Intramolecular Activation of a *N*-Methyl C–H Bond by an Electron Rich Iridium Centre: a Novel Chemoselective Reduction Catalyst

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The iridium complex $\{H_2\overline{Ir[(P)-NCH_2Me]}[(P)-NMe_2]\}$ [(P)–NMe_2 = *o*-(diphenylphosphino)-*N*,*N*-dimethyl aniline] formed by intramolecular C–H oxidative addition, as shown by *X*-ray analysis, behaves as a chemoselective catalyst in hydrogen transfer reduction of α,β-unsaturated ketones to unsaturated alcohols.

Anchimeric assistance by the methoxy group of *o*-anisylphosphine plays a key role[1] in determining the selectivity of iridium complexes in the reduction of α,β-unsaturated aldehydes to allylic alcohols by hydrogen transfer from propan-2-ol. Such chemoselectivity was proposed to be related to the co-ordination of the *o*-methoxy group, which increases the electron density of the metal and therefore enhances the nucleophilic character of the co-ordinated hydride.

This effect is expected to be enhanced by substituting the oxygen atom with a nitrogen donor atom, as in the hybrid phosphine amine (P)–NMe_2 ligand.[2]

Reaction of $[Ir(cod)(OMe)]_2$ (cod = cyclo-octa-1,5-diene) with (P)–NMe_2 (P/Ir = 2) in benzene at room temperature gives the hydridic complex $\{HIr(cod)[(P)-NMe_2]\}$, probably *via* β-hydrogen elimination from the methoxy ligand.[3] After refluxing the resulting solution (or, at variance, a propan-2-ol solution) under hydrogen for 1 h a new species is formed, which can be isolated by addition of n-hexane. The air and light sensitive yellow solid obtained is a hydridic bisphosphino complex (**1**), with two non-equivalent phosphorous atoms in a mutually *cis* position, as deduced on the basis of n.m.r. data {^{1}H n.m.r. (80 MHz, C_6D_6): δ 8.3 (m, 2H, *o*-Ar), 8.0—6.5 (m, 26H, Ar), 3.52 (br. s, 6H, NMe_2), 3.38 (s, 3H, CH_2–N–*Me*), 3.5—2.3 (partially overlapped multiplet, 2H, *CH_2*–N–Me), −7.73 (t, 2H, Ir–H, J_{PH} 14.2 Hz); ^{31}P {^{1}H} n.m.r. (32 MHz, C_6H_6): δ +33.4 and +12.5 (2d, J_{PP} 5 Hz), [free (P)-NMe_2 δ −13.6]† p.p.m.}. No unco-ordinated NMe_2 groups are present in the molecule, as indicated by results from the analysis of the aliphatic region of the ^{1}H n.m.r. spectrum, and by the absence in the i.r. spectrum of the band at 2780 cm^{-1}, which is typical of a free NMe_2 group.[4]

Single crystals suitable for *X*-rays analysis were obtained by slow diffusion of propan-2-ol in a CH_2Cl_2 solution of (**1**), and covered with epoxydic cement.‡ The molecular structure is shown in Figure 1. The original iridium complex (**1**) has been partially chlorinated by CH_2Cl_2 to give $\{H\overline{IrCl[(P)-NCH_2Me]}[(P)-NMe_2]\}$ (**2**). Such chlorination can be followed by monitoring the ^{1}H and ^{31}P n.m.r. spectra (CD_2Cl_2) of (**1**): after 12 h this species is completely converted into (**2**) [^{1}H n.m.r. (C_6D_6): δ 8.2—6.4 (m, 28H, Ar), 3.48 and 3.37 (2s, 6H, NMe_2), 2.94 (s, 3H, CH_2–N–*Me*), 3.4—2.4 (partially overlapped multiplet, 2H, *CH_2*–N–Me), −21.50 (dd, 1H, Ir–H, J_{PH} 12.8 and 21.5 Hz); ^{31}P {^{1}H} n.m.r. (CH_2Cl_2): δ +19.3 and +3.8 (2d, J_{PP} 4 Hz) p.p.m.]. The close similarity between the

† ^{31}P n.m.r. chemical shifts are referred to H_3PO_4 85% as external standard, with positive sign for low field shifts.

‡ *Crystal data*: $C_{40}H_{40}ClIrN_2P_2 \cdot 0.5CH_2Cl_2$, triclinic, space group $P\bar{1}$, a = 9.881(2), b = 12.501(3), c = 16.798(4) Å, α = 88.70(3), β = 83.05(3), γ = 61.18(2)°, U = 1898(3) Å^3, D_c = 1.54 g cm^{-3}, M_w = 880.8, Z = 2, μ(Mo-K_α) = 39.7 cm^{-1}, $F(000)$ = 878, R = 0.039, R_w = 0.052 for 5712 independent reflections with $I > 3\sigma(I)$ and 4° < θ <27° after absorption correction. The structure was solved by Patterson and Fourier methods. The Fourier maps, showing broad peaks attributable to a non-stoicheiometric amount of solvent of crystallization, suggest a partial loss of CH_2Cl_2. Hydrogen atoms were located at calculated positions and held fixed (B = 5 Å^2) during final refinement. Scattering factors, anomalous dispersion terms and programs were taken from Enraf-Nonius SPD.[5] Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

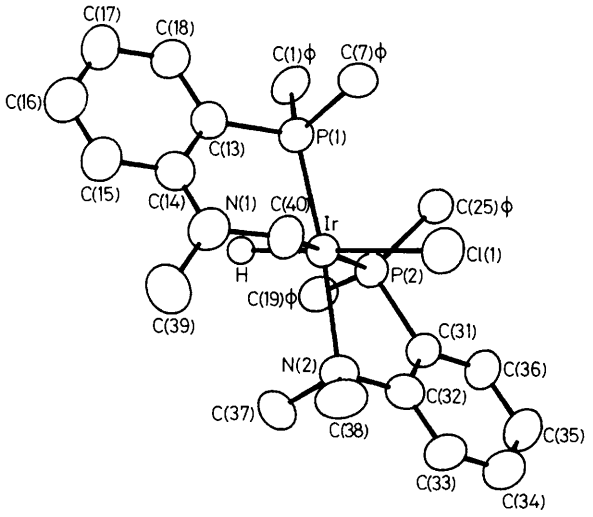

Figure 1. An ORTEP plot of {HIrCl[(P)–NCH$_2$Me][(P)–NMe$_2$]} (**2**), showing atom numbering scheme. Atoms are drawn at the 50% probability level. Phenyl groups [C(1), C(7), C(19) and C(25)] and hydrogen atoms are omitted.

n.m.r data of (**1**) and (**2**) indicates that (**1**) is the *trans*-dihydride {H$_2$Ir[(P)–NCH$_2$Me][(P)–NMe$_2$]} [equation (1)].

$$\{\mathrm{HIr(cod)[(P)\text{–}NMe_2]}\} \xrightarrow[80\,^\circ\mathrm{C}]{\mathrm{H_2,\ P\text{–}NMe_2}} \underset{(\mathbf{1})}{\{\mathrm{H_2Ir[(P)\text{–}NCH_2Me][(P)\text{–}NMe_2]}\}} \xrightarrow{\mathrm{CH_2Cl_2}} \underset{(\mathbf{2})}{\{\mathrm{HIrCl[(P)\text{–}NCH_2Me][(P)\text{–}NMe_2]}\}} \quad (1)$$

The most interesting feature of the structure is the presence of a six-membered chelate ring formed by oxidative addition of the *N*-methyl C–H bond. A similar C–H activation was proposed, on the basis of deuteriation experiments, to account for an unusual isomerization of *o*-chelated aryl iridium(I) complexes.[6] The (P)–NMe$_2$ ligand we used creates an electron rich metal centre, which will activate a C–H bond through a three centred transition state.[7]

The high electron density on the metal is expected, by enhancing the nucleophilic character of the co-ordinated hydride, to promote its selective attack to the carbon atom of the keto group of an organic substrate, even in the presence of other reducible functions. Complex (**1**) proves to be a selective catalyst for the hydrogen transfer reduction of α,β-unsaturated ketones to allylic alcohols, using propan-2-ol as hydrogen donor, as can be seen from the results reported in Table 1. Activity and selectivity are in some cases remarkable, supporting the hypothesis that one of the main factors in determining selectivity in such reductions is the extent of negative charge on the co-ordinated hydride. In these reactions, no basic cocatalyst is required, which is a very unusual feature for a catalyst of hydrogen transfer from propan-2-ol. To the best of our knowledge, this is the first example of catalytic chemoselective reduction of α,β-unsaturated ketones to allylic alcohols by hydrogen transfer.

Table 1. Reduction of α,β-unsaturated ketones catalysed by {H$_2$Ir[(P)–NCH$_2$Me][(P)–NMe$_2$]}.[a]

Substrate	% Conversion (h)	% Saturated ketone	% Saturated alcohol	% Unsaturated alcohol	% Selectivity[b]
PhCH=CHCOMe	99(1)	1	6	92	93
PhCH=CHCOPh	94(1)	13	14	67	71
Me$_2$C=CHCOMe	65(7)	2	1	62	95
MeCH=CHCOEt	35(7)	23	0	12	34
CH$_2$=CHCOEt	9(7)	8	0	1	11

[a] *Reaction conditions*: [Ir] = 4 × 10^{-4} M; [substrate]/[Ir] = 500; solvent propan-2-ol; T = 83 °C. [b] % Selectivity = (% unsaturated alcohol/% conversion) × 100.

The authors thank C.N.R. Progetti Finalizzati and M.P.I. for partial financial support.

Received, 28th February 1989; Com. 9/00869A

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