Synthesis and Characterisation of New Iridium Complexes with the (4*S*)-2-[2-(Diphenylphosphanyl)phenyl]-4-isopropyl-1,3-oxazoline Ligand That Catalyse Asymmetric Michael Reactions

Daniel Carmona,*[a] Joaquina Ferrer,[a] Mónica Lorenzo,[a] Fernando J. Lahoz,[a] Isabel T. Dobrinovitch,[a] and Luis A. Oro[a]

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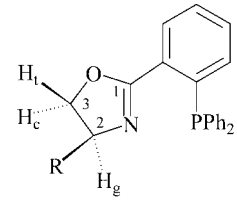
The chiral iridium compounds [IrCl(COE){(*S*)-PN}] {COE = cyclooctene, PN = (4*S*)-2-[2-(diphenylphosphanyl)phenyl]-4-isopropyl-1,3-oxazoline, (**1**)}, [Ir(acac)ClH{(*S*)-PN}] {Hacac = acetylacetone, (**2**)} and [Ir{(*S*)-PN}$_2$]A {A = Cl (**3a**,**b**); BF_4 (**4a**,**b**); PF_6 (**5a**,**b**)} have been prepared, characterised and employed as catalysts for the asymmetric Michael addition of keto or cyano esters to α,β-unsaturated carbonyl compounds. The X-ray molecular structures of compounds **2** and **5b** are reported. The model catalytic intermediates [IrH(NCCHCO$_2$R){(*S*)-PN}$_2$]Cl {R = Me (**12**), Et (**13**)} have also been isolated and characterised.

Introduction

The catalytic asymmetric Michael reaction is a powerful and valuable method for the formation of C–C bonds β to a carbonyl group[1] that often allows construction of quaternary carbon centres.[2] Pioneering work was performed by Wynberg et al., who studied the use of chincona alkaloids as catalysts.[3] In 1984, Brunner and Hammer reported the first example of a transition-metal-catalysed asymmetric Michael addition, employing a complex derived from Co(acac) and (*S*,*S*)-1,2-diphenyl-1,2-ethylenediamine.[4] Since then, much attention has been paid to transition-metal-based systems for the asymmetric catalysis of the Michael reaction, and a variety of chiral transition-metal-based catalysts have been developed by several groups.[2b,5–11] Particularly important are the results achieved by Shibasaki et al. with their heterodimetallic catalysts in the Michael reaction of β-dicarbonyls or hydroxyketones with α,β-unsaturated carbonyls.[12] Related heterodimetallic catalysts have been subsequently developed by others.[13] However, although a few platinum-metal-based compounds have been employed as Michael reaction catalysts, the use of iridium derivatives for this reaction is very scarce.[14] On the other hand, most of the metallic catalytic systems are generated in situ by mixing the appropriate metallic precursor and the chiral ligand, and therefore the actual structure of the involved coordination compound(s) is usually unknown.

[a] Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, C.S.I.C. – Universidad de Zaragoza, Instituto Universitario de Catálisis Homogénea, Universidad de Zaragoza,
Pedro Cerbuna 12, 50009 Zaragoza, Spain
Fax: +34-76-761187
E-mail: dcarmona@posta.unizar.es

During our studies on phosphanyloxazoline iridium complexes,[15] we realised that the iridium(I) compound [IrCl(COE){(*S*)-PN}] {COE = cyclooctene, PN = (4*S*)-2-[2-(diphenylphosphanyl)phenyl]-4-isopropyl-1,3-oxazoline, (Scheme 1)} (**1**) activated the sp^3 CH methylene bonds of the acetylacetone (Hacac), affording the hydrido(enolato)-iridium(III) [Ir(acac)ClH{(*S*)-PN}] (**2**). The diastereoselective formation of **2** from **1** prompted us to test complex **1** as a catalyst for Michael addition reactions. In this context, Murahashi, Komiya, et al. have reported the formation of the hydrido(enolato)ruthenium(II) complexes, *mer*-[RuH(acac)(PPh$_3$)$_3$] and *mer*-[RuH(NCCHCO$_2$R)(NCCH$_2$CO$_2$R)(PPh$_3$)$_3$], by reacting either the dihydride [RuH$_2$(PPh$_3$)$_4$] or the orthometalated ethylene complex [RuH(PPh$_2$C$_6$H$_4$)(C$_2$H$_4$)(PPh$_3$)$_2$] with Hacac or alkylcyanoacetates, respectively.[16] Notably, it has been shown that a variety of transition-metal α-cyanocarbanion complexes, including the aforementioned, are intermediates in the catalytic Michael reactions of nitriles.[16,17] Furthermore, very recently, Ikayira et al. have isolated and characterised a chiral metal-carbon-bound ruthenium–malonato complex,



R = *i*Pr, (*S*)-PN;
*i*Bu, (*S*)-PN'

Scheme 1. Phosphanyloxazoline ligands.

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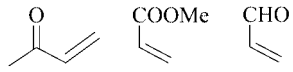
which is the plausible intermediate in the asymmetric Michael reaction of α-substituted acetates with cyclic enones.[18]

Here we report on the synthesis and characterisation of the phosphanyloxazoline iridium complexes **1** and **2**, the related bis(*S*)-PN ligand cationic compounds [Ir{(*S*)-PN}$_2$]A {A = Cl (**3a,b**); BF_4 (**4a,b**); PF_6 (**5a,b**)}, as well as, on their use as catalysts for the Michael addition of cyano or keto esters **6** and **7** to α,β-unsaturated carbonyls **8**–**10** (Scheme 2). The X-ray molecular structures of compounds **2** and **5b** are also included. Furthermore, we also report the preparation and characterisation of the hydrido(enolate)-iridium(III) complexes [IrH(NCCHCO$_2$R){(*S*)-PN}$_2$]Cl {R = Me (**12**), Et (**13**)}, derived from **11a** and **11b**, as possible model intermediates in the catalytic Michael process.

R^1 = Me; R = Me, **6a**; Et, **6b**
R^1 = H; R = Me, **11a**; Et, **11b**

R = Me, **7a**; Et, **7b**



8 **9** **10**

Scheme 2. Catalytic Michael reaction substrates.

Results and Discussion

Treatment of the dimer [Ir(μ-Cl)(COE)$_2$]$_2$[19] with two equivalents of (*S*)-PN, in pentane at –60 °C, afforded [IrCl(COE){(*S*)-PN}] (**1**). Since solutions of **1** in common organic solvents slowly decompose, attempts to obtain an analytically pure sample of this complex failed. However, the spectroscopic data for the generated species, collected at –60 °C, leave no doubt that the proposed formulation for **1** is correct (see Experimental Section).

Complex **1** reacted with acetylacetone, through activation of an sp^3 CH methylene bond, affording the hydrido(enolato)iridium(III) complex [Ir(acac)ClH{(*S*)-PN}] (**2**) stereoselectively. The spectroscopic data indicated the formation of a major isomer (95%) together with trace amounts of some other uncharacterised stereoisomers. The molecular structure of **2** has been determined by a single-crystal X-ray diffraction study (Figure 1). Selected bond parameters are reported in Table 1. Complex **2** has a distorted octahedral coordination environment. The metal centre is coordinated to the two oxygen atoms of an acetylacetonate anion and to the phosphorus and nitrogen atoms of the (*S*)-PN ligand. A chloride anion and a hydride ligand, mutually *trans* (Cl–Ir–H, 169.7°), complete the coordination sphere of the iridium atom. The metal atom is chiral, and the isomer present in the crystal is the *OC*-6–53-*A* diastereomer. The Ir–Cl bond length, 2.512(2) Å, is significantly longer than the mean value observed for terminal chlorides in octahedral Ir complexes, 2.426(7) Å;[20] most probably this fact is a consequence of the high *trans* influence of the hydride that elongates the Ir–Cl bond length to a mean value of 2.500(2) Å when both ligands are situated in a *trans* position relative to each other.[20]

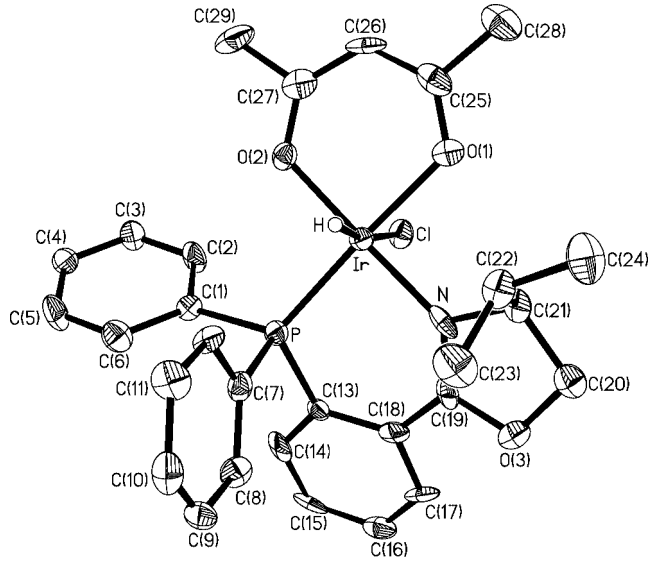


Figure 1. Molecular structure of **2** (organic hydrogen atoms are omitted for clarity).

The highly diastereoselective formation of **2** from **1** prompted us to test complex **1** as a catalyst for Michael addition reactions. A mixture of [Ir(μ-Cl)(COE)$_2$]$_2$ and two equivalents of (*S*)-PN catalysed the addition of the α-cyano propionate **6b** or the β-keto ester **7b** to methyl vinyl ketone with 23 and 26.5% *ee*, respectively. To improve the stereoselectivity, we tried to incorporate one additional (*S*)-PN group to the iridium coordination sphere. Thus, treatment of the dimer [Ir(μ-Cl)(COE)$_2$]$_2$ with 4.5 equivalents of (*S*)-PN, in acetone or dichloromethane, at room temperature, afforded cationic [Ir{(*S*)-PN}$_2$]Cl (**3**) in 75% yield. Complex **3** was isolated as a mixture of two isomers in relative amounts of about 60% (**3a)** and 40% (**3b**). Pure samples of both isomers could be obtained: pure **3b** was obtained when the reaction was carried out in toluene, and complex **3b** isomerised quantitatively to **3a** after refluxing two hours in acetone.

Furthermore, the chloride can be metathetically replaced by the reaction of **3** with $NaBF_4$ or KPF_6, affording the corresponding [Ir{(*S*)-PN}$_2$]A {A = BF_4 (**4a,b**); PF_6 (**5a,b**)} salts.

To obtain further structural information about these complexes, the molecular structure of compound **5b** was determined by X-ray diffractometric methods (Figure 2). Selected bond parameters are reported in Table 1. The cation presents a highly distorted square-planar geometry with relative *trans* arrangement of nitrogen and phosphorus atoms of both (*S*)-PN ligands. Both Ir–P–C–C–C–N six-membered metallacycles adopt an $^1S_2$ screw-boat conformation[21] with a relative *anti* disposition to each other (Figure 3). A similar arrangement has been previously found in

Table 1. Selected bond lengths [Å] and angles [°] for metal complexes **2** and **5b**.

Complex **2**					
Ir–Cl	2.512(2)		C(13)–C(18)	1.418(10)	
Ir–P	2.197(2)		C(18)–C(19)	1.459(12)	
Ir–N	2.002(7)		N–C(19)	1.289(11)	
Ir–O(1)	2.093(6)		O(1)–C(25)	1.244(11)	
Ir–O(2)	2.009(6)		O(2)–C(27)	1.273(10)	
Ir–H	1.61		C(25)–C(26)	1.407(13)	
P–C(13)	1.815(8)		C(26)–C(27)	1.366(13)	
Cl–Ir–P	97.30(8)		N–Ir–O(2)	177.9(3)	
Cl–Ir–N	91.1(2)		N–Ir–H	95.3	
Cl–Ir–O(1)	88.65(16)		O(1)–Ir–O(2)	91.0(2)	
Cl–Ir–O(2)	87.01(16)		O(1)–Ir–H	83.5	
Cl–Ir–H	169.7		O(2)–Ir–H	86.5	
P–Ir–N	87.89(19)		Ir–P–C(13)	111.0(3)	
P–Ir–O(1)	172.84(16)		Ir–N–C(19)	131.2(6)	
P–Ir–O(2)	93.28(17)		P–C(13)–C(18)	118.1(6)	
P–Ir–H	91.0		C(13)–C(18)–C(19)	124.0(8)	
N–Ir–O(1)	88.0(2)		N–C(19)–C(18)	128.9(8)	
Complex **5b**[a]					
Ir–P(1)	2.2063(14)	2.2103(13)	Ir–N(1)	2.088(4)	2.115(4)
P(1)–C(13)	1.853(5)	1.851(5)	C(18)–C(19)	1.476(8)	1.478(7)
C(13)–C(18)	1.405(7)	1.410(7)	N(1)–C(19)	1.277(7)	1.283(7)
P(1)–Ir–P(51)	101.29(5)		P(51)–Ir–N(1)	167.50(13)	
P(1)–Ir–N(1)	85.05(12)		P(51)–Ir–N(51)	87.07(12)	
P(1)–Ir–N(51)	168.94(13)		N(1)–Ir–N(51)	88.16(16)	
Ir–P(1)–C(13)	108.69(18)	108.22(17)	C(13)–C(18)–C(19)	121.4(5)	123.5(5)
Ir–N–C(19)	130.5(4)	126.6(4)	N–C(19)–C(18)	128.0(5)	128.8(5)
P(1)–C(13)–C(18)	120.8(4)	121.1(4)			

[a] When two values are given in the table, they represent analogous parameters from the two independent (*S*)-PN ligands of complex **5b**.

the related rhodium compound[22] $[Rh\{(S)\text{-}PN\}_2]BF_4$, as well as in the nickel(II) derivative[23] $[Ni\{(S)\text{-}PN'\}_2][O_3SCF_3]_2$, where (*S*)-PN′ represents the *iso*-butyl derivative shown in Scheme 1.

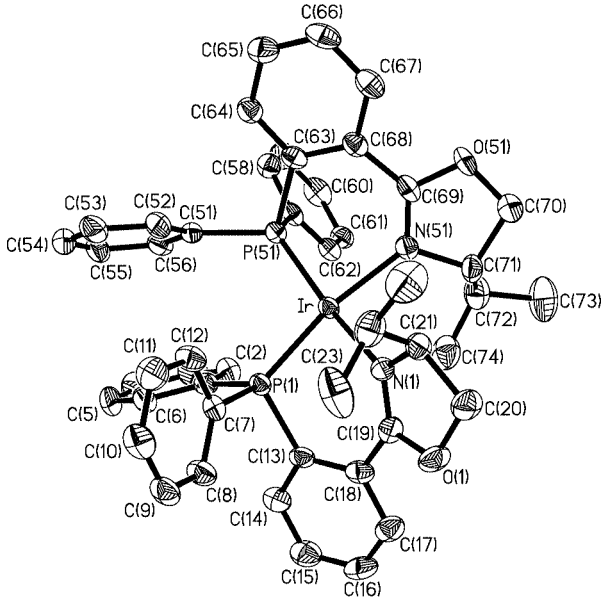


Figure 2. Molecular drawing of the cationic metal complex of **5b** (hydrogen atoms are omitted for clarity).

The NMR spectroscopic data of isomers only differing in the counter-anion are very similar, indicating that they

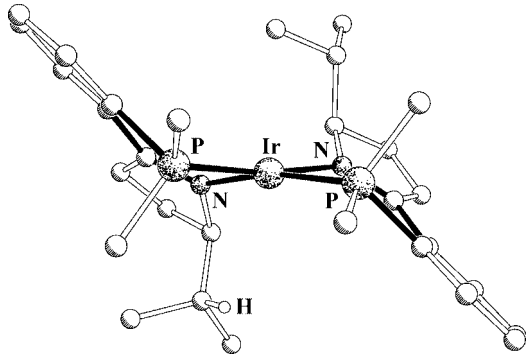


Figure 3. Relative *anti* conformation observed for the metallacycles Ir–P–C–C–C–N in the solid structure of **5b** (view along the pseudo C_2 axis).

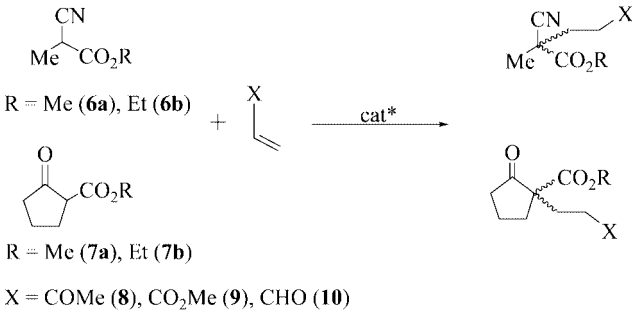
should have similar structure. However, while the NMR spectra of **3b-5b** present only one set of signals for the (*S*)-PN ligand, those of **3a-5a** reveal that the two (*S*)-PN ligands are not equivalent. From the molecular structure of **5b**, we propose that, in compounds labelled **b**, the equivalence in solution of the two (*S*)-PN ligands arises from the existence of a C_2 axis, contained in the coordination plane, that bisects the P–Ir–P and N–Ir–N angles (Figure 3). The value of the PP′ coupling constant in **3a**–**5a** is about 15 Hz. Thus, in both types of isomers the phosphorus atoms adopt a *cis* geometry.

Concerning the **3a-5a** isomers, the most notable feature of their ^1H NMR spectra is the shielding of about 1.4 ppm

of one of the CH isopropyl protons with respect to the other. Inspection of molecular models reveals that one of the CH isopropyl protons lies below the iridium coordination plane pointing to the metal (Figure 3). In fact, this proton is only 3.111(1) Å apart from the iridium in the solid structure of **5b**. From these data, we tentatively propose that the isomerization from **b** to **a** consists of the formation of a C–H···Ir agostic interaction[24] between the iridium atom and one of the CH isopropyl protons.

Preliminary results indicate that compounds **3**–**5** are active catalysts for the Michael addition of cyano or keto esters **6** and **7** to α,β-unsaturated carbonyls **8**–**10** (Scheme 3). Table 2 collects some selected results. Chloride **3b** is a very active catalyst for the Michael additions (entries 1–12), achieving quantitative conversion in most of the cases. However, the *ee* obtained are low. Unsymmetrical chloride **3a** (entries 13–15) is less active but more selective, affording *ee* of up to 39%. Surprisingly, changing the anion to BF_4 or PF_6 strongly decreases the activity (entries 16–22), rendering enantioselectivities ranging from 20 to 30% *ee*.

To obtain mechanistic information about the catalytic system, **3a** or **3b** were treated with excess of ethyl-2-cyanopropionate (**6b**) in catalytic conditions; no conclusive results were obtained, most of the starting substrates remained unaltered. However, when **3a** was reacted with the closely related α-cyanoacetates **11a** or **11b** (Scheme 2), the corresponding hydrido enolate iridium(III) complexes [IrH(NCCHCO$_2$R){(*S*)-PN}$_2$]Cl {R = Me (**12**), Et (**13**)} were diastereoselectively isolated in 85 and 88% yield, respectively. The IR spectra of compounds **12** and **13** show characteristic absorption bands at about 2175 and 2205 cm^{-1} assignable to ν(C≡N) and ν(Ir–H), respectively.



Scheme 3. Catalytic reactions.

An intense band due to ν(C=O) of the enolato ligand appears ca. 1667 cm^{-1}. The ^{1}H NMR spectra show a doublet of doublets at δ = –19.28 ppm (**12**) or –19.23 ppm (**13**) ($^2J_{PH}$ = 13.5, 26.6 Hz) attributed to a hydride ligand coupled to two nonequivalent phosphorus nuclei. Two singlets at δ = 3.57 and 3.18 ppm, assignable to the methyl and methine protons of the enolato ligand, are observed in the spectrum of **12**. For compound **13**, the methyl, methylene and methine protons of the enolato ligand resonate as a triplet at 1.21, a quartet at 4.08 and a singlet at 3.22 ppm, respectively. In both compounds the methine proton has no coupling with the phosphorus nuclei, suggesting that the enolate is N-bonded. The isolation of **12** and **13** from **3a** indicates that most probably, the oxidative addition of the sp^3 CH activated bond of the Michael donors to the iridium(I) complexes **3**–**5** would be the first step in the catalytic path. Interaction of the coordinated enolate with the Michael acceptor followed by adduct elimination would complete the catalytic cycle.

Table 2. Asymmetric Michael reactions using the new iridium compounds **3**–**5** as catalysts.[a]

Entry	Catalyst	Donor	Acceptor	Yield (%)[b]	*ee* (%)
1	[Ir{(*S*)-PN}$_2$]Cl (**3b**)	**6a**	MeCOCH=CH$_2$ (**8**)	100	1.5[c] (*R*)[d]
2		**6a**	COOMeCH=CH$_2$ (**9**)	100	1[c]
3		**6a**	CHOCH=CH$_2$ (**10**)	100	5.5[c]
4		**6b**	MeCOCH=CH$_2$ (**8**)	100	1.3[c] (*R*)[d]
5		**6b**	COOMeCH=CH$_2$ (**9**)	100	15.5[c]
6		**6b**	CHOCH=CH$_2$ (**10**)	100	3.5[c]
7		**7a**	MeCOCH=CH$_2$ (**8**)	66	25[e]
8		**7a**	COOMeCH=CH$_2$ (**9**)	1	10[e]
9		**7a**	CHOCH=CH$_2$ (**10**)	100	22.5[e]
10		**7b**	MeCOCH=CH$_2$ (**8**)	100	8.5[e]
11		**7b**	COOMeCH=CH$_2$ (**9**)	57	2[e]
12		**7b**	CHOCH=CH$_2$ (**10**)	100	2[e]
13	[Ir{(*S*)-PN}$_2$]Cl (**3a**)	**6b**	MeCOCH=CH$_2$ (**8**)	100	39[c] (*R*)[d]
14		**7b**	MeCOCH=CH$_2$ (**8**)	54	20.5[e]
15		**7b**	COOMeCH=CH$_2$ (**9**)	23	2.5[e]
16	[Ir{(*S*)-PN}$_2$]BF_4 (**4b**)	**6b**	MeCOCH=CH$_2$ (**8**)	18	28[c] (*R*)[d]
17		**7b**	MeCOCH=CH$_2$ (**8**)	9.5	24.5[e]
18	[Ir{(*S*)-PN}$_2$]PF_6 (**5b**)	**6b**	MeCOCH=CH$_2$ (**8**)	64	35[c] (*R*)[d]
19		**7b**	MeCOCH=CH$_2$ (**8**)	11	27.5[e]
20	[Ir{(*S*)-PN}$_2$]PF_6 (**5a**)	**7a**	CHOCH=CH$_2$ (**10**)	8	28[e]
21		**7b**	MeCOCH=CH$_2$ (**8**)	10	32[e]
22		**7b**	CHOCH=CH$_2$ (**10**)	90	22[e]

[a] All reactions run at room temperature, using 1 mol-% Ir catalyst, 1 equiv. of donor, 1.5 equiv. of acceptor, in toluene (5 mL). [b] After 22 h of reaction; determined by ^{1}H NMR spectroscopy. [c] Determined by gas chromatography using CP-Chirasil-CB column. [d] Determined by comparison to reported $[\alpha]_D$ data (see ref.[7a]). [e] Determined by gas chromatography using Lipodex-E column.

In summary, we report the first chiral iridium(I) compounds that are active catalysts for the Michael addition of keto or cyano esters to α,β-unsaturated carbonyl compounds. The enantioselectivity obtained is modest. In fact, few examples of highly enantioselective catalytic Michael addition versions for the synthesis of quaternary stereocentres have been demonstrated to date.[2,11n] However, the catalytic efficiency in these clean quaternary-carbon-centre-forming reactions is promising. Further studies to extend the catalytic reaction to other related metallic systems and substrates are currently under progress in our laboratory.

Experimental Section

General Comments: The compounds described herein were handled with exclusion of air by using standard Schlenk techniques. All solvents were dried by known procedures and distilled under argon prior to use. NMR spectra were recorded with a Varian Gemini 2000 or a Bruker Avance 400 spectrometer. Chemical shifts are expressed in ppm upfield from $SiMe_4$ (^1H, ^{13}C) or 85% H_3PO_4 in D_2O (^{31}P). Coupling constants (*J*) are given in Hertz. For proton and carbon labelling, see Scheme 1. Infrared spectra were recorded with a Perkin–Elmer 783 spectrophotometer. Carbon, hydrogen, and nitrogen analyses were performed with a Perkin–Elmer 240B microanalyser. Molar conductivities were measured in approximately 5×10^{-4} mol dm^{-3} acetone solutions with a Philips PW 9509 digital conductivity meter. Gas chromatographic analyses were performed with a Hewlett–Packard 8590A gas chromatograph equipped with CP-Chirasil-CB or Lipodex-E columns. Optical rotations were measured with a Jasco P-1020 polarimeter. [Ir(μ-Cl)(COE)$_2$]$_2$[19] and (4*S*)-2-[2-(diphenylphosphanyl)phenyl]-4-isopropyl-1,3-oxazoline[25] were prepared according to published procedures. Acetylacetone and compounds **7a**, **7b**, **8**, **9**, **10**, **11a**, and **11b** were purchased from Aldrich Co. Ltd. The α-cyanopropionates **6a** and **6b** were prepared as previously reported.[11f]

Preparation of [IrCl(COE){(*S*)-PN}] (1): (*S*)-PN (83.0 mg, 0.22 mmol) was added to a suspension of [Ir(μ-Cl)(COE)$_2$]$_2$ (100.0 mg, 0.11 mmol) in pentane (10 mL) at –60 °C, under argon. The suspension was stirred for 1 h. During this time, a change of colour from orange to brown took place. The solid formed was filtered off, washed with pentane and vacuum-dried. Yield: 66.0 mg (65%). ^1H NMR (400.13 MHz, $CDCl_3$, –60 °C): δ = 8.8–6.6 (m, 14 H, Ph), 5.93 (m, 1 H, H_g), 4.50 (br., 2 H, CH=CH), 4.34 (m, 2 H, H_c and H_t), 2.81 (m, 1 H, CH *i*Pr), 2.6–0.7 (m, 14 H, COE), 0.83 (d, *J* = 6.0 Hz, 3 H, Me *i*Pr), 0.09 (d, *J* = 6.0 Hz, 3 H, *i*Pr) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$, –60 °C): δ = 161.88 (C_1), 134.4–123.6 (Ph), 69.06 (C_2), 68.29 (C_3), 64.44 (br., CH=CH), 31.14 (CH *i*Pr), 31.94, 29.97, 26.93, 25.80 (CH_2 COE), 19.36, 13.83 (Me *i*Pr) ppm. $^{31}P\{^1H\}$ NMR (161.97 MHz, $CDCl_3$, –60 °C): δ = 10.1 (s) ppm. IR (Nujol mulls): $\tilde{\nu}$ = 1616 ($\nu_{C=N}$) cm^{-1}.

Preparation of [Ir(acac)ClH{(*S*)-PN}] (2): (*S*)-PN (83.0 mg, 0.22 mmol) was added to a solution of [Ir(μ-Cl)(COE)$_2$]$_2$ (100.0 mg, 0.11 mmol) in acetone (10 mL), under argon. The solution was stirred for 30 min, and then Hacac (0.3 mL) was added. The resulting solution was heated under reflux for 6 h and then concentrated under vacuum. Addition of *n*-hexane led to the precipitation of **2** as a yellow solid, which was filtered off, washed with *n*-hexane, and air-dried. Yield: 134.8 mg (86%). ^1H NMR (300.1 MHz, $CDCl_3$, r.t.): δ = 8.2–6.9 (m, 14 H, Ph), 5.35 (s, 1 H, CH acac), 5.09 (ddd, *J* = 10.2, 5.7, 3.0 Hz, 1 H, H_g), 4.48 (dd, *J* = 10.2, 9.0 Hz, 1 H, H_c), 4.29 (dd, *J* = 9.0, 5.7 Hz, 1 H, H_t), 2.57 (m, 1 H,CH *i*Pr), 1.91 (s, 3 H, Me acac), 1.54 (s, 3 H, Me acac), 0.72 (d, *J* = 7.0 Hz, 3 H, Me *i*Pr), –0.09 (d, *J* = 7.0 Hz, 3 H, Me *i*Pr), –22.86 (d, *J* = 18.5 Hz, 1 H Ir–H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$, r.t.): δ = 184.63 (CO acac), 183.81 (CO acac), 161.38 (C_1), 135.4–125.3 (Ph), 101.37 (CH acac), 69.02 (C_2), 66.52 (C_3), 30.93 (CH *i*Pr), 28.42 (Me acac), 26.82 (Me acac), 18.73 (Me *i*Pr), 11.93 (Me *i*Pr) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, r.t.): δ = –2.32 (s) ppm. IR (Nujol mulls): $\tilde{\nu}$ = 2216 (ν_{IrH}), 1617 ($\nu_{C=N}$) cm^{-1}. $C_{29}H_{32}ClIrNO_3P$ (701.223): calcd. C 49.74, H 4.61, N 2.00; found C 49.59, H 4.70, N 1.99.

Preparation of [Ir{(*S*)-PN}$_2$]Cl (3a, 3b): (*S*)-PN (187.7 mg, 0.50 mmol) was added to a solution of [Ir(μ-Cl)(COE)$_2$]$_2$ (100.0 mg, 0.11 mmol) in acetone (10 mL), under argon. The solution was refluxed for 2 h and then concentrated under vacuum. Addition of *n*-hexane led to the precipitation of **3a** as a red powder. Yield 185.1 mg (85%). Pure **3b** can also be obtained as a red powder by following the same procedure but using toluene as solvent. Yield 174.1 mg (80%). Compounds **3a** and **3b** had to be stored under argon. **3a:** ^1H NMR (300.1 MHz, CD_2Cl_2, r.t.): δ = 8.2–6.4 (m, 28 H, Ph), 5.25 (m, 1 H, H_g), 4.63 (m, 1 H, $H_{g'}$), 4.54 (m, 1 H, H_t), 4.36 (m, 2 H, $H_{t'}$, $H_{c'}$), 4.23 (m, 1 H, H_c), 2.78 (m, 1 H, CH *i*Pr), 1.42 (m, 1 H, CH *i*Pr′), 0.81 (d, *J* = 6.9 Hz, 3 H, Me *i*Pr′), 0.76 (d, *J* = 7.0 Hz, 3 H, Me *i*Pr), 0.22 (d, *J* = 6.6 Hz, 3 H, Me *i*Pr′), –0.09 (d, *J* = 6.9 Hz, 3 H, Me *i*Pr) ppm. ^{13}C NMR (75.4 MHz, CD_2Cl_2, r.t.): δ = 167.33 (d, *J* = 6.6 Hz), 164.39 (t, *J* = 4.8 Hz) (C_1, $C_{1'}$), 135.5–122.2 (Ph), 77.94, 70.16 (C_2, $C_{2'}$), 69.17, 69.09 (C_3, $C_{3'}$), 30.48, 29.40 (CH *i*Pr), 18.81, 18.34, 12.85, 12.78 (Me *i*Pr) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, r.t.): δ = –11.83 (d, *J* = 14.7 Hz), –13.09 (d) ppm. Molar conductivity (acetone) = 71.9 ohm^{-1} cm^2 mol^{-1}. $C_{48}H_{48}ClIrN_2O_2P_2$ (974.54): calcd. C 59.16, H 4.96, N 2.87; found C 58.64, H 6.44, N 2.58. **3b:** ^1H NMR (300.1 MHz, CD_2Cl_2, r.t.): δ = 8.2–6.4 (m, 28 H, Ph), 4.88 (dd, *J* = 9.6, 9.3 Hz, 1 H, H_c), 4.44 (dd, *J* = 9.6, 3.6 Hz, 1 H, H_t), 4.24 (m, 1 H, H_g), 2.26 (m, 1 H, CH *i*Pr), 0.90 (d, *J* = 6.9 Hz, 3 H, Me *i*Pr), 0.31 (d, *J* = 6.6 Hz, 3 H, Me *i*Pr) ppm. ^{13}C NMR (75.4 MHz, CD_2Cl_2, r.t.): δ = 163.48 (C_1), 135.5–122.2 (Ph), 73.54 (C_2), 69.90 (C_3), 32.36 (CH *i*Pr), 19.90, 15.60 (Me *i*Pr) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, r.t.): δ = 16.20 (s) ppm. $C_{48}H_{48}ClIrN_2O_2P_2$ (974.54): calcd. C 59.16, H 4.96, N 2.87; found C 58.54, H 6.35, N 2.96.

Preparation of [Ir{(*S*)-PN}$_2$]A {A = BF_4 (4a), PF_6 (5a)}: (*S*)-PN (187.7 mg, 0.50 mmol) and $NaBF_4$ or $NaPF_6$ (1 mmol) were added to a solution of [Ir(μ-Cl)(COE)$_2$]$_2$ (100.0 mg, 0.11 mmol) in acetone (10 mL), under argon. The resulting suspension was refluxed for 6 h, and the solvent was evaporated under vacuum. The residue was extracted with CH_2Cl_2 (10 mL) and filtered through a pad of Celite. The resulting solution was concentrated to ca. 1 mL, and the addition of diethyl ether led to the precipitation of a red solid, which was filtered off, washed with the precipitant and vacuum-dried. Yield 167.3 mg (73%) (**4a**) or 188.9 mg (78%) (**5a**). Complexes **4a** and **5a** had to be stored under argon. **4a:** ^1H NMR (300.1 MHz, CD_2Cl_2, r.t.): δ = 8.2–6.4 (m, 28 H, Ph), 5.32 (m, 1 H, H_g), 4.62 (m, 1 H, $H_{g'}$), 4.52 (m, 1 H, H_t), 4.34 (m, 2 H, $H_{t'}$, $H_{c'}$), 4.25 (m, 1 H, H_c), 2.83 (m, 1 H, CH *i*Pr), 1.50 (m, 1 H, CH *i*Pr′), 0.82 (d, *J* = 7.1 Hz, 3 H, Me *i*Pr′), 0.78 (d, *J* = 6.9 Hz, 3 H, Me *i*Pr), 0.23 (d, *J* = 6.4 Hz, 3 H, Me *i*Pr′), 0.07 (d, *J* = 6.9 Hz, 3 H, Me *i*Pr) ppm. ^{13}C NMR (75.4 MHz, CD_2Cl_2, r.t.): δ = 167.43 (d, *J* = 6.5 Hz), 164.49 (t, *J* = 4.8 Hz) (C_1, $C_{1'}$), 134.5–127.2 (Ph), 78.21, 70.25 (C_2, $C_{2'}$), 69.45, 69.26 (C_3, $C_{3'}$), 30.79, 29.74 (CH *i*Pr), 19.13, 18.55, 13.13, 13.13 (Me *i*Pr) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, r.t.): δ = –10.91 (d, *J* = 15.1 Hz), –12.33 (d) ppm. $C_{48}H_{48}BF_4IrN_2O_2P_2$ (1025.89): calcd. C 56.19, H 4.71, N

2.72; found C 55.63, H 4.07, N 2.11. **5a:** ^{1}H NMR (300.1 MHz, CD_2Cl_2, r.t.): δ = 8.2–6.4 (m, 28 H, Ph), 5.31 (m, 1 H, H_g), 4.60 (m, 1 H, $H_{g'}$), 4.58 (m, 1 H, $H_{t'}$), 4.51 (dd, J = 9.6, 2.2 Hz, 1 H, H_t), 4.31 (m, 1 H, $H_{c'}$), 4.24 (pt, J = 9.0 Hz, 1 H, H_c), 2.81 (m, 1 H, CH *i*Pr), 1.41 (m, 1 H, CH *i*Pr′), 0.81 (d, J = 7.2 Hz, 3 H, Me *i*Pr′), 0.77 (d, J = 6.9 Hz, 3 H, Me *i*Pr), 0.22 (d, J = 6.6 Hz, 3 H, Me *i*Pr′), –0.09 (d, J = 6.9 Hz, 3 H, Me *i*Pr) ppm. ^{13}C NMR (75.4 MHz, CD_2Cl_2, r.t.): δ = 167.43 (d, J = 6.5 Hz), 164.52 (t, J = 4.8 Hz) (C_1, $C_{1'}$), 134.5–127.2 (Ph), 78.07, 70.09 (C_2, $C_{2'}$), 69.26, 69.08 (C_3, $C_{3'}$), 30.55, 29.51 (CH *i*Pr), 18.86, 18.29, 12.84, 12.84 (Me *i*Pr) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, r.t.): δ = –10.72 (d, J = 14.7 Hz), –12.03 (d) ppm. $C_{48}H_{48}F_6IrN_2O_2P_3$ (1084.049): calcd. C 53.18, H 4.46, N 2.58; found C 52.56, H 4.89, N 2.60.

Preparation of [Ir{(*S*)-PN}$_2$]A {A = BF$_4$ (4b), PF$_6$ (5b)}: Complexes **4b** and **5b** were prepared as described for **4a** or **5a**, but the reactions were carried out at room temperature. Complexes **4b** and **5b** had to be stored under argon. **4b:** ^{1}H NMR (300.1 MHz, CD_2Cl_2, r.t.): δ = 8.0–6.8 (m, 28 H, Ph), 4.48 (pt, J = 9.6 Hz, 1 H, H_c), 4.46 (dd, J = 10.0, 3.7 Hz, 1 H, H_t), 4.28 (m, 1 H, H_g), 2.27 (m, 1 H, CH *i*Pr), 0.90 (d, J = 6.9 Hz, 3 H, Me *i*Pr), 0.30 (d, J = 6.6 Hz, 3 H, Me *i*Pr) ppm. ^{13}C NMR (75.4 MHz, CD_2Cl_2, r.t.): δ = 163.48 (C_1), 135.5–122.2 (Ph), 73.54 (C_2), 69.90 (C_3), 32.36 (CH *i*Pr), 19.90, 15.60 (Me *i*Pr) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, r.t.): δ = 17.16 (s) ppm. $C_{48}H_{48}BF_4IrN_2O_2P_2$ (1025.89): calcd. C 56.19, H 4.71, N 2.72; found C 55.69, H 4.11, N 2.09. **5b:** ^{1}H NMR (300.1 MHz, CD_2Cl_2, r.t.): δ = 8.2–6.4 (m, 28 H, Ph), 4.48 (pt, J = 9.6 Hz, 1 H, H_c), 4.44 (dd, J = 9.9, 3.7 Hz, 1 H, H_t), 4.20 (m, 1 H, H_g), 2.21 (m, 1 H, CH *i*Pr), 0.90 (d, J = 6.9 Hz, 3 H, Me *i*Pr), 0.30 (d, J = 6.6 Hz, 3 H, Me *i*Pr) ppm. ^{13}C NMR (75.4 MHz, CD_2Cl_2, r.t.): δ = 163.48 (C_1), 135.5–122.2 (Ph), 73.54 (C_2), 69.90 (C_3), 32.36 (CH *i*Pr), 19.90, 15.60 (Me *i*Pr) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, r.t.): δ = 17.09 (s) ppm. $C_{48}H_{48}F_6IrN_2O_2P_3$ (1084.049): calcd. C 53.18, H 4.46, N 2.58; found C 52.61, H 4.89, N 2.08.

Preparation of [IrH(NCCHCO$_2$R){(*S*)-PN}$_2$]Cl {R = Me (12), Et (13)}: A solution of (*S*)-PN (187.7 mg, 0.50 mmol) in acetone (2 mL) was added to a solution of $[Ir(\mu\text{-}Cl)(COE)_2]_2$ (100.0 mg, 0.11 mmol) in the same solvent (12 mL) at ambient temperature under argon. The solution was stirred for 6 h, and then methyl or ethyl α-cyanoacetate (0.3 mL) was added. The resulting solution was stirred for 22 h and then concentrated to ca. 1 mL. Addition of diethyl ether led to the precipitation of **12** or **13** as a yellow solid, which was filtered off, washed with diethyl ether and air-dried. Yield 197.2 mg (85%) (**12**) or 206.9 mg (88%) (**13**). **12:** ^{1}H NMR (300.1 MHz, $CDCl_3$, r.t.): δ = 8.3–6.6 (m), 5.65 (m, 28 H, Ph), 4.73 (m), 4.64 (m), 4.56 (m), 4.52 (m), 4.32 (m), 4.16 (m, 6 H, H_g, $H_{g'}$, H_c, $H_{c'}$, H_t, $H_{t'}$), 3.57 (s, 3 H, OCH_3), 3.18 (s, 1 H, NCCH), 2.78 (m, 1 H, CH *i*Pr), 2.30 (m, 1 H, CH *i*Pr′), 0.86 (d, J = 6.6 Hz, 3 H, Me *i*Pr′), 0.70 (d, J = 6.9 Hz, 3 H, Me *i*Pr), 0.02 (d, J = 6.6 Hz, 3 H, Me *i*Pr′), –0.40 (d, J = 6.9 Hz, 3 H, Me *i*Pr), –19.28 (dd, J = 26.6, 13.5 Hz, 1 H, Ir-H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$, r.t.): δ = 184.77 (CO), 167.46, 164.85 (C_1, $C_{1'}$), 134.9–127.8 (Ph), 73.88, 71.97 (C_2, $C_{2'}$), 69.72, 68.22 (C_3, $C_{3'}$), 51.26 (OCH_3), 50.15 (NC-*C*H), 31.16, 28.99 (CH *i*Pr), 19.56, 18.25, 13.83, 12.70 (Me *i*Pr) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, r.t.): δ = 1.16 (d, J = 14.5 Hz), –13.30 (d) ppm. IR (Nujol): $\tilde{\nu}$ = 2207 sh. (ν_{IrH}), 2177 s (ν_{CN}) cm^{-1}. $C_{52}H_{53}ClIrN_3O_4P_2$ (1073.63): cacld. C 58.17, H 4.97, N 3.91; found C 58.64, H 5.47, N 4.25. **13:** ^{1}H NMR (300.1 MHz, $CDCl_3$, r.t.): δ = 8.3–6.6 (m), 5.68 (m, 28 H, Ph), 4.81 (m), 4.78 (m), 4.62 (m), 4.55 (m), 4.38 (m), 4.22 (m, 6 H, H_g, $H_{g'}$, H_c, $H_{c'}$, H_t, $H_{t'}$), 4.08 (q, J = 6.8 Hz, 2 H, OCH_2CH_3), 3.22 (s, 1 H, NCCH), 2.83 (m, 1 H, CH *i*Pr), 2.36 (m, 1 H, CH *i*Pr′), 1.21 (t, 3 H, OCH_2CH_3), 0.91 (d, J = 6.9 Hz, 3 H, Me *i*Pr′), 0.74 (d, J = 6.9 Hz, 3 H, Me *i*Pr), –0.03 (d, J = 6.9 Hz, 3 H, Me *i*Pr′), –0.36 (d, J = 6.9 Hz, 3 H, Me *i*Pr), –19.23 (dd, J = 26.6, 13.5 Hz, 1 H, Ir-H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$, r.t.): δ = 182.92 (CO), 167.40, 164.75 (C_1, $C_{1'}$), 137.3–124.7 (Ph), 73.75, 71.81 (C_2, $C_{2'}$), 69.79, 68.51 (C_3, $C_{3'}$), 58.64 (OCH_2CH_3), 51.04 (NC*C*H), 31.14, 29.01 (CH *i*Pr), 19.51, 18.21 (Me *i*Pr), 14.90 (OCH_2CH_3), 13.90, 12.74 (Me *i*Pr) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, r.t.): δ = 1.18 (d, J = 14.5 Hz), –13.30 (d) ppm. IR(Nujol): $\tilde{\nu}$ = 2206 sh. (ν_{IrH}), 2176 s (ν_{CN}), 1666 s (ν_{CO}) cm^{-1}. $C_{53}H_{55}ClIrN_3O_4P_2$ (1087.65): calcd. C 58.53, H 5.09, N 3.86; found C 57.94, H 4.87, N 3.93.

Catalytic Michael Addition Procedure: The catalyst (0.01 mmol), donor **6** or **7** (1 mmol) and acceptor **8**–**10** (1.5 mmol) were dissolved in toluene (5 mL) under argon at room temperature, and the mixture was stirred for 22 h. After removal of all volatile materials, [D$_8$]toluene (500 μL) was added to the residue. The yield based on the donor was determined by ^{1}H NMR. The crude product was extracted with *n*-hexane, and the extract was purified by chromatography on silica gel. The products were identified by NMR spectroscopy.[7a,11l,26] Enantiomeric excesses were determined by GLC.

X-ray Structure Analyses of Complexes 2 and 5b: Single crystals of both complexes were glued to a glass fiber and mounted on a Bruker SMART APEX (equipped with a CCD area detector) (**2**) or Siemens-Stoe AED-2 diffractometer (**5b**) and examined using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Crystal data for **2** (from 4392 reflections, 2.2 < θ < 23.5°): $C_{29}H_{32}ClIrNO_3P{\cdot}0.5(C_4H_8O)$, tetragonal, space group $P4_12_12$; a = 11.2664(6), c = 46.726(4) Å, V = 5931.1(7) Å^3, Z = 8, D_c = 1.651 Mg m^{-3}, μ(Mo-K_α) = 4.680 mm^{-1}; crystal size 0.13 × 0.12 × 0.07 mm; T = 100.0(2) K, ω scans, max. 2θ = 55.1°; 38251 measured reflections, 6835 unique (R_{int} = 0.0835). Crystal data for **5b** (from 44 reflections, 12.5< θ < 15.0°): $C_{48}H_{48}F_6IrN_2O_2P_3$, M = 1083.99, orthorhombic, space group $P2_12_12_1$; a = 12.9657(10), b = 16.2713(17), c = 21.278(3) Å, V = 4489.1(8) Å^3, Z = 4, D_c = 1.604 Mg m^{-3}, μ(Mo-K_α) = 3.148 mm^{-1}; crystal size 0.23 × 0.20 × 0.19 mm; T = 200.0(2) K, $\theta/2\theta$ scans, max. 2θ = 50.0°; 9769 measured reflections, 7840 unique (R_{int} = 0.0213). Orange crystals of **5b** suitable for X-ray diffraction were grown by slow diffusion of diethyl ether into a solution of the complex in dichloromethane.

Data were integrated with the Bruker SAINT[27] (**2**) and Stoe REDU4 (**5b**) programs. Absorption correction was applied by using the SADABS program[28] (**2**) or the psi-scan approach[29] (**5b**). Structures were solved by direct methods[30] and completed by subsequent difference Fourier techniques. Refinement on F^2 was carried out for both structures by full-matrix least-squares (SHELXL-97).[30] In **2**, half a THF molecule was observed as crystallisation solvent in the structure. All non-hydrogen atoms, including those of the solvent molecule, were refined with anisotropic displacement parameters. The organic hydrogen atoms were included in calculated positions and refined with riding positional and thermal parameters. The hydride ligand was clearly observed in the last cycles of refinement, but it did not support a proper refinement as free isotropic atom. It was incorporated in the refinement with a restrained position and with a fixed displacement parameter. All non-hydrogen atoms in **5b**, except the F atoms in the PF_6^- anion, were refined with anisotropic displacement parameters. The PF_6^- anion was found to be disordered. A model for static disorder was established and the anion was refined with all atoms in two positions; occupancy factors were refined holding the sum of their occupancies equal to one. The hydrogen atoms were included accord-

ing to their geometry with restrained thermal and positional parameters.

The absolute configuration for both complexes were determined on the basis of the Flack parameter[31] [–0.008(11) for **2** and –0.018(6) for **5b**] and using as internal reference the previously known chirality of the asymmetric carbon atom in the phosphanyloxazoline ligand. Conventional final agreement factors[30] were: R_1 = 0.0506 [for 5588 reflections with $F^2>4\sigma(F^2)$], ωR_2 = 0.0937 and S = 0.968 for all independent reflections of **2**; R_1 = 0.0289 [for 7259 reflections with $F^2>4\sigma(F^2)$], ωR_2 = 0.0651 and S = 1.046 for all independent reflections of **5b**.

CCDC-240695 and CCDC-240696 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/data_request/cif.

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