction study were obtained by carefully placing a layer of pentane over a concentrated solution of IV in methylene chloride; after several unsuccessful attempts, very small yellow plates were finally obtained. Although the number of reflections collected was fairly low, the study unambiguously showed that the new species $Ir(P\text{–}NH)_3$ (V) had been formed, in which the iridium is coordinated to three chelating P–NH ligands. The coordination polyhedron around iridium can be described as a distorted octahedron, with the phosphorus and nitrogen atoms arranged in a facial configuration (see Fig. 1). Bond lengths and angles of interest are listed in Table 4. From the structural data it is evident that loss of H_2 has occurred, together with a rearrangement of the ligands from a meridional to a facial configuration: such isomerization could be ascribed to the high *trans* influence of the amido groups, which would cause the meridional configuration to be less stable than the facial one, since the latter contains no mutually *trans* NH groups.

From the findings discussed above, species IV appears to be a close precursor of the catalytically active species. However, when IV was used as catalyst precursor there was a poor selectivity for the unsaturated alcohol (only 12%). The chemoselectivity of the system can be raised to 92% if the reaction is performed in the presence of an excess of the phosphine; a comparison of the results obtained with species IV with those for the *in situ* system at comparable [P]/[Ir] ratio is presented in Table 5.

A question arising from this is why an excess of ligand is also required to obtain high chemoselectivity even when the preformed complex IV is used. In order to find

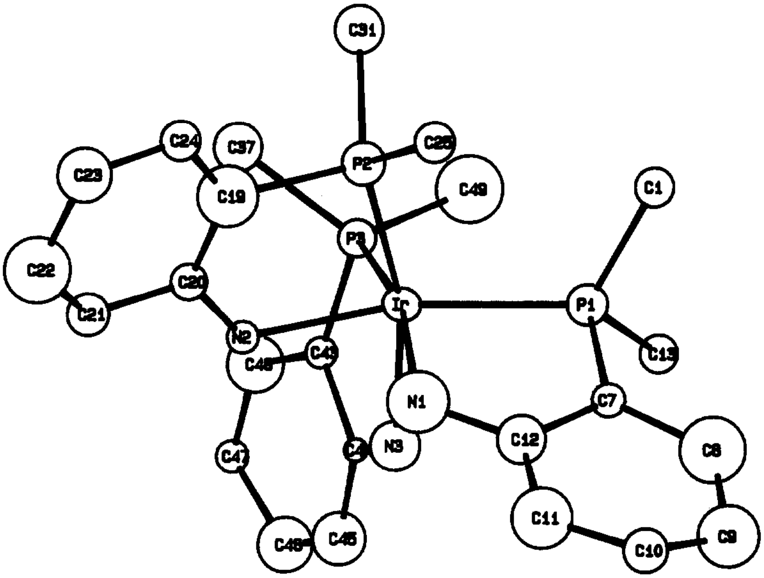


Fig. 1. ORTEP plot of Ir(P–NH)$_3$ (V) showing the atom numbering. Atoms are drawn at the 50% probability level. Phenyl groups [C(1), C(13), C(25), C(31), C(47) and C(49)] and hydrogen atoms are omitted.

an answer it was necessary to investigate the fate of species IV in the catalytic conditions.

When a benzene solution of species IV is kept at 80 °C under a hydrogen flow in the presence of two equivalents of P–NH$_2$ the starting complex remains unchanged even after 6 hours. In contrast, if the reaction is performed under hydrogen but without an excess of phosphine, even after only 10 min there is a precipitate of a yellow solid, VI. The low solubility of VI prevents its spectroscopic characterization; the only informative feature of the IR spectrum is a band at 2231 cm^{-1} attributable

Table 4

Selected bond lengths (Å) and angles (°) for Ir(P–NH)$_3$ (V) with esd's in parentheses

Ir–P(1)	2.35(1)	Ir–N(1)	2.10(6)
Ir–P(2)	2.32(2)	Ir–N(2)	2.09(4)
Ir–P(3)	2.32(1)	Ir–N(3)	2.10(5)
P(1)–Ir–P(2)	102.2(5)	P(3)–Ir–N(1)	164(2)
P(1)–Ir–P(3)	104.0(5)	P(3)–Ir–N(2)	90(1)
P(1)–Ir–N(1)	84(1)	P(3)–Ir–N(3)	80(1)
P(1)–Ir–N(2)	164(1)	N(1)–Ir–N(2)	80(2)
P(1)–Ir–N(3)	92(1)	N(1)–Ir–N(3)	85(2)
P(2)–Ir–P(3)	102.3(5)	N(2)–Ir–N(3)	84(2)
P(2)–Ir–N(1)	89(2)	Ir–N(1)–C(12)	114(4)
P(2)–Ir–N(2)	81(1)	Ir–N(2)–C(20)	121(3)
P(2)–Ir–N(3)	164(1)	Ir–N(3)–C(44)	122(4)

Table 5

Hydrogenation of PhCH=CHCOMe catalyzed by Ir/P-NH_2 systems [a]

Precursor	P_{tot}/Ir	% conversion (hours)	% saturated ketone	% saturated alcohol	% unsaturated alcohol
[Ir]+P-NH_2	3	97 (24)	39	7	51
IV	3	88 (24)	68	9	11
[Ir]+P-NH_2	5	99 (24)	1	19	79
IV+P-NH_2	5	96 (24)	4	4	88

[a] Reaction conditions: same as in Table 1. [Ir] = [Ir(cod)(OMe)]$_2$.

to ν(Ir–H). Further characterization was made by treating a suspension of IV in hot benzene with CO. After 1 h a yellow solution was obtained, the ^{31}P NMR spectrum of which consisted of two AB spin patterns with a relative intensity of about 2 : 1, indicating that two species, VII and VIII, respectively, are present, each containing two phosphines in a reciprocally *trans* position (^{31}P NMR for VII δ +38.8 d and +18.5 d, J(P–P) 297 Hz; for VIII δ +30.2 d and +20.7 d, J(P–P) 295 Hz). The hydridic part of the ^{1}H NMR spectrum of this solution shows a pseudotriplet at δ −7.69 (J(P–H) 16.6 Hz) and a doublet of doublets at δ −12.51 (J(P–H) 14.6 Hz). Moreover, both species contain coordinated CO, as indicated by the presence of bands in the IR spectrum at 2099, 2016 and 1941 cm^{-1}, attributable to Ir–H and C≡O stretching vibrations. Likely structures for VII and VIII are shown in Scheme 1.

As both of the products of the carbonylation reaction are hydridic bisphosphino complexes, and since no free P–NH_2 is detected in the ^{31}P NMR spectrum of the resulting solution, it can be inferred that the starting species VI also contains two phosphines coordinated to each iridium atom. As concerns the nuclearity of VI, its extremely low solubility suggests that it is a polynuclear species.

We now have enough information to allow rationalization of the catalytic data. When species IV is used as catalyst precursor, dissociation of a phosphine readily takes place under catalytic conditions to give bisphosphino species, which are, not surprisingly, poorly selective in carbonyl group hydrogenation. In order to keep three phosphines in the coordination sphere of iridium it is necessary to operate in the presence of an excess of P–NH_2: under such conditions a highly chemoselective reaction is obtained.

We believe that at high hydrogen pressures, such as the 20 atm. used in the catalytic reactions, complex IV undergoes reversible oxidative addition to give a species of type H_3IrP_3. Support for this hypothesis comes from the results of the catalytic reactions performed in the presence of the ligands $PPh_2(CH_2)_2NMe_2$, $PPh_2(CH_2)_3NMe_2$ or $PCy_2(CH_2)_2NMe_2$. The systems prepared *in situ* starting from [Ir(cod)(OMe)]$_2$ and an excess of one of these ligands promote the hydrogenation of benzylideneacetone to give the unsaturated alcohol in yields of up to 95%. NMR studies reveal that under a hydrogen flow the species $H_3Ir(PR_2(CH_2)_nNMe_2)_3$ is formed. Thus it is likely that, also in the case of the ligand P–NH_2, formation of the trihydride takes place, but only under more drastic conditions, and this is probably related to the higher chelating ability of P–NH_2 than of the $PR_2(CH_2)_nNMe_2$ ligands.

Conclusions

As mentioned in the Introduction, one of the main reasons why we used P–N type ligands in our iridium-based hydrogenation catalysts was to provide better understanding of the factors determining the selectivity. Our interest was focused on the connection between steric and electronic properties of the species formed on one hand and the chemoselectivity on the other. The results presented above are in line with our previous data obtained with iridium complexes containing mono- and di-phosphines. Once more we have experimental evidence that the presence of three coordinated phosphorous atoms is crucial for selective carbonyl group reduction in α,β-unsaturated ketones. According to our interpretation, steric effects determine the selectivity: the presence of three bulky phosphines prevents the coordination of the substrate through its C=C bond, while the less sterically demanding carbonyl group can approach iridium even in this crowded situation because of its end-on coordination mode. The coordinated function is then selectively reduced.

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