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Dehydrogenation of Hydridoirida-β-diketones in Methanol: The Selective Formation of Mono- and Dinuclear Acyl Complexes

Roberto Ciganda,[a] María A. Garralda,*[a] Lourdes Ibarlucea,[a] Claudio Mendicute,[a] Elena Pinilla,[b] and M. Rosario Torres[b]

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The hydridoirida-β-diketone [IrH{(PPh_2(*o*-C_6H_4CO))$_2$H}Cl] (**1**) reacts with diimines (NN) or with pyridine (py) in refluxing methanol to undergo dehydrogenation. The reactions afford selectively the *cis*-acyl, *trans*-phosphane isomers of the cationic [Ir(PPh_2(*o*-C_6H_4CO))$_2$(NN)]$^+$ {NN = 2,2′-bipyridine (**2**); R–N=C(CH_3)–C(CH_3)=N–R′ [R = R′ = NH_2 (**3**); R = R′ = OH (**4**); R = OH, R′ = NH_2 (**5**)]} or neutral [IrCl(PPh_2(*o*-C_6H_4CO))$_2$(py)] (**6**) derivatives. The reactions are faster for ligands containing amino substituents. Refluxing **1** in MeOH affords the formation of an equimolar mixture of dimer cationic species [Ir_2(μ-Cl)(μ-PPh_2(*o*-C_6H_4CO))$_2$(PPh_2(*o*-C_6H_4CO))$_2$]$^+$ (**7a** and **7b**) containing two acyls and a chloride as bridging groups. The isomers could be separated by fractional precipitation. Compound [**3**]Cl, containing amino substituents in the imino functionalities, catalyses the hydrogen transfer from 2-propanol to cyclohexanone to afford cyclohexanol. All the complexes were fully characterised spectroscopically. Single crystal X-ray diffraction analysis was performed on complexes **6** and [**7b**]ClO_4.

Introduction

Hydridoirida-β-diketones can be easily prepared by activation of aldehydes, tethered to N- or P-ligands, by hydridoacyliridium complexes.[1] Metalla-β-diketones, also described as acylhydroxycarbene complexes, are rather stable due to the formation of a strong intramolecular hydrogen bond between the acyl and the hydroxycarbene moieties. Recently it has been reported that this hydrogen bond is stronger than that in acetylacetone, an organic β-diketone.[2] The hydridoirida-β-diketone complex [IrH{(PPh_2(*o*-C_6H_4CO))$_2$H}Cl] (**1**) being an electronically saturated species is remarkably stable. In solvents of low polarity, **1** is unreactive toward σ-donors such as pyridine or triphenylphosphane. It requires the abstraction of chloride to afford cationic mononuclear [IrH{(PPh_2(*o*-C_6H_4CO))$_2$H}(L)][ClO_4] complexes, or the dinuclear species [Ir_2H(PPh_2(*o*-C_6H_4CO)){μ-PPh_2(*o*-C_6H_4CO)}$_3$]BF_4, containing three acylphosphane bridging ligands and a single terminal hydride, in a reversible process.[3] In methanol the reaction of **1** with bases such as KOH or Et_3N, at room temperature, led to dehydrodechlorination and afforded the acyl-bridged hydrido iridium derivative [Ir_2H_2(PPh_2(*o*-C_6H_4CO))$_2$(μ-PPh_2(*o*-C_6H_4CO))$_2$]. When the reaction was performed in refluxing methanol, KOH led to a novel dihydridoirida-β-diketone [IrH_2{(PPh_2(*o*-C_6H_4CO))$_2$H}] while Et_3N gave [Ir_2(μ-H){μ-PPh_2(*o*-C_6H_4CO)}$_2$(PPh_2(*o*-C_6H_4CO))$_2$]Cl, with two acylphosphane chelate-bridging ligands and a bridging hydride.[4] In some of these reactions dehydrogenation reactions also occurred. We report now on the reactivity of **1** in methanol in the presence or absence of N-donor ligands such as diimines: 2,2′-bipyridine (bipy), R–N=C(CH_3)–C(CH_3)=N–R′ [dihydrazone, R = R′ = NH_2 (bdh); dioxime, R = R′ = OH (dmg); oxime hydrazone, R = OH, R′ = NH_2 (boh)] or pyridine (py). In all cases dehydrogenation occurs to afford mono- or dinuclear diacyl complexes.

Results and Discussion

Complex **1** reacts with diimines in refluxing methanol, to undergo dehydrogenation affording the cationic diacyl derivatives [Ir(PPh_2(*o*-C_6H_4CO))$_2$(NN)]$^+$ (NN = bipy, **2**; bdh, **3**; dmg, **4**; boh, **5**) shown in Scheme 1. The reactions are slow and require reaction times in a 90 min–9 h range to reach completion. The corresponding complexes have been isolated as perchlorate compounds by addition of sodium perchlorate (see Exp. Sect.). High stereochemical selectivity is observed in these reactions that afford a single isomer. The obtained complexes show the expected features in their IR spectra, their FAB spectra show the parent peaks and they behave as 1:1 electrolytes in acetone solution.[5] For complexes containing symmetric diimines, **2**–**4**, the diimine ligand shows one set of resonances due to equivalent imino fragments, their $^{31}P\{^1H\}$ NMR spectra contain only one singlet in the 27–33 ppm range, indicating equivalent P-

[a] Facultad de Química de San Sebastián, Universidad del País Vasco,
Apdo. 1072, 20080 San Sebastián, Spain
[b] Departamento de Química Inorgánica, Laboratorio de Difracción de Rayos X, Facultad de Ciencias Químicas, Universidad Complutense,
28040 Madrid, Spain

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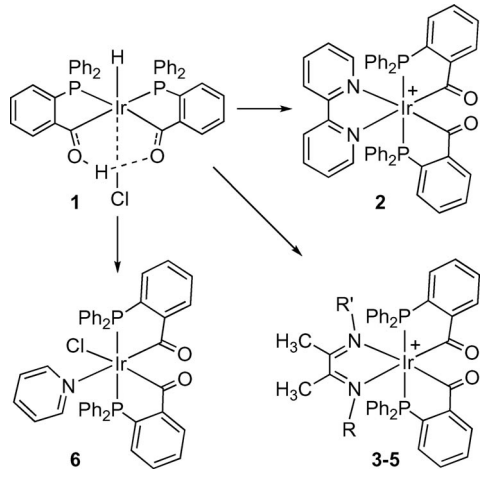
atoms and the $^{13}C\{^1H\}$ NMR spectra show also only one singlet in the 216–224 ppm range, corresponding to equivalent acyl groups. According to these data two isomers are possible for these complexes, the *cis*-acyl, *trans*-phosphane species or the *trans*-acyl, *cis*-phosphane compound. Taking into account electronic considerations, the most stable isomer would be the *cis*-acyl, *trans*-phosphane isomer, with the acyl groups *trans* to the imino groups, since acyls, having the largest *trans* influence and being the best σ-donors, would prefer to be *trans* to the imino group with the lowest *trans* influence, being the weakest σ-donor, when compared to phosphanes.[6] This is confirmed by the reaction of **1** with boh, containing nonsymmetrical imino groups, which shows that the stereochemistry of **5** corresponds to that shown in Scheme 1. The oxime hydrazone ligand shows two sets of resonances due to nonequivalent imino fragments, the $^{31}P\{^1H\}$ NMR spectrum shows two doublets (AB pattern) at δ = 37.3 and 26.7 ppm corresponding to two nonequivalent phosphanes mutually *trans* [J(P,P) = 323 Hz] and the $^{13}C\{^1H\}$ NMR spectrum contains two acyl resonances at δ = 233.9 and 214.6 ppm.



Scheme 1. NN = bipy, **2**; bdh (R = R′ = NH_2), **3**; dmg (R = R′ = OH) **4**; boh, (R = NH_2, R′ = OH), **5**.

Complex **1** contains a hydride, which may behave as a proton acceptor, and an alcoholic O···H···O proton. In $CDCl_3/CD_3OD$ solution H/D exchange of this proton is observed. We believe that the dehydrogenation reaction most likely occurs by interaction of H^- and H^+. Because of the low rate of our reactions we were unable to observe any hydrogen evolution by NMR during the dehydrogenation reaction. Nevertheless, the interaction between late transition-metal hydrides and alcoholic or hydroxycarbene protons that may result in hydrogen formation is documented.[7] Furthermore, we observe some relation between the reaction rate and the type of ligand. The slowest reaction occurs for the dioxime ligand containing OH groups (ca. 9 h), the reaction with a good "proton acceptor" ligand such as bipyridine is faster (ca. 150 min) and the reaction with ligands containing amino groups, bdh or boh, are the fastest (ca. 90 min). Recent studies on a reversible reaction involving dehydrogenation of $[Ru(H)_2(PMe_3)\{HN(CH_2CH_2P\textit{i}Pr_2)_2\}]$ and hydrogenation of $[RuH(PMe_3)\{N(CH_2CH_2P\textit{i}Pr_2)_2\}]$, via heterolytic splitting of hydrogen, suggest that the barrier for the hydrogen splitting may be lowered by hydrogen bond formation with added water.[8] In the present case the different dehydrogenation rates may be related to initial hydrogen bond formation between the hydroxycarbene proton and the free N-donor ligand which may lead to the proton being closer to the hydride thus allowing for easier formation of hydrogen when better proton acceptor ligands are available. X-ray diffraction studies on hydridoirida-β-diketones have shown that the iridacycle comprising the acyl(hydroxycarbene) group is essentially planar.[3a] In these reactions complete dehydrogenation occurs while previously we have observed that the reaction of **1** with Et_3N in refluxing methanol led only to partial dehydrogenation.[4] We believe that this different behaviour may be related to the better coordinating ability of diimines, when compared to Et_3N, which may favour the removal of the hydride in the present case.

The reaction of $[IrHCl\{(PPh_2(o\text{-}C_6H_4CO))_2H\}]$ (**1**) with pyridine in refluxing methanol also leads to dehydrogenation to afford the neutral diacyl $[IrCl(PPh_2(o\text{-}C_6H_4CO))_2(py)]$ (**6**). Its IR spectrum contains the band due to coordinated acyl groups at 1624 cm^{-1} and the FAB spectrum shows the peak due to pyridine loss. The $^{31}P\{^1H\}$ NMR spectrum contains an AB spin pattern due to *trans* phosphorus atoms [J(P,P) = 347 Hz] and the $^{13}C\{^1H\}$ NMR spectrum contains two resonances in the 210 ppm region, attributed to two acyl groups bonded to iridium. These spectral features indicate *trans* P-atoms and *cis*-acyl groups *trans* to chloride and to pyridine, which are the groups with lower *trans* influence, as shown in Scheme 1.

Complex **6** could be characterised by single-crystal X-ray diffraction, which confirms the spectroscopic findings. Complex **6** crystallises in the $P2_1/c$ monoclinic group. Figure 1 shows an ORTEP view of complex **6**. Selected bond lengths and angles are listed in Table 1. The coordinative environment of the rhodium atom is distorted octahedral, with four positions occupied by the phosphorus and carbon atoms of the two bidentate ligands, and the other two positions are occupied by the nitrogen atom of the pyridine and by chloride. As also proposed for complexes **2**–**5**, the phosphorus atoms are mutually *trans*, and the acyl groups are mutually *cis*. A similar feature has also been observed in a related rhodium complex.[7d] The bond lengths in **6** are in the expected ranges.[9] The Ir–P distances are similar and the Ir–N1 [2.229(4) Å] and Ir–Cl [2.515(1) Å] distances are rather long, because of the high *trans* influence of the acyl groups.

Attempts to obtain a diacyl complex similar to **6** using more sterically demanding ligands such as 2-methylpyridine proved unsuccessful. Instead, the formation of an equimolar mixture of dimer cationic species $[Ir_2(\mu\text{-}Cl)(\mu\text{-}PPh_2(o\text{-}C_6H_4CO))_2(PPh_2(o\text{-}C_6H_4CO))_2]^+$ (**7a** and **7b**) occurred (see Scheme 2). Refluxing **1** in MeOH affords also the formation of **7**. The two isomers could be separated by addition of $NaClO_4$. The precipitation of [**7a**]ClO_4 was quantitative and from the remaining solution [**7b**]ClO_4

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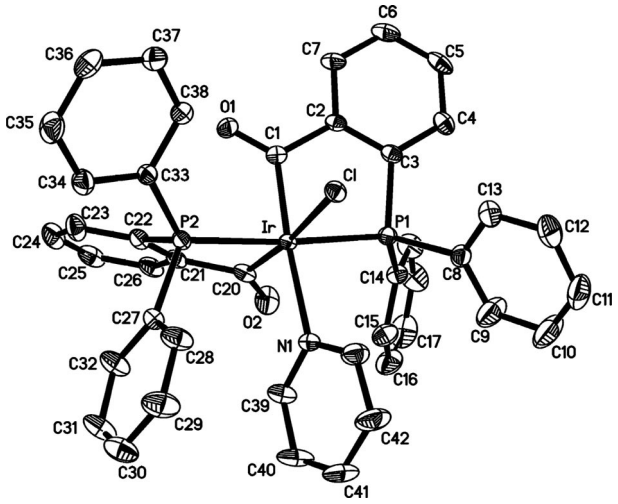
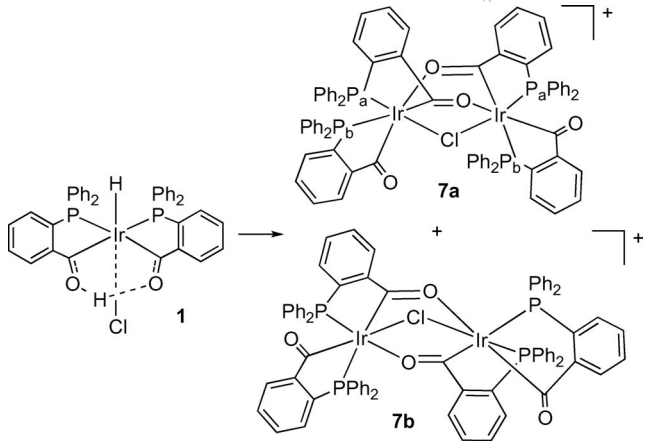


Figure 1. ORTEP view of compound **6** showing the atomic numbering (20% probability ellipsoids). The hydrogen atoms and some carbon atoms have been omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for **6** and [**7b**]ClO_4.

6		[**7b**]ClO_4			
Ir–P1	2.342(1)	Ir1–P1	2.373(3)	Ir2–P3	2.382(3)
Ir–P2	2.321(1)	Ir1–P2	2.270(2)	Ir2–P4	2.258(3)
Ir–C20	2.020(6)	Ir1–C20	2.02(1)	Ir2–C58	2.04(1)
Ir–Cl	2.029(5)	Ir1–C1	2.00(1)	Ir2–C39	2.01(1)
Ir–N1	2.229(4)	Ir1–Cl1	2.418(4)	Ir2–Cl1	2.496(4)
Ir–Cl	2.515(1)	Ir1–O4	2.267(7)	Ir2–O2	2.126(7)
C20–O2	1.210(6)	C20–O2	1.27(1)	C58–O4	1.24(1)
C1–O1	1.214(6)	C1–O1	1.23(1)	C39–O3	1.22(1)
		Ir1–Ir2	3.564(1)		
P1–Ir–P2	175.01(5)	P1–Ir1–P2	99.1(1)	P3–Ir2–P4	101.4(1)
P1–Ir–C20	96.4(2)	P1–Ir1–C20	177.0(3)	P3–Ir2–C58	175.3(3)
P1–Ir–Cl	89.1(5)	P1–Ir1–Cl1	88.8(1)	P3–Ir2–O2	85.5(2)
P1–Ir–C1	84.3(2)	P1–Ir1–C1	83.8(3)	P3–Ir2–Cl1	99.4(1)
P1–Ir–N1	91.0(1)	P1–Ir1–O4	95.9(2)	P3–Ir2–C39	83.6(3)
P2–Ir–C20	82.4(2)	P2–Ir1–C20	82.0(2)	P4–Ir2–C58	81.7(3)
P2–Ir–Cl	91.9(1)	P2–Ir1–Cl1	168.6(1)	P4–Ir2–O2	169.5(2)
P2–Ir–C1	90.8(2)	P2–Ir1–C1	84.9(3)	P4–Ir2–Cl1	101.2(1)
P2–Ir–N1	93.9(1)	P2–Ir1–O4	104.0(2)	P4–Ir2–C39	89.9(3)
C20–Ir–Cl	173.3(2)	C20–Ir1–Cl1	89.7(3)	C58–Ir2–O2	90.9(3)
C20–Ir–C1	86.1(2)	C20–Ir1–C1	93.6(4)	C58–Ir2–Cl1	84.4(3)
C20–Ir–N1	94.6(2)	C20–Ir1–O4	86.4(3)	C58–Ir2–C39	92.9(4)
C1–Ir–Cl	90.6(2)	C1–Ir1–Cl1	87.8(3)	O2–Ir2–Cl1	85.3(2)
N1–Ir–Cl	89.1(1)	C1–Ir1–O4	171.0(3)	O2–Ir2–C39	82.9(3)
C1–Ir–N1	175.3(2)	Cl1–Ir1–O4	83.2(2)	Cl1–Ir2–C39	167.6(3)
		Ir1–Cl1–Ir2	93.0(2)		
		Ir1–C1–O1	122.3(8)	Ir2–C39–O3	123.4(8)
		Ir1–C20–O2	124.0(7)	Ir2–C58–O4	125.4(8)
		Ir1–O4–C58	119.5 (7)	Ir2–O2–C20	123.0 (6)

could be obtained. Both compounds behave as 1:1 electrolytes in acetone solution and the FAB spectra show the $[M]^+$ peak at 1577 as expected for such dinuclear species. Their IR spectra show stretches at 1633 cm^{-1} due to the terminal acyl groups and a strong stretch at 1515 cm^{-1} that can be assigned to bridging acyl groups.



Scheme 2.

The $^{13}C\{^1H\}$ NMR spectrum of **7a** contains two doublets due to acyl groups. In both resonances the coupling to one of the phosphorus atoms is observed while the coupling to the other phosphorus is unobservable. The resonance at lower field is due to acyl groups with carbon atoms *trans* to phosphorus atoms [J(P,C) = 99 Hz]. The chemical shift, 264.9 ppm, is in the upper end of the range 274–240 ppm, reported for bridging acyl groups between iridium atoms in dinuclear complexes,[3b,4,10] and is similar to that of the related rhodium $[Rh_2(\mu\text{-}Cl)(\mu\text{-}PPh_2(o\text{-}C_6H_4CO))_2(PPh_2(o\text{-}C_6H_4CO))_2]^+$ complex.[6d] The resonance at higher field, 197.6 ppm, is attributed to terminal acyl groups and appears at higher field than that of the related rhodium derivative, 219.0 ppm. The $^{31}P\{^1H\}$ NMR spectrum contains two doublets consistent with an AX pattern. For this isomer we propose the structure depicted in Scheme 2, with two equivalent iridium fragments, and with phosphorus atoms *trans* to acyl and to chlorine. It contains the weakest σ-donor oxygen atoms *trans* to the strongest σ-donor acyl groups, which represents the most electronically favourable geometry. Nevertheless, a disposition with phosphorus atoms being *trans* to acyl and to oxygen cannot be excluded. For **7b**, the spectra are due to the presence of four nonequivalent acyl-phosphane fragments, two per iridium atom. In the $^{13}C\{^1H\}$ NMR spectrum two close doublets due to terminal acyl groups [ca. 198.9 ppm, J(P,C) = 8 Hz] and two close doublets due to bridging acyl groups [ca. 264 ppm, J(P,C) = 102 Hz] are observed. The $^{31}P\{^1H\}$ NMR spectrum consists of four doublets. The J(P,P) coupling constants agree with both phosphorus atoms bonded to the same iridium atom being mutually *cis*.

It is noteworthy that by refluxing **1** in MeOH in the presence of NEt_3, partial dehydrochlorination and partial dehydrogenation occurred, thus yielding the dinuclear $[Ir_2(\mu\text{-}H)(\mu\text{-}PPh_2(o\text{-}C_6H_4CO))_2(PPh_2(o\text{-}C_6H_4CO))_2]Cl$, with a hydride and two acyl groups bridging the two iridium atoms.[4] An isomer, $[Ir_2H(PPh_2(o\text{-}C_6H_4CO))\{\mu\text{-}PPh_2(o\text{-}C_6H_4CO)\}_3]BF_4$, containing three acylphosphane bridging ligands and a single terminal hydride, could be obtained by complete halide abstraction and partial dehydrogenation of **1** promoted by halide abstractors.[3] In the present case, complete

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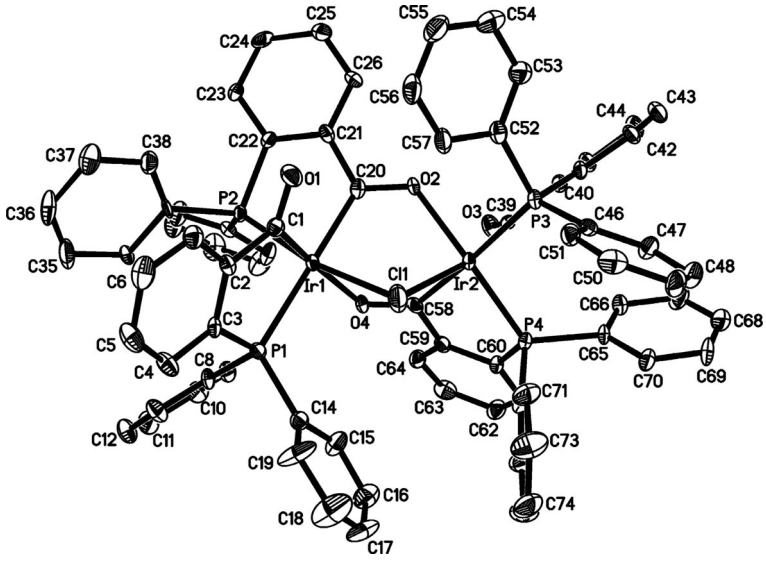

Figure 2. ORTEP view of the cation in compound [**7b**]ClO_4 showing the atomic numbering (20% probability ellipsoids). The hydrogen atoms and some carbon atoms have been omitted for clarity.

dehydrogenation leads the chloride to occupy a bridging position in **7**. The formation of these triply bridged iridium dimers appears easy. In all cases two of the bridging groups between the two iridium atoms are acyls and the nature of the third bridge appears to depend markedly on the reaction conditions.

We succeeded in isolating compound [**7b**]ClO_4 as single crystals suitable for X-ray diffraction. This compound crystallises in the $P2_1/n$ monoclinic group. The asymmetric unit consists of a dinuclear cation and a ClO_4^- anion. Figure 2 shows an ORTEP view of the cation. Selected bond lengths and angles are listed in Table 1. Two acyl groups in a head-to-tail arrangement and a chloride bridge the Ir atoms. The geometry around each Ir atom is pseudo-octahedral with the chloro ligand *trans* to a phosphorus atom through the Ir1 atom and *trans* to the carbon atom of a terminal acyl group through the Ir2 atom. The bridging Ir2–Cl1 distance [2.496(4) Å] is longer than the Ir1–Cl1 distance [2.418(4) Å] reflecting the higher *trans* influence of the acyl group.[11] The bridging Ir2–Cl1 distance is slightly shorter than that observed in the mononuclear complex **6** [2.515(1) Å], and is similar to that reported for complexes containing a bridging chloride *trans* to vinyl [2.495(6) and 2.464(6) Å].[10] The Ir1–Ir2 distance [3.564(1) Å] and the Ir1–Cl1–Ir2 angle [93.0(2)°] exclude any Ir–Ir interaction. As in other dinuclear species,[12] the Ir1–Ir2 distance in **7b** is longer than that in the related $[Ir_2(\mu\text{-}H)(\mu\text{-}PPh_2(o\text{-}C_6H_4CO))_2(PPh_2(o\text{-}C_6H_4CO))_2]^+$ [2.9629(4) Å] containing hydride instead of chloride as the bridge. The Ir–C and the C–O distances of the bridging and terminal acyl groups are practically equal. The average Ir–C and C–O bond lengths, 2.02(1) Å and 1.24(1) Å respectively are as expected for coordinated acyl groups with low carbene-like character.[10] The Ir–P distances also reflect the decreasing *trans* influence in the series: acyl [Ir1–P1 2.373(3) and Ir2–P3 2.382(4) Å] >> chlorine [Ir1–P2 2.270(2) Å] > oxygen [Ir2–P4 2.258(3) Å].

It is well known that metal hydrides may catalyse the transfer hydrogenation of ketones.[13] Chelated Ir^{III} bis-carbene complexes, proposed to involve a monohydride active species, or hemilabile pincer-type hydride Ir^{III} derivatives have been reported to promote the transfer hydrogenation of cyclohexanone, reaching TOF values higher than 1000 mol/h.[14] We have recently shown that in methanol and in the presence of strong bases iridium acyls may afford iridium acylhydrides,[4] and that the presence of P- and N-donor ligands, instead of only P-donor ligands, make the corresponding iridium hydrides more useful for transfer hydrogenation reactions of ketones.[1c] We have tested the catalytic activity of complexes **2**–**7** in the transfer hydrogenation of cyclohexanone in *i*PrOH, in the presence of a strong base. From the transfer hydrogenation data it is apparent that compound [**3**]Cl, containing amino substituents in both the imino functionalities shows the highest activity reaching 88% conversion to cyclohexanol after 180 min (TOF[15] of 134 after 10 min). The dimer compound [**7**]Cl reaches 59% conversion after 180 min (TOF[15] of 85 after 10 min) and the pyridine complex **6** shows lower activity, reaching 44% conversion after 180 min. For compounds [**2**]Cl, [**4**]Cl and [**5**]Cl less than 10% conversion was attained after 180 min. The corresponding perchlorate compounds show a lower activity than the chloride compounds, probably due to their low solubility. Compound [**3**]Cl shows a comparable catalytic activity to that of Cp^*Ir^{III} complexes containing functionalised carbenes.[16]

Conclusions

The hydridoirida-β-diketone $[IrH\{(PPh_2(o\text{-}C_6H_4CO))_2H\}Cl]$ (**1**) undergoes dehydrogenation in protic solvents to afford dimer complexes with bridging acyl and chloride groups. The presence of N-donors makes the dehydrogena-

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tion reaction faster, suggesting hydrogen bond formation favouring the dehydrogenation reaction, affording selectively cationic or neutral diacyl complexes of the *cis*-acyl, *trans*-phosphane type. The dihydrazone-containing complex can be used as a pre-catalyst for transfer hydrogenation of ketones.

Experimental Section

General Procedures: The preparation of the metal complexes was carried out at room temperature under nitrogen using standard Schlenk techniques. [IrHCl{(PPh_2(*o*-C_6H_4CO))$_2$H}] (**1**) was prepared as previously reported.[1a] Microanalyses were carried out with a Leco CHNS–932 microanalyser. Conductivities were measured in acetone solution with a Metrohm 712 conductimeter. IR spectra were recorded with a Nicolet FTIR 510 spectrophotometer in the range 4000–400 cm^{-1} using KBr pellets. NMR spectra were recorded with Bruker Avance DPX 300 or Bruker Avance 500 spectrometers, ^1H and $^{13}C\{^1H\}$ (TMS internal standard), $^{31}P\{^1H\}$ (H_3PO_4 external standard), were measured from $CDCl_3$ solutions. Mass spectra were recorded with a VG Autospec, by liquid secondary ion (LSI) MS using nitrobenzyl alcohol as matrix and a caesium gun (Universidad de Zaragoza).

[Ir(PPh_2(*o*-C_6H_4CO))$_2$(bipy)]ClO_4 (2): To a methanol suspension of [IrH{(PPh_2(*o*-C_6H_4CO))$_2$H}Cl] (**1**) (50 mg, 0.062 mmol) was added 2,2′-bipyridine (bipy) (9.7 mg, 0.062 mmol). The suspension was refluxed for 150 min whereupon a yellow solution was formed. The solution was cooled and a methanol solution of $NaClO_4{\cdot}H_2O$ (8.7 mg, 0.062 mmol) was added to afford a yellow solid that was decanted, washed with methanol and dried under vacuum. Yield 50.3 mg, 79%. IR (KBr): $\tilde{\nu}$ = 1627 (s) (C=O) cm^{-1}. Λ_M ($ohm^{-1}cm^2mol^{-1}$): 128 (acetone). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 27.2 (s) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 216.0 (s) ppm. $C_{48}H_{36}ClIrN_2O_6P_2$ (1026.14): calcd. C 56.17, H 3.53, N 2.73; found C 55.79, H 3.16, N 2.71.

[Ir(PPh_2(*o*-C_6H_4CO))$_2$(bdh)]ClO_4 (3): To a methanol suspension of [IrH{(PPh_2(*o*-C_6H_4CO))$_2$H}Cl] (**1**) (50 mg, 0.062 mmol) was added biacetyldihydrazone (bdh) (7.1 mg, 0.062 mmol). The suspension was refluxed for 90 min whereupon a yellow solution was formed. The solution was cooled and a methanol solution of $NaClO_4{\cdot}H_2O$ (8.7 mg, 0.062 mmol) was added to afford a yellow solid that was decanted, washed with methanol and dried under vacuum. Yield 45.2 mg, 74%. IR (KBr): $\tilde{\nu}$ = 3398 (m) (OH), 3299 (m), 3201 (m) (NH_2), 1597 (s) (C=O) cm^{-1}. Λ_M ($ohm^{-1}cm^2mol^{-1}$): 134 (acetone). ^1H NMR ($CDCl_3$): δ = 5.68 (s, 4 H, NH); 1.57 (s, 3 H, CH_3) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 31.4 (s) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 218.3 (s, Ir*C*O); 15.1 (s, CH_3) ppm. FAB-MS: calcd. for $C_{42}H_{38}IrN_4O_2P_2$, 885; obsd. 885 [M^+]. $C_{42}H_{38}ClIrN_4O_6P_2{\cdot}CH_3OH$ (1016,18): calcd. C 50.81, H 4.17, N 5.51; found C 50.62, H 4.18, N 5.78.

[Ir(PPh_2(*o*-C_6H_4CO))$_2$(dmg)]ClO_4 (4): To a methanol suspension of [IrH{(PPh_2(*o*-C_6H_4CO))$_2$H}Cl] (**1**) (50 mg, 0.062 mmol) was added dimethylglyoxime (dmg) (8.7 mg, 0.062 mmol). The suspension was refluxed for 9 h whereupon a yellow solution was formed. The solution was cooled and a methanol solution of $NaClO_4{\cdot}H_2O$ (7.6 mg, 0.062 mmol) was added to afford a yellow solid that was decanted, washed with methanol and dried under vacuum. Yield 29.4 mg, 48%. IR (KBr): $\tilde{\nu}$ = 3611 (m) (OH), 1624 (s) (C=O) cm^{-1}. Λ_M ($ohm^{-1}cm^2mol^{-1}$): 140 (acetone). ^1H NMR ($CDCl_3$): δ = 1.73 (s, 3 H, CH_3) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 32.8 (s) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 224.6 (s, Ir*C*O); 14.7 (s, CH_3) ppm. $C_{42}H_{36}ClIrN_2O_8P_2{\cdot}CH_3OH$ (1018.16): calcd. C 50.71, H 3.96, N 2.75; found C 50.57, H 4.10, N 2.94.

[Ir(PPh_2(*o*-C_6H_4CO))$_2$(boh)]ClO_4 (5): To a methanol suspension of [IrH{(PPh_2(*o*-C_6H_4CO))$_2$H}Cl] (**1**) (50 mg, 0.062 mmol) was added biacetyloxime hydrazone (boh) (8.7 mg, 0.062 mmol). The suspension was refluxed for 90 min whereupon a yellow solution was formed. The solution was cooled and a methanol solution of $NaClO_4{\cdot}H_2O$ (7.6 mg, 0.062 mmol) was added to afford a yellow solid that was decanted, washed with methanol and dried under vacuum. Yield 37.3 mg, 61%. IR (KBr): $\tilde{\nu}$ = 3341 (w) (OH), 3395 (w), 3201 (w) (NH), 1607 (s) (C=O) cm^{-1}. Λ_M ($ohm^{-1}cm^2mol^{-1}$): 94 (acetone). ^1H NMR ($CDCl_3$): δ = 10.6 (s, 1 H, OH); 6.17 (s, 2 H, NH); 1.72 (s, 3 H, CH_3); 1.56 (s, 3 H, CH_3) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 37.3 (d) and 26.7 (d) [J(P,P) = 273 Hz] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 233.9 [d, J(P,CO) = 4 Hz, Ir*C*O]; 214.6 [d, J(P,CO) = 4 Hz, Ir*C*O]; 13.6 (s, CH_3); 13.2 (s, CH_3) ppm. $C_{42}H_{37}ClIrN_3O_7P_2{\cdot}CH_3OH$ (1017,17): calcd. C 50.76, H 4.06, N 4.13; found C 50.40, H 4.01, N 4.02.

[IrCl(PPh_2(*o*-C_6H_4CO))$_2$(py)] (6): To a methanol suspension of [IrH{(PPh_2(*o*-C_6H_4CO))$_2$H}Cl] (**1**) (50 mg, 0.062 mmol) was added pyridine (py) (5 μL, 0.062 mmol). The suspension was refluxed for 3 h whereupon a yellow solution was formed. The solution was cooled and evaporation of the methanol solution under vacuum afforded a yellow solid that was decanted, washed with methanol and dried under vacuum. Yield 31.8 mg, 58%. IR (KBr): $\tilde{\nu}$ = 1624 (s) (C=O) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 33.5 (d) and 29.0 (d) [J(P,P) = 347 Hz] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 211.4 [d, J(P,C) = 2 Hz, Ir*C*O]; 209.8 [d, J(P,C) = 4 Hz, Ir*C*O] ppm. FAB-MS: calcd. for $C_{43}H_{33}ClIrNO_2P_2$, 885; obsd. 806 [M – py^+]. $C_{43}H_{33}ClIrNO_2P_2{\cdot}CH_3OH$ (917.16): calcd. C 57.61, H 4.07, N 1.53; found C 57.30, H 3.95, N 1.84.

Reaction of 1 with 2-Methylpyiridine. Formation of [Ir_2(μ-Cl)(μ-PPh_2(*o*-C_6H_4CO))$_2$(PPh_2(*o*-C_6H_4CO))$_2$]Cl [7]Cl: To a methanol suspension of [IrH{(PPh_2(*o*-C_6H_4CO))$_2$H}Cl] (**1**) (30 mg, 0.037 mmol) was added 2-methylpyridine (3.7 μL, 0.037 mmol). The suspension was refluxed for 90 min whereupon a yellow solution was formed. The solution was cooled and evaporation of the methanol solution under vacuum afforded an equimolar mixture of [**7a**]Cl and [**7b**]Cl that was identified by NMR spectroscopy.

[Ir_2(μ-Cl)(μ-PPh_2(*o*-C_6H_4CO))$_2$(PPh_2(*o*-C_6H_4CO))$_2$]ClO_4 [7a]ClO_4 and [7b]ClO_4: A methanol suspension of [IrH{(PPh_2(*o*-C_6H_4CO))$_2$H}Cl] (**1**) (50 mg, 0.062 mmol) was refluxed for 10 h whereupon a yellow solution was formed. The solution was cooled and a methanol solution of $NaClO_4{\cdot}H_2O$ (1.8 mg, 0.031 mmol) was added to afford a yellow solid, [**7a**]ClO_4, which was decanted, washed with methanol and dried under vacuum. Yield 24.9 mg, 48%. To the remaining solution a methanol solution of $NaClO_4{\cdot}H_2O$ (1.8 mg, 0.031 mmol) was added to afford a yellow solid, [**7b**]ClO_4, which was decanted, washed with methanol and dried under vacuum. Yield 15.6 mg, 30%. Data for [**7a**]ClO_4. IR (KBr): $\tilde{\nu}$ = 1638 (s) $(C=O)_t$, 1516 (s) $(C=O)_b$ cm^{-1}. Λ_M ($ohm^{-1}cm^2mol^{-1}$): 137 (acetone). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 21.9 [d, J(P,P) = 3 Hz, P_a]; 9.9 (d, P_b) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 264.9 [d, J(P,C) = 99 Hz, IrC_aO]; 197.6 [d, J(P,C) = 6 Hz, IrC_bO] ppm. FAB-MS: calcd. for $C_{76}H_{56}ClIr_2O_4P_4$, 1577; obsd. 1577 [M^+]. $C_{76}H_{56}Cl_2Ir_2O_8P_4{\cdot}2CH_3OH$ (1740.22): calcd. C 53.82, H 3.71; found C 53.49, H 3.55. Data for [**7b**]ClO_4. IR (KBr): $\tilde{\nu}$ = 1633 (s) $(C=O)_t$, 1515 (s) $(C=O)_b$ cm^{-1}. Λ_M ($ohm^{-1}cm^2mol^{-1}$): 95 (acetone). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 20.2 (d) and 17.4 (d) [J(P,P) = 9 Hz]; 17.8 (d) and 13.4 (d) [J(P,P) = 6 Hz] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 263.8 [d, J(P,C) = 102 Hz]; 263.1 [d, J(P,C) = 102 Hz]; 198.9 [d, J(P,C) = 8 Hz] and 195.7 (m) for Ir*C*O ppm. FAB-MS: calcd. for $C_{76}H_{56}Cl$-

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$Ir_2O_4P_4$, 1577; obsd. 1577 [M^+]. $C_{76}H_{56}Cl_2Ir_2O_8P_4$ (1676.16): calcd. C 54.45, H 3.37; found C 54.46, H 3.71.

Catalytic Reactions: The transfer hydrogenation reactions were carried out under nitrogen in refluxing 2-propanol with magnetic stirring. The equipment consisted of a 100-mL round-bottomed flask, fitted with a condenser and provided with a septum cap. The catalysts, as chloride compounds, were prepared "in situ" by refluxing equimolar amounts (0.02 mmol) of **1** and the corresponding ligand in MeOH to obtain solutions. After cooling, the methanol was eliminated under vacuum. The solid residue was dissolved in 30 mL of 2-propanol and 0.2 mmol of potassium hydroxide in 10 mL of 2-propanol were added. The resulting solutions were heated to 83 °C and 4 mmol of the substrate was injected. The analysis of the catalytic reactions was carried out with a Shimadzu GC-14A chromatograph, connected to a Shimadzu C-R6A calculation integrator.

X-ray Structure Determination of 6 and [7b]ClO_4: Prismatic yellow crystals of $[C_{43}H_{33}Cl_1N_1O_2P_2Ir]$ and $[C_{76}H_{56}Cl_1O_4P_4Ir_2]ClO_4$ suitable for X-ray experiments were obtained by slow diffusion of diethyl ether into chloroform solutions of **6** or [**7b**]ClO_4. A summary of the fundamental crystal and refinement data are given in Table 2. The crystals were resin epoxy coated and mounted on a Bruker Smart CCD diffractometer, with graphite-monochromated Mo-K_α (λ = 0.71073) radiation, operating at 50 kV and 20 mA. Data were collected over a hemisphere of the reciprocal space by combination of three exposure sets. Each frame exposure time was of 20s, covering 0.3° in ω. The cell parameters were determined and refined by a least-squares fit of all reflections collected. The first 100 frames were recollected at the end of the data collection to monitor crystal decay, and no appreciable decay was observed. In both cases a semi-empirical absorption correction was applied. The structures were solved by direct methods and conventional Fourier techniques and refined by applying full-matrix least-squares on F^2 with anisotropic thermal parameters for the non-hydrogen atoms, with the exception of the oxygen atoms of the perchlorate anions of **7b**, which were refined isotropically. The hydrogen atoms were included at their calculated positions determined by molecular geometry and refined riding on the corresponding bonded atom. All the calculations were carried out with SHELX-97.[17]

CCDC-767995 (for **6**) and -767996 (for **7b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

Table 2. Crystal data and structure refinement for compounds **6** and [**7b**]ClO_4.

Crystal data	**6**	[**7b**]ClO_4
Empirical formula	$[C_{43}H_{33}Cl_1IrN_1O_2P_2]$	$[C_{76}H_{56}Cl_1Ir_2O_4P_4]ClO_4$
Formula weight	885.29	1676.39
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a [Å]	12.0866(5)	20.471(1)
b [Å]	17.2053(7)	11.864(1)
c [Å]	17.7139(7)	28.438(2)
[°]	99.837(1)	99.352(1)
Volume [Å^3]	3629.5(3)	6814.5(8)
Z	4	4
D(calcd.) [g cm^{-3}]	1.620	1.634
Absorption coefficient [mm^{-1}]	3.879	4.130
Scan technique	ω and ϕ	ω and ϕ
F(000)	1752	3296
Range for data collection [°]	1.66 to 25.00	1.14 to 25.00
Index ranges	–14, –20, –20 to 13,19,20	–21, –14, –33 to 24,14,22
Reflections collected	25701	34851
Independent reflections	6091 [R(int) = 0.0450]	12015 [R(int) = 0.065]
Completeness to theta	95.2%	100.0%
Data / restraints / parameters	6091 / 0 / 451	12015 / 0 / 805
Goodness-of-fit on F^2	1.063	1.082
R[a] (refl. obsd.) [$I > 2\sigma(I)$]	0.0303 (4490)	0.0516 (7132)
Rw_F[b](all data)	0.0698	0.1463
Largest diff. peak and hole	0.922 and –0.649 eÅ^{-3}	1.329 and –1.181 eÅ^{-3}

[a] $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

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[1] a) M. A. Garralda, R. Hernández, L. Ibarlucea, E. Pinilla, M. R. Torres, *Organometallics* **2003**, *22*, 3600–3603; b) M. A. Garralda, *Dalton Trans.* **2009**, 3635–3645; c) R. Ciganda, M. A. Garralda, L. Ibarlucea, E. Pinilla, M. R. Torres, *Dalton Trans.* **2009**, 4227–4235.
[2] a) C. M. Lukehart, *Acc. Chem. Res.* **1981**, *14*, 109–116; b) C. M. Lukehart, *Adv. Organomet. Chem.* **1986**, *25*, 45–71; c) D. Steinborn, *Dalton Trans.* **2005**, 2664–2671; d) D. Steinborn, S. Schwieger, *Chem. Eur. J.* **2007**, *13*, 9668–9678.
[3] a) F. Acha, M. A. Garralda, L. Ibarlucea, E. Pinilla, M. R. Torres, *Inorg. Chem.* **2005**, *44*, 9084–9091; b) F. Acha, M. A. Garralda, R. Hernández, L. Ibarlucea, E. Pinilla, M. R. Torres, M. Zarandona, *Eur. J. Inorg. Chem.* **2006**, 3893–3900.
[4] F. Acha, R. Ciganda, M. A. Garralda, R. Hernández, L. Ibarlucea, E. Pinilla, M. R. Torres, *Dalton Trans.* **2008**, 4602–4611.
[5] W. J. Geary, *Coord. Chem. Rev.* **1971**, *7*, 81–122.
[6] a) T. G. Appleton, H. C. Clark, L. E. Manzer, *Coord. Chem. Rev.* **1973**, *10*, 335–422; b) O. Blum, R. Carmielli, J. M. L. Martin, D. Milstein, *Organometallics* **2000**, *19*, 4608–4612; c) M. A. Garralda, R. Hernández, L. Ibarlucea, E. Pinilla, M. R. Torres, M. Zarandona, *Organometallics* **2007**, *26*, 5369–5376; d) M. A. Garralda, R. Hernández, E. Pinilla, M. R. Torres, M. Zarandona, *Dalton Trans.* **2009**, 9860–9869.
[7] a) J. N. Coalter III, J. C. Huffman, K. G. Caulton, *Organometallics* **2000**, *19*, 3569–3578; b) W. Yao, R. H. Crabtree, *Inorg. Chem.* **1996**, *35*, 3007–3011; c) L. M. Epstein, E. S. Shubina, *Coord. Chem. Rev.* **2002**, *231*, 165–181; d) M. A. Garralda, R. Hernández, L. Ibarlucea, E. Pinilla, M. R. Torres, M. Zarandona, *Organometallics* **2007**, *26*, 1031–1038.
[8] A. Friedrich, M. Drees, J. Schmedt auf der Günne, S. Schneider, *J. Am. Chem. Soc.* **2009**, *131*, 17552–17553.
[9] a) G. R. Clark, T. R. Greene, W. R. Roper, *J. Organomet. Chem.* **1985**, *293*, C25–C28; b) M. V. Jiménez, E. Sola, A. P. Martínez, F. J. Lahoz, L. A. Oro, *Organometallics* **1999**, *18*, 1125–1136; c) S. N. Paisner, P. Burger, R. G. Bergman, *Organometallics* **2000**, *19*, 2073–2083.
[10] J. M. O'Connor, R. Merwin, A. L. Rheingold, M. L. Adams, *Organometallics* **1995**, *14*, 2102–2105.
[11] A. Albinati, H. Lehner, L. M. Venanzi, *Inorg. Chem.* **1985**, *24*, 1483–1488.
[12] a) A. Musco, R. Naegeli, L. M. Venanzi, A. Albinati, *J. Organomet. Chem.* **1982**, *228*, C15–C18; b) H. Lehner, D. Matt, A. Togni, R. Thouvenot, L. M. Venanzi, A. Albinati, *Inorg. Chem.* **1984**, *23*, 4254–4261.

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[13] a) J. E. Bäckvall, *J. Organomet. Chem.* **2002**, *652*, 105–111; b) S. E. Clapham, A. Hadzovic, R. H. Morris, *Coord. Chem. Rev.* **2004**, *248*, 2201–2237; c) J. S. M. Samec, J. E. Bäckvall, P. G. Andersson, P. Brandt, *Chem. Soc. Rev.* **2006**, *35*, 237–248; d) S. Gladiali, E. Alberico, *Chem. Soc. Rev.* **2006**, *35*, 226–236.
[14] a) M. Albrecht, J. R. Miecznikowski, A. Samuel, J. W. Faller, R. H. Crabtree, *Organometallics* **2002**, *21*, 3596–3604; b) A. Choualeb, A. J. Lough, D. G. Gusev, *Organometallics* **2007**, *26*, 5224–5229.
[15] TOF calculated after 10 min and expressed in mol of product/(mol of pre-catalyst × h).
[16] A. Pontes da Costa, M. Viciano, M. Sanaú, S. Merino, J. Tejeda, E. Peris, B. Royo, *Organometallics* **2008**, *27*, 1305–1309.
[17] G. M. Sheldrick, *SHELX-97*, *Program for Crystal Structure Determination*, University of Göttingen, Göttingen, Germany, **1997**.

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