42. The Dynamic Behaviour and NMR Solution Structures of Complexes of the Type (Bisphosphine)(cycloocta-1,5-diene)iridium(I) and the X-Ray Crystal Structure of (Cycloocta-1,5-diene)((−)-norphos)iridium(I) Hexafluorophosphate

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A square-planar coordination geometry was found for the complex [Ir(cod){(−)-norphos}][PF_6] (**1b**[PF_6]; cod = cycloocta-1,5-diene and (−)-norphos = [(2*R*,3*R*)-8,9,10-trinorborn-5-ene-2,3-diyl]bis(diphenylphosphine)) in the solid state by X-ray diffraction. Crystal data: monoclinic, space group $P2_1$, a = 10.751(6), b = 18.669(14), c = 12.037(8) Å, β = 114.82(5)°, Z = 2. A total structural assignment including the configurational and conformational aspects of this and the related compounds [Ir(bisphosphine)(cod)]X (bisphosphine = (−)-chiraphos = (2*S*,3*S*)-2,3-bis(diphenylphosphino)butane and (−)-norphos, X = Cl, CF_3SO_3, or PF_6) was carried out in solution by one- and two-dimensional NMR spectroscopy. The complexes containing the $CF_3SO_3^-$ and PF_6^- anions are four-coordinate cations with square-planar geometry, whereas the chlorides are five-coordinate neutral compounds showing solvent-dependent dynamic behaviour. In toluene, two diastereoisomers of [IrCl(cod){(−)-norphos}] (**2b**) exist and interconvert slowly at room temperature. This interchange is fast in $CDCl_3$ solution, and it is likely to involve Cl dissociation and the formation of the cation [Ir(cod){(−)-norphos}]$^+$ as an intermediate.

Introduction. – Chiral bidentate phosphines continue to be of much interest as ligands in transition-metal catalysts for the enantioselective transformations of organic substrates [1]. In some of the ligands which are commonly employed, such as 2,3-bis(diphenylphosphino)butane (= chiraphos) [2], 4,5-bis[(diphenylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane (= diop) [3], and (8,9,10-trinorborn-5-ene-2,3-diyl)bis(diphenylphosphine) (= norphos) [4], the actual chirality resides in the backbone of the chelate and, therefore, is remote from the potential binding site of the organic substrate. Thus, the observed asymmetric induction was attributed to the arrangement of the Ph groups which play a crucial role in forming a pocket, whose sense of chirality is felt by the approaching prochiral substrate [5]. A model for such a chiral pocket, based on X-ray crystallographic results, was proposed; this essentially involves an alternating equatorial-axial conformational array of the Ph groups on the chelate ring. Growing interest [6] [7] is noted also in modelling these or related situations in the solution state with the help of one- and two-dimensional NMR spectroscopic techniques. For this purpose, a combination of the incorporation of additional suitable ligands serving as 'reporters' [8] and NOE

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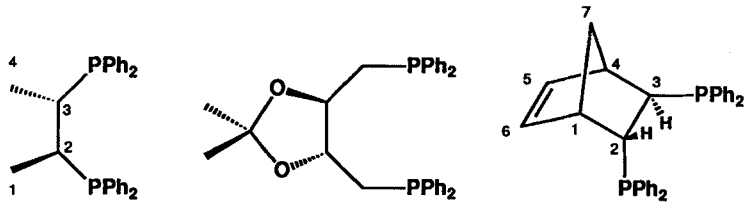
spectroscopy to characterize close non-bonding contacts between ligands helps in mapping the configurational and conformational aspects around the metal site.



(–)-chiraphos (–)-diop (–)-norphos

This paper demonstrates the use of the cyclooctadiene ligand for this purpose and describes the synthesis and solution NMR properties of the cationic complexes [Ir(cod){(–)-chiraphos}]$^+$ (**1a**; cod = cycloocta-1,5-diene, (–)-chiraphos = (2*S*,3*S*)-2,3-bis(diphenylphosphino)butane), [Ir(cod){(–)-norphos}]$^+$ (**1b**; (–)-norphos = [(2*R*,3*R*)-8,9,10-trinorborn-5-ene-2,3-diyl]bis(diphenylphosphine)), and of the neutral five-coordinate complexes [IrCl(cod){(–)-chiraphos}] (**2a**) and [IrCl(cod){(–)-norphos}] (**2b**). The X-ray crystal structure of **1b** is also reported.

Experimental. – *General.* All reactions involving air- or moisture-sensitive materials (free phosphines and silver salts, resp.) were carried out under Ar using standard *Schlenk* techniques. (–)-Chiraphos (*Aldrich*), (–)-norphos (*Merck*), and solvents (*puriss. p.a., Fluka*) were used without further purification. The organometallic starting materials $[Ir_2Cl_2(cod)_2]$ [9] and $[Ir(cod)_2][PF_6]$ [10] were prepared as described in the literature. NMR Spectra: *Bruker-AMX-400* (or *AMX-500*) spectrometer operating at 400.13 (500.13), 162.0 (202.5), and 100.6 (125.9) MHz for ^1H, ^{31}P, and ^{13}C, resp.; solns. in 5-mm o.d. tubes; ^{31}P- and ^{13}C-NMR with full ^1H-decoupling employing the waltz-16 sequence [11]; δ in ppm rel. to external H_3PO_4 for ^{31}P and TMS for ^{13}C and ^1H, using the solvent resonance as a secondary standard, J in Hz; homonuclear COSY [12] and NOESY [13] (with a mixing time of 0.5 s) and heteronuclear HMQC [14], HMBC [15], and XH-COSY [16] 2D-NMR experiments were acquired for pure absorption mode representation [17] according to the literature. Elemental analyses were carried out at the Laboratory of the Organic Chemistry, ETH-Zürich. Conductivity measurements were performed with 10^{-3} M solns. on a *Metrohm* conductometer *E 527*.

[(–)-Chiraphos](cycloocta-1,5-diene)iridium(I) Trifluoromethanesulfonate ([Ir(cod){(–)-chiraphos}]-(CF_3SO_3); **1a**(CF_3SO_3)). To a suspension of $[Ir_2Cl_2(cod)_2]$ (201.5 mg, 300 μmol) in acetone (20 ml) was added silver triflate (154.2 mg, 600 μmol). Addition of (–)-chiraphos (255.9 mg, 600 μmol), dissolved in CH_2Cl_2 (10 ml), to the resulting yellow suspension afforded a red suspension. The solid AgCl was filtered off, the filtrate evaporated and the residue extracted with CH_2Cl_2 (3 ml). The red soln. was covered with a 20-ml layer of petroleum ether (30–60°). The product separated from this mixture as a deep red powder which was dried *in vacuo* (494.2 mg, 94%). ^{31}P-NMR ($CDCl_3$, 101.3 MHz, r.t.): 43.3. Anal. calc. for $C_{37}H_{40}F_3IrO_3P_2S$: C 50.73, H 4.60; found: C 50.52, H 4.98.

(Cycloocta-1,5-diene)[(–)-norphos]iridium(I) Trifluoromethanesulfonate ([Ir(cod){(–)-norphos}](CF_3SO_3); **1b**(CF_3SO_3)). (–)-Norphos (308.1 mg, 666 μmol) and $[Ir_2Cl_2(cod)_2]$ (223.7 mg, 333 μmol) were dissolved in CH_2Cl_2 (30 ml), and the soln. was stirred for ½ h, after which the solvent was evaporated. The residue was then suspended in acetone (30 ml) and a soln. of $Ag(CF_3SO_3)$ (171.1 mg, 666 μmol) in acetone (10 ml) added. After stirring for 1 h, the precipitate formed was filtered off and the filtrate evaporated. The crude product was recrystallized from CH_2Cl_2/Et_2O: 440 mg (72%). ^{31}P-NMR ($CDCl_3$, 101.3 MHz, r.t.): 16.0, 14.6, J(P,P) = 17.5.

(Cycloocta-1,5-diene)[(–)-norphos]iridium(I) Hexafluorophosphate–Diethyl Ether (1/1) [Ir(cod){(–)-norphos}][PF_6]·Et_2O; **1b**[PF_6]·Et_2O. A soln. of (–)-norphos (98.4 mg, 213 μmol) and $[Ir(cod)_2][PF_6]$ (117.8 mg, 213 μmol), in CH_2Cl_2 (15 ml) was refluxed for 1 h, and then Et_2O (40 ml) was added. A small amount of a precipitate

was filtered off and the mother liquor concentrated in a stream of Ar, whereupon deep-red crystals separated. These were collected and dried *in vacuo:* 193.5 mg (71%). ^{31}P-NMR ($CDCl_3$, 81.0 MHz, r.t.): 16.0, 14.6, J(P,P) = 17.5. Anal. calc. for $C_{43}H_{50}F_6IrOP_3$: C 52.60, H 5.13; found: C 52.95, H 5.07.

[(−)-Chiraphos]chloro(cycloocta-1,5-diene)iridium(I)–Dichloromethane (1/0.5) ([IrCl(cod){(−)-chiraphos}]·0.5 CH_2Cl_2; **2a**·0.5 CH_2Cl_2). (−)-Chiraphos (87.5 mg, 205 μmol) and $[Ir_2Cl_2(cod)_2]$ (68.9 mg, 102 μmol) were dissolved in CH_2Cl_2 (10 ml), and the soln. was stirred for 2 h. After filtration, the solvent was removed and the residue dried *in vacuo* at 10 Pa for 5 d: 131 mg (80%). ^{1}H-NMR: 0.5 equiv. of CH_2Cl_2. ^{31}P-NMR ($CDCl_3$, 101.3 MHz, r.t.): 35.6. Anal. calc. for $C_{36.5}H_{41}Cl_2$: C 54.47, H 5.13; found: C 54.88, H 5.21.

Chloro(cycloocta-1,5-diene)[(−)-norphos]iridium(I) ([IrCl(cod){(−)-norphos}]; **2b**). (−)-Norphos (197 mg, 420 μmol) and $[Ir_2Cl_2(cod)_2]$ (143 mg, 210 μmol) were suspended in MeOH (20 ml) and stirred for 3 h. The solvent was removed and the residue dried *in vacuo:* 303 mg (50%). ^{31}P-NMR ($CDCl_3$, 81.0 MHz, r.t.): 3.9, 0.3, J(P,P) = 24.5. Anal. calc. for $C_{39}H_{40}ClIrP_2$: C 58.67, H 5.05; found: C 57.94, H 5.37.

NMR-Resonance Assignments in [Ir(cod){(−)-norphos}]$^+$, Representative Example. The assignments of the NMR resonances in [Ir(cod){(−)-norphos}]$^+$ and related complexes was achieved in five steps: 1) The trinorbornene protons were assigned from a NOESY experiment, where H–C(2) was located from a diagnostic NOE to one of the bridge protons. From H–C(2), a chain of NOE's led to H–C(1), H–C(6), H–C(5), H–C(4), and H–C(3). The C-resonances of the trinorbornene fragment were then assigned from an inverse ^{13}C,^{1}H correlation. 2) The cyclooctadiene resonances were assigned from a COSY spectrum in combination with a ^{13}C,^{1}H correlation. 3) A ^{31}P,^{1}H correlation led to an assignment of the ^{31}P spectrum, since P–C(2) coupled to H–C(1) and H–C(7), and P–C(3) showed scalar interaction with H–C(4), whereas both P-atoms coupled to H–C(2) and H–C(3). 4) The assignment of the Ph groups was carried out as follows: The ^{31}P,^{1}H correlation was used to relate pairwise the H_o's of the Ph groups to their respective P-substituent and to distinguish between the 'left' and 'right' halves of the ligand (this conclusion was supported by the observation of NOE's from the corresponding bridgehead protons H–C(1) and H–C(4) to the same H_o's). The 'lower' and 'upper' Ph's were then entirely assigned from the NOESY spectra. The *exo*-oriented H–C(2) and one of the bridge protons (H′–C(7)) point toward the 'upper' Ph's, which were then assigned to Ph^2_{eq} and Ph^3_{ax}, whereas the *endo*-positioned H–C(3) and the olefinic protons of trinorbornene showed spatial closeness to the 'lower' Ph groups Ph^2_{ax} and Ph^3_{eq}. 5) Having obtained a configurational assignment of relevant Ph resonances, one proceeded to obtain those for the cyclooctadiene *via* interligand NOE's. Close contacts were established between the H_o's of the equatorial Ph rings and the olefinic H–C(2′) and H–C(6′). The second type of olefinic resonances (H–C(1′) and H–C(5′)) showed interactions with both equatorial and axial Ph's (an example is given in *Fig. 3* see below).

X-Ray Crystallography. A deep red crystal of *{[(2R,3R)-bicyclo[2.2.1]hept-5-ene-2,3-diyl]bis(diphenylphosphine)}(cycloocta-1,5-diene)iridium hexafluorophosphate–diethyl ether* ([Ir(cod){(−)-norphos}][PF_6]·Et_2O; **1b**[PF_6]·Et_2O), with the size 0.1 × 0.2 × 0.2 mm, was obtained by slow evaporation of a CH_2Cl_2/Et_2O soln. Crystal and acquisition data are given in *Table 1.* During data collection, a strong decrease in the diffracted intensities was observed at high 2Θ values. Indeed, there was no significant intensity left above 2Θ = 35°; this was taken as an indication of molecular disorder, and the data collection was stopped at this 2Θ value.

Table 1. *Crystal Data, Data Collection, and Structure Solution for* **1b**[PF_6]·Et_2O

Empirical formula	$C_{43}H_{50}F_6IrOP_3$	Density (calc.)	1.487 Mg/m^3
Color, habit	deep red	Absorption coefficient	3.210 mm^{-1}
Crystal size [mm]	0.1 × 0.2 × 0.2	Radiation	MoK_α (λ = 0.71073 Å)
Crystal system	monoclinic	2Θ Range	3.0 to 35.0°
Space group	$P2_1$	Index ranges	$0 \leq h \leq 9, -15 \leq k \leq 15,$
Cell constants	a = 10.751 (6) Å		$-10 \leq l \leq 9$
	b = 18.669 (14) Å	Reflections collected	3020
	c = 12.037 (8) Å	Independent reflections	2795 (R_{int} = 8.47%)
	β = 114.82 (5)°	Observed reflections	1643 ($F > 6.0\sigma(F)$)
Volume	2193 (3) Å^3	Number of parameters refined	198
Z	2	Final R indices (obs. data)	R = 6.32%, R_w = 6.37%
Formula weight	981.9	Goodness-of-fit	1.36

The structure was solved using *Patterson* and difference *Fourier* methods. A full-matrix least-squares refinement was used, and the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. Anisotropic displacement parameters were used

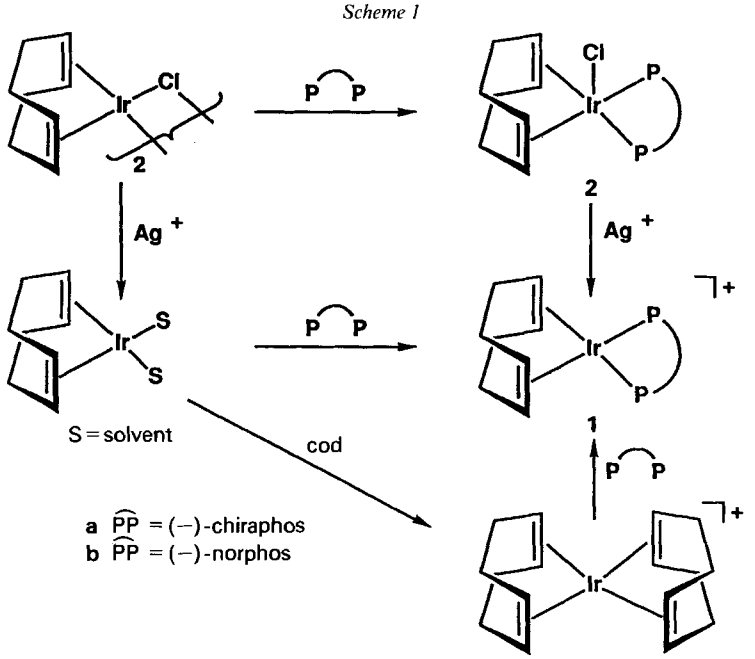
for Ir- and P-atoms. The contributions of the H-atoms in their idealized positions (C–H = 0.96 Å, U = 80 Å^2) were taken into account but not refined. At the end of the refinement, a Et_2O solvent molecule was found in the *Fourier* difference map, and was refined.

As expected from the falloff of the intensities, there is a high degree of disorder in **1b**[PF_6]·Et_2O, as can also be judged from the large values of the U_{ij} of the PF_6^- moiety, the atoms of the cod and norphos ligand, and those of the solvent molecule. The six strongest peaks in the *Fourier* difference map around the P-atom in the PF_6^- counterion were taken as the starting values for the refinement. Thus, only an approximate geometry of this ion was obtained.

The handedness of the crystal was tested by refining the two possible sets of coordinates. Those corresponding to the lower R_w value (0.064 *vs.* 0.081 for the other set) were taken. All calculations were carried out on a *Micro-VAX II* using the SHELXTL-Plus program. Final positional and displacement parameters and tables of observed and calculated structure factors are available upon request from *V.G.* and have been deposited with the *Cambridge Crystallographic Data Centre.*

Results and Discussion. – 1. *Synthetic Studies.* The complexes [Ir(cod)(bisphosphine)]$^+$ **1a** (bisphosphine = (–)-chiraphos) and **1b** (bisphosphine = (–)-norphos), the counterion being $CF_3SO_3^-$ or PF_6^-, can conveniently be prepared as shown in *Scheme 1.* Starting from [$Ir_2Cl_2(cod)_2$], one first abstracts the Cl-ligand by Ag^+ to give an intermediate solvento complex which is then transformed into the desired product by the addition of the bisphosphine ligand. While this method works for chiraphos, diphos ($Ph_2PCH_2CH_2PPh_2$), or diop, it fails in the case of norphos, which gives untractable materials, presumably of polymeric nature. The different behaviour of the norphos ligand in this reaction may be related to the large change in the P–C–C–P torsional angle (from *ca.* 120 to *ca.* 60–65°) required for chelate formation. The energy gained by chelate formation may not be sufficient to compensate this imposed strain, and thus polynuclear species may be formed. In an alternative synthetic procedure, the solvento complex is transformed into the bis(cyclooctadiene) complex, which can be isolated and kept as a

Scheme 1



very convenient starting material for the preparation of complexes of type **1** by reacting it with the bisphosphine. The norphos derivative **1b**[PF_6] is obtained in good yields by the latter method.

The chloro complexes [IrCl(bisphosphine)(cod)] **2a** (bisphosphine = (−)-chiraphos) and **2b** (bisphosphine = (−)-norphos) are directly obtained from the chloro-bridged dimer and the corresponding bisphosphines. These materials can also be transformed into complexes of type **1** by halogen abstraction with silver salts. Diluted solutions of stoichiometric amounts of phosphines and metal complexes should be used to avoid the formation of [Ir(bisphosphine)$_2$]X or polynuclear species [18]. Although ^{31}P-NMR spectroscopy indicates the quantitative formation of a single product for both the cationic and the neutral complexes **1** and **2**, respectively, it sometimes proved difficult to obtain some of these materials in an analytically pure form, as inclusion of solvents into the crystals occur quite easily, *e.g.* [Ir(cod){(−)-norphos}][PF_6] is obtained as its Et_2O adduct, and [IrCl(cod){(+)-diop}] [19] and the related [Rh(cod){(−)-chiraphos}][ClO_4] [20a] were reported as containing clathrated ethanol and tetrahydrofuran, respectively.

2. *The X-Ray Crystal Structure of [Ir(cod){(−)-norphos}][PF_6]·Et_2O* (**1b**[PF_6]·Et_2O). In the solid state, this salt contains discrete [Ir(cod){(−)-norphos}] cations, in which slight disorder of the cod and the norphos ligands is found, disordered [PF_6] anions and a highly disordered Et_2O molecule, without any significant interaction between them. An ORTEP view of the cation **1b** is shown in *Fig. 1*, and a selection of bond distances and angles is given in *Table 2*. No unusual values for the bond distances and angles are found as compared to other related diene [20] or norphos [21] complexes. Despite this disorder, several significant features can be unambiguously identified. The two P-atoms and the

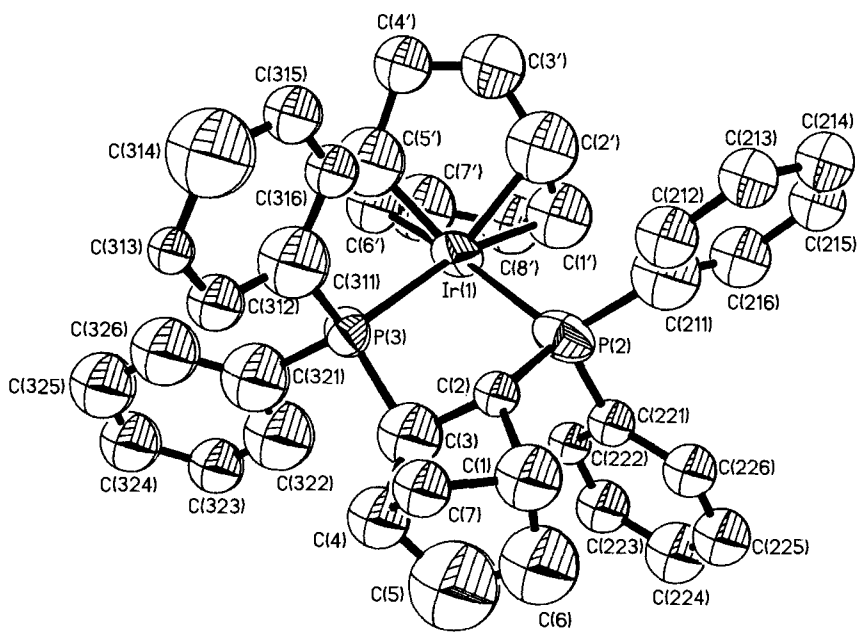


Fig. 1. *ORTEP view of [Ir(cod){(−)-norphos}]$^+$* (**1b**)

midpoints of the cyclooctadiene double bonds form approximately a square-planar arrangement around the Ir-atom with the Ir–P and Ir–olefin separations in the expected range.

Of particular interest with respect to the transmission of chirality to a prochiral substrate are the conformation of the Ir–P(2)–C(2)–C(3)–P(3) chelate ring and the orientations of the Ph groups in the norphos ligand. The trinorbornene backbone of this ligand, in contrast to systems with larger rings like diop or, to a lesser extent, chiraphos, imposes a rigid puckered conformation on the five-membered ring. Chelate formation

Table 2. *Selected Bond Distances* [Å] *and Angles* [deg] *for [Ir(cyclo-1,5-octadiene){(–)-norphos}][PF_6]·Et_2O* (**1b**[PF_6]·Et_2O)

Bond lengths		Bond angles	
Ir(1)–P(2)	2.29(2)	P(2)–Ir(1)–P(3)	85.5(5)
Ir(1)–P(3)	2.31(1)	P(2)–Ir(1)–C(1′)	90(2)
Ir(1)–C(1′)	2.27(5)	P(2)–Ir(1)–C(2′)	97(2)
Ir(1)–C(2′)	2.16(6)	P(2)–Ir(1)–C(5′)	163(2)
Ir(1)–C(5′)	2.02(5)	P(2)–Ir(1)–C(6′)	165(1)
Ir(1)–C(6′)	2.18(4)	P(3)–Ir(1)–C(1′)	166(1)
C(1)–C(2)	1.60(7)	P(3)–Ir(1)–C(2′)	157(2)
C(1)–C(6)	1.45(7)	P(3)–Ir(1)–C(5′)	93(2)
C(1)–C(7)	1.52(5)	P(3)–Ir(1)–C(6′)	99(2)
C(2)–C(3)	1.52(6)	P(2)–C(2)–C(1)	131(2)
P(2)–C(2)	1.85(4)	P(2)–C(2)–C(3)	106(3)
C(3)–C(4)	1.54(8)	P(3)–C(3)–C(2)	103(3)
P(3)–C(3)	1.84(5)	P(3)–C(3)–C(4)	131(3)
C(4)–C(5)	1.45(6)	C(1′)–C(2′)–C(3′)	123(6)
C(4)–C(7)	1.53(7)	C(2′)–C(3′)–C(4′)	117(4)
C(5)–C(6)	1.26(8)	C(3′)–C(4′)–C(5′)	109(45)
C(1′)–C(2′)	1.41(8)	C(4′)–C(5′)–C(6′)	116(6)
C(1′)–C(8′)	1.56(9)	C(5′)–C(6′)–C(7′)	139(6)
C(2′)–C(3′)	1.53(7)	C(6′)–C(7′)–C(8′)	115(4)
C(3′)–C(4′)	1.40(6)	C(1′)–C(8′)–C(7′)	119(4)
C(4′)–C(5′)	1.59(6)	C(2′)–C(1′)–C(8′)	122(5)
C(5′)–C(6′)	1.18(8)		
C(6′)–C(7′)	1.56(6)		
C(7′)–C(8′)	1.49(5)		

requires some flattening of this ring, as is indicated by the enlarged angles C(1)–C(2)–P(2) and C(4)–C(3)–P(3), 131(3)° each, and a small value of the dihedral angle P(2)–C(2)–C(3)–P(3), –66(3)°. The observed values for these parameters are in agreement with previously reported data of other norphos or renorphos (= 2,3-bis(diphenylphosphino)-8,9,10-trinorbornane) complexes [21]. The puckered conformation of the chelate ring fixes also the spatial orientations of the Ph rings on the diphenylphosphino moieties. Their spatial arrangement (see *Fig. 2*) is close to that of a typical C_2 phosphine ligand like chiraphos [21a], having two equatorial and two axial Ph groups in an alternating sequence, although this particular ligand itself lacks any symmetry.

The cyclooctadiene ligand shows severe distortions imposed by steric interactions with the four Ph groups of norphos. In an idealized geometry, *e.g.*, of local C_{2v} or C_v symmetry, one would expect the two olefinic bonds to be perpendicular to the coordination plane. In **1b** [PF_6], however, one notes a tilt around the axis defined by the midpoints

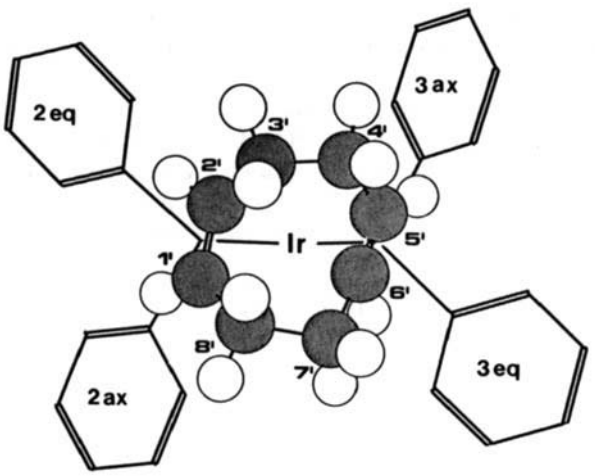


Fig. 2. *Spatial orientation of the Ph rings of the diphenylphosphino moieties at the chelate ring of* **1b**

of the olefinic bonds and the metal (see *Fig. 2*) bringing the olefinic protons H–C(1′) and H–C(5′) into a cavity left between the axial and equatorial Ph group attached to the same P-atom, thus reducing steric strain in the molecule. This specific distortion or skewed conformation of the cyclooctadiene is also manifested by the torsional angles found in cod, although the high experimental errors involved preclude a more detailed analysis.

3. *NMR Studies of the Solution Structures of 'IrX(bisphosphine)(cod)' Complexes.* 3.1. *General.* Complexes of the composition IrX(bisphosphine)(cod) exist in solution either as cationic four-coordinate [Ir(bisphosphine)(cod)]X or a neutral five-coordinate [IrX(bisphosphine)(cod)] species, depending on the coordinating properties of the anion X and the polarity of the solvent [22]. For weakly coordinating anions, such as $CF_3SO_3^-$ or PF_6^-, the square-planar form is found in the solid and in solution. The Cl^- anion, present in complexes of type **2**, often takes an intermediate position in this respect, and dynamic equilibria between the four- and five-coordinate species are frequently encountered in solution. The equilibria and exchange processes occurring in solutions of the complexes $[IrCl(cod)(EPh_3)_2]$ (E = P or As) were interpreted by *Vrieze* and coworkers [23] in terms of steps shown in *Eqn. 1* on the basis of NMR kinetics and conductivity measurements. The position of such equilibria can generally be influenced by the choice of solvent. A similar NMR study was carried out for the chelate-phosphine derivatives **1** and **2**.

$$[IrCl(cod)(EPh_3)] + EPh_3 \rightleftarrows [IrCl(cod)(EPh_3)_2] \rightleftarrows [Ir(cod)(EPh_3)_2]^+Cl^- \qquad (1)$$

3.2. *Four-Coordinate [Ir(bisphosphine)(cod)]*$^+$. The chiraphos complex [Ir(cod){(−)-chiraphos}]$^+$ (**1a**), as its $CF_3SO_3^-$ salt, exists in $CDCl_3$ solution as a cation with a C_2 molecular symmetry. This deduction is evident from the NMR data (see *Table 3*) and, in particular, *i*) the equivalence of the P-nuclei in the ^{31}P-NMR spectra, *ii*) the observation of only two sets of Ph groups in the ^{1}H- and ^{13}C-NMR spectra, assignable to the axial and equatorial positions, respectively, and *iii*) the equivalence of the Me (and CH) groups in the chiraphos backbone. The cod ligand itself senses the chirality imposed by the bisphosphine and shows two sets of olefinic resonances and also two different types of aliphatic

Table 3. *^{31}P-, ^{13}C-, and ^{1}H-NMR Data of Complexes [Ir(Bisphosphine)(cod)]X* (bisphosphine = (−)-chiraphos, **1a**; (−)-norphos **1b**; X = CF_3SO_3 or PF_6[a])

	$\delta(^{13}C)$	$J(P,C)$[b]	$\delta(^{1}H)$	$\delta(^{13}C)$	$J(P,C)$	$\delta(^{1}H)$
	1a[c]			**1b**[d]		
Cyclooctadiene						
1′	87.8	9.3	4.79	83.5	10.1	4.77
2′	93.3	11.3	3.98	91.2[e]	10.9	3.91
3′	28.2		1.92[f], 1.82	28.2		1.93[f], 1.68
4′	33.2		2.48, 2.23[f]	33.6	4	2.42, 2.4
5′				83.0	10.4	4.79
6′				90.7[e]	10.8	3.91
7′				28.2		1.93[f], 1.68
8′				33.5	4	2.38, 2.4
Phosphine						
1	13.2	12.2	1.04	41.8	9.8, 7.2	2.97
2	34.6	19.2	2.17	46.1	39.0, 17.4	3.12
3				47.4	31.7, 15.8	2.53
4				39.2	12.4, 6.3	2.66
5				140.2	7.7	6.13
6				131.3		5.30
7				52.0	9.9	1.81, 0.78[g]
Phenyls (ortho)[h]						
2_{ax}	136.6	11.8	7.76	136.6	12.0	7.78
2_{eq}	130.8	8.8	7.37	130.9[e]	8.8	7.38
3_{ax}				135.9	11.6	7.86
3_{eq}				130.8[e]	8.7	7.35

[a]) The spectra were recorded in $CDCl_3$ solution at room temperature. Chemical shifts are in ppm relative to TMS (^{13}C and ^{1}H) and H_3PO_4 (^{31}P). Coupling constants are in Hz.

[b]) *AXX′* spin systems; values quoted correspond to $J(P,C) + J(P',C)$.

[c]) $\delta(^{31}P) = 43.3$ ppm.

[d]) $\delta(^{31}P) = 14.6$ (P^2) and 16.0 ppm (P^3), $J(P,P) = 17.5$ Hz.

[e]) Assignments within the same ligand could be reversed.

[f]) *exo*-Oriented.

[g]) Oriented towards the metal.

[h]) Remaining Ph ^{13}C resonances: **1a**, *ipso*: 127.0, 126.4; *meta*: 130.0 {9.8}[b]), 129.4 {10.6}; *para*: 133.3, 131.9. **1b**, *ipso*: 127.7 (49.9), 127.5 (49.4), 127.4 (50.9), 125.2 (51.8); *meta*: 129.9, 129.8, 129.8, 129.2 (10.8 all); *para*: 133.3, 133.2, 131.8, 131.7 (2.4 all).

CH_2 moieties. The C_2-related equivalences within both the bisphosphine and the diolefin, as well as the observation of specific interligand NOE's are consistent with the formulation of this complex as a square-planar four-coordinate cation. Alternatively, a neutral five-coordinate complex in fast exchange with such a cation could be envisaged. However, this is unlikely in view of the dynamic behaviour of such species to be discussed later.

In the analogous norphos complex [Ir(cod){(−)-norphos}]$^+$ (**1b**), as its $CF_3SO_3^-$ or PF_6^- salt, the presence of the trinorbornene backbone prevents a C_2 molecular symmetry and, consequently, leads to inequivalent P-spins and four different Ph groups which can be distinguished and assigned. While the ^{13}C-NMR spectrum clearly reveals four different olefinic C-resonances for the cod moiety in this complex, the ^{1}H-NMR spectrum seems to show only two types of olefinic H-atoms (see also the projection in *Fig. 3*). Most likely,

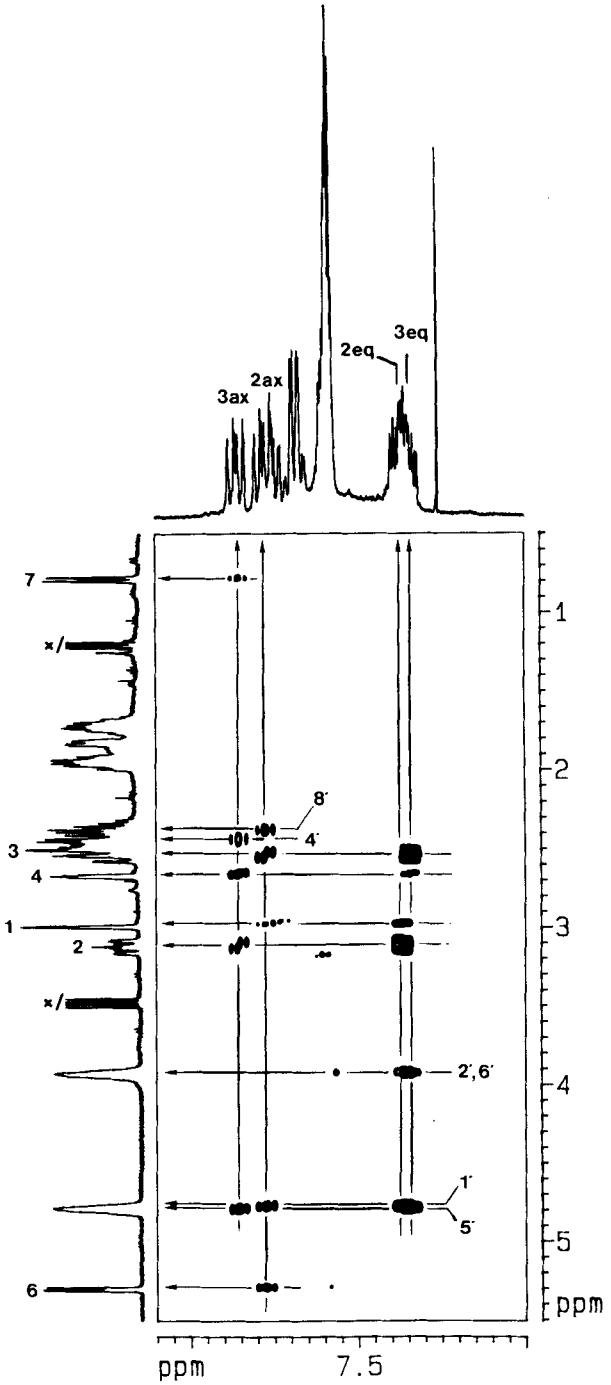


Fig. 3. *Section of the 400-MHz NOESY spectrum of [Ir(cod)((−)-norphos)]*$^+$ (**[1b]**$^+$), *relating the cod and the norbornene resonances to those of the Ph rings.* Note the near degeneracy of H–C(2′)/H–C(6′) and H–C(1′)/H–C(5′), respectively.

this apparently higher local symmetry originates from similar shielding of *e.g.* H–C(1′) and H–C(5′) imposed by the quasi C_2 relationship of the Ph's as it is observed in its X-ray crystal and NMR solution structures. Although lowering the temperature to 220 K does not result in a dispersion of the resonances within the two pairs of almost isochronous nuclei, it leads to larger shift differences between the H–C(1′)/H–C(5′) and H–C(2′)/H–C(6′) pairs ($\Delta\delta$ = 1.09 and 0.88 ppm at 220 and 298 K, resp.). An unambiguous assignment for H–C(1′) and H–C(5′), however, could be made from selective and diagnostic NOE's to the Ph groups at P–C(2) and P–C(3), respectively (*Fig. 3*), whereas H–C(2′) and H–C(6′) could not be resolved sufficiently by any homo- or heteronuclear technique.

The observation of interligand NOE's in **1a** and **1b** between the olefinic protons H–C(1′) and H–C(5′) of the cyclooctadiene and the axial and equatorial Ph groups of the phosphine moieties suggests that the olefinic bonds are not perpendicular to the coordination plane, as such an arrangement would lead to exclusive contact with only the axial Ph substituents. However, a skew arrangement of the cod, similar to that observed in the crystal structure, would bring H–C(1′) close to the H_o's of both the equatorial and the axial Ph groups. These structural features of the cod ligand would be consistent with the interligand distance constraints implied by the NOESY spectra. As such a conformational adaption of an olefinic ligand to the steric requirements of the chiral phosphines chiraphos and norphos seemed of general interest in view of optical induction in asymmetric catalysis, the conformation of cod in **1a** and **1b** was determined more precisely.

It should be noted that olefins whose positions are non-orthogonal with respect to the coordination plane would require additional changes in dihedral angles in the cod molecule and in particular also around the C(3′)–C(4′) and C(7′)–C(8′) bonds. A knowledge of the magnitudes of the vicinal ^{1}H,^{1}H-coupling constants within the cyclooctadiene (see *Table 4*) should allow the determination of the corresponding torsion angles *via* the *Karplus* relationship [24] and, therefore, its conformation. For [Ir(cod){(−)-chiraphos}]$^+$ (**1a**), the relevant coupling parameters are obtained from linear combinations of a series of one-dimensional COSY spectra [25], whereas for [Ir(cod){(−)-norphos}]$^+$ (**1b**), the data from the two-dimensional experiment are used in combination with the DISCO method [26]. The vicinal coupling constants ^3J(H,H) in **1a** and **1b** are equal within the

Table 4. *Vicinal ^{1}H,^{1}H-Coupling Constants for cod in [Ir(Bisphosphine)(cod)]$^+$ Complexes* [**1a**]$^+$ *and* [**1b**]$^{+a}$)

	[**1a**]$^+$	[**1b**]$^{+b}$)
J(1′,2′)	7.7	8
J(1′,7′*n*)	2.8	2
J(1′,7′*x*)	7.5	7
J(2′,3′*n*)	7.0	7
J(2′,3′*x*)	8.0	8
J(3′*n*,4′*n*)	8.3	8
J(3′*n*,4′*x*)	9.3	8
J(3′*x*,4′*n*)	3.0	2
J(3′*x*,4′*x*)	9.5	10

a) Values are given in Hz. Abbreviations: *n* = *endo*, *x* = *exo* proton.

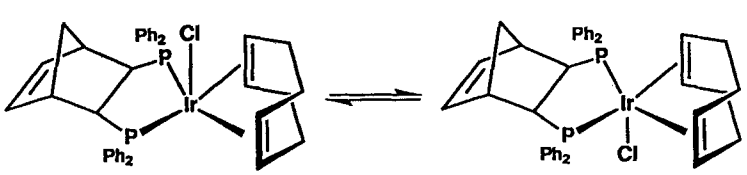
b) Values are deduced from the COSY experiment and are accurate to ± 1 Hz.

experimental uncertainty and thus reflect a similar conformation of the cyclooctadiene moiety in both complexes. From the coupling data, the dihedral angles C(2′)–C(3′)–C(4′)–C(5′) and C(6′)–C(7′)–C(8′)–C(1′) are estimated to be *ca.* –20°, in close agreement with those found by X-ray diffraction in **1b** (–18(9) and –10(8)°, resp.) and in the corresponding rhodium complex [Rh(cod){(–)-chiraphos}]$^+$ (25.9 and 33.2°, resp.) [20a]. It can then be concluded that the solution structures of **1a** and **1b**, as derived by NMR spectroscopy, are similar to the solid-state structures of [Rh(cod){(–)-chiraphos}]$^+$ [20a] and [Ir(cod){(–)-norphos}]$^+$, respectively, both having a C_2-like chiral array of the Ph groups in the diphenylphosphino moieties and a skewed conformation of the cyclooctadiene ligand.

3.3. *Five-Coordinate [IrCl(cod)(bisphosphine)].* Five-coordinate metal complexes are prone to dynamic processes and those occurring with the systems [IrCl(cod)$(PPh_3)_2$] are summarized in *Eqn. 1*. In view of these facile ligand-dissociation processes, particularly of chloride, the results obtained in toluene solution will be discussed first, as the formation of charged species is likely to be less favoured.

In toluene solution at room temperature, the bisphosphine ligand in [IrCl(cod){(–)-chiraphos}] (**2a**) shows the presence of two inequivalent P-spins, four different Ph groups and diastereotopic CH-Me moieties, a shown by its ^{31}P-, ^{13}C- and ^{1}H-NMR spectra (see *Table 5*). From these results it is deduced that *a*) the metal is a stereogenic centre and *b*) the bisphosphine moiety is in a static relationship with respect to the Ir–Cl fragment. These two features are also present in the norphos analog **2b**, where one expects, and finds, the two diastereoisomers originating from the chirality imposed at the Ir-centre. The latter stereoisomers are most easily visualized on the basis of the two square pyramids shown in *Scheme 2* (see **2b′** and **2b″**). However, these features remain, if one assumes that **2b** has the trigonal bipyramidal structure as reported [19] for [IrCl(cod){(+)-diop}] (**2c**), as long as the orientations of the Cl-atom relative to the norphos ligand remains identical. The major stereoisomer (*ca.* 70%) is likely to have structure **2b″** based on expected low-field shifts observed for protons caused by the neighbouring-group anisotropy of a Cl-substituent close in space[2]). Thus, in **2b″** one finds downfield shifts for H–C(3) and the H_o's of the axial Ph group at P–C(2), whereas in **2b′**, besides the axial Ph on P–C(3), H–C(2) and one of the H–C(7) are affected most. The assignment of **2b″** is further supported by the observation of a weak NOE between the axial Ph group on P–C(3) and the *exo*-proton H–C(4′).

Scheme 2



2b′ **2b″**

[2]) *E.g.*, the cyclohexyl (Cy) protons in α-position of *trans*-[Pt(XY)$(PCy_3)_2$] resonate at 1.91, 2.24, and 2.68 ppm for XY = H_2, HCl, and Cl_2, respectively [27].

Table 5. *^{31}P-, ^{13}C-, and ^{1}H-NMR Data of Complexes [IrCl(Bisphosphine)(cod)],* (biphosphine = (−)-chiraphos, **2a**; (−)-norphos **2b**)[a]

	$\delta(^{13}C)$	$J(P,C)$[b]	$\delta(^{1}H)$	$\delta(^{13}C)$	$J(P,C)$	$\delta(^{1}H)$
	2a[c]			**2b**[d]		
Cyclooctadiene						
1′	71.7	br.	3.67	66.6	8.0, 5.6	3.96
2′	71.4	br.	3.51	72.4	8.0, 5.4	3.27
3′	28.1		2.05, 1.48	29.8		2.02[e]), 1.48
4′	37.3		2.63, 2.37	34.9		2.49[e]), 2.12
Phosphine						
1	14.1	12.5	1.13	42.2	11.7, 8.2	2.91
2	39.7	48.3	2.52	48.1	34.3, 21.3	3.25
3				47.8	29.1, 18.1	3.18
4				39.9	13.3, 7.0	2.68
5				140.2	7.2	6.21
6				132.4		5.49
7				51.7	9.0	1.69, 0.75[f])
Phenyls (ortho)[h])						
2_{ax}	133.6	8.6	7.68	136.8	10.4	7.88
2_{eq}	135.5	10.2	7.56	128.2	10.0	7.40
3_{ax}				136.4	10.8	8.00
3_{eq}				127.4	9.6	7.35

[a]) The spectra were recorded in $CDCl_3$ solution at room temperature. Chemical shifts are in ppm relative to TMS (^{13}C and ^{1}H). Coupling constants are in Hz.

[b]) *AXX′* spin systems; values quoted correspond to $J(P,C) + J(P',C)$.

[c]) $\delta(^{31}P) = 35.6$ ppm.

[d]) $\delta(^{31}P) = 0.3$ (P–C(2)) and 3.9 ppm (P–C(3)).

[e]) *exo*-Oriented.

[f]) Oriented towards the metal.

[g]) Remaining Ph ^{13}C resonances: **1a**, *ipso*: 130.7 {50.1}[b]), 129.5 {41.6}; *meta*: 128.1 {9.4}, 127.4 {9.5}; *para*: 130.3, 130.2. **1b**, *ipso*: 132.6 (50), 131.4 (45.2), 128.8 (41,8), 127.4 (40.8); *meta*: 132.3, 132.3, 128.0, 128.0 (10 all); *para*: 131.2, 130.8, 129.8, 129.7 (2.2 all).

The cyclooctadiene ligands in the complexes **2a** and **2b** show unexpected equivalences in the ^{1}H- and ^{13}C-NMR spectra, *e.g.* of H–C(1′) and H–C(5′), which are inconsistent with the overall molecular symmetry (all spins in the cod fragment should be inequivalent in a static structure like the ones shown in *Scheme 2*). However, this feature can be rationalized by assuming a fast rotation (or a jump by 180°) of the cod moiety on the NMR time scale. It should be noted, however, that the skewed conformation of this unit is maintained despite this dynamic process. This is indicated from *a*) the vicinal coupling constants between the olefinic and the adjacent CH_2 protons, *b*) NOE's between the CH_2 protons, and *c*) interligand NOE's from the cod protons to the Ph groups of norphos in **2b**. The conservation of the conformation of the cod is best explained by assuming a two-site jump process, which brings this fragment from one equivalent position to the other. Cyclooctadiene rotation was also observed [28] in the related complexes [Ir(R)(cod)(diphos)], R = Me and H, and interpreted in terms of *Berry* or pseudorotational rearrangements [29] in trigonal-bipyramidal complexes.

In summary, the NMR solution structures of the neutral five-coordinate complexes [IrCl(cod)(bisphophine)] can be described as having basic square-pyramidal (or trigonal-

bipyramidal) geometries in fast intramolecular exchange, where, however, the geometrical relationship between the phosphine chelate and the Ir–Cl bond is conserved. In view of the rotational behaviour of the cod, the complexes could also be considered as being pseudo-tetrahedral, if one formally considers the diene as one single ligand.

It has been observed that the two diastereoisomers of [IrCl(cod){(–)-norphos}] exchange slowly at room temperature, and that this process can be monitored *via* two-dimensional ^{31}P (and ^{1}H) exchange spectroscopy [30] (see *Fig. 4*). Higher rates of interconversion can be obtained by heating to 100° or by adding catalytic amounts of the $CF_3SO_3^-$ salt of **1b**, which is sparingly soluble in toluene. This exchange can be rationalized on the basis of an intermolecular Cl-exchange, a process which readily occurs in $CDCl_3$ solution.

The chiraphos derivative **2a** in $CDCl_3$ and at room temperature shows *a*) equivalent P-nuclei in the ^{31}P-NMR spectrum and *b*) C_2-related equivalences within both the chiraphos and the cyclooctadiene ligands in the ^{13}C- and ^{1}H-NMR spectra. Furthermore, in the norphos derivative **2b** in $CDCl_3$, one observes signals indicating the presence of only one species, while two diastereoisomers are found in toluene solution, and it is proposed that, in the former solvent, the observed signals arise for dynamic averaging of the two diastereoisomers. The general symmetry aspects observed in $CDCl_3$ solution are reminis-

Table 6. *^{31}P-, ^{13}C-, and ^{1}H-NMR Data of Complexes [Ir(Bisphosphine)(cod)]* (biphosphine = (–)-chiraphos, **2a**; (–)-norphos **2b**[a])

	$\delta(^{13}C)$	$\delta(^{1}H)$	$\delta(^{1}H)$	
	2a		**2b**	
Cyclooctadiene				
1′	69.1	3.62	3.27	n.o.
2′	68.4	3.50	3.96	3.95
3′	38.0	2.80[b]), 2.36	2.64[b]), 2.10	n.o.
4′	28.5	2.01[b]), 1.42	2.05[b]), 1.43	n.o.
Phosphine				
1	13.8	0.76	2.54	2.76
2	40.9	3.74	2.97	4.26
	37.3[c])		–9.1[c])	7.1[c])
3	40.2	1.39	3.90	2.51
	30.8[c])		5.6[c])	–8.3[c])
4	14.5	0.98	2.34	2.40
5			6.01	5.49
6			5.45	5.01
7			1.43, 0.40[d])	1.54, 1.25[d])
Phenyls (ortho)				
2_{ax}	137.5	7.66	8.14	7.92
2_{eq}	133.9	7.43	7.33	7.43
3_{ax}	135.0	7.97	7.99	8.33
3_{eq}	134.5	7.59	7.46	7.32

[a]) The spectra were recorded in (D_8)toluene solution at room temperature. Chemical shifts are in ppm relative to TMS (^{13}C and ^{1}H) and H_3PO_4 (^{31}P).

[b]) *exo*-Oriented.

[c]) $\delta(^{31}P)$.

[d]) Oriented towards the metal.

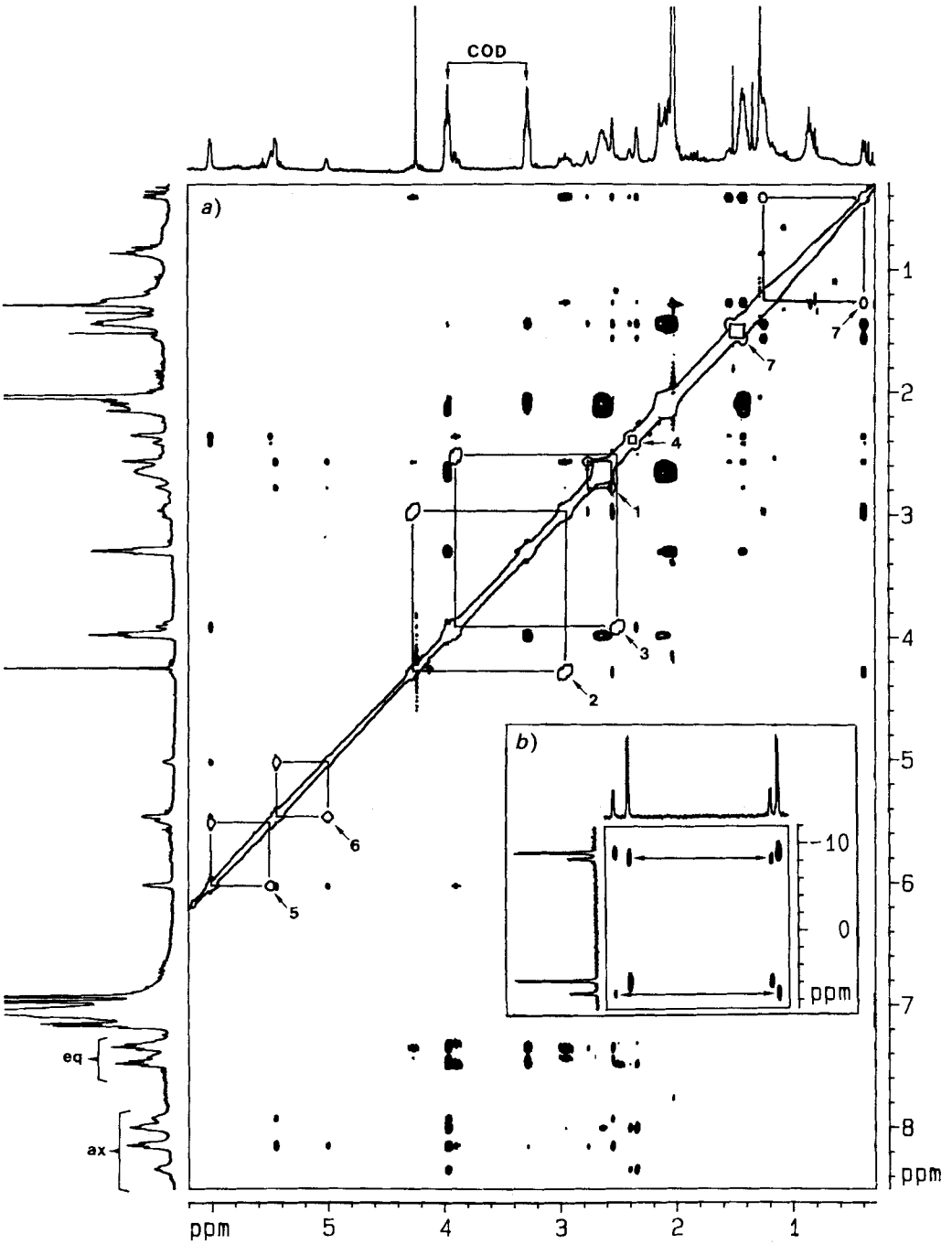


Fig. 4. a) *Section of the 400-MHz NOESY spectrum of [IrCl(cod)((−)-norphos)]* (**2b**) *in* (D_8)*toluene.* Chemically exchanging protons are indicated by squares connecting peaks arising from interconversion of isomers **2b′** and **2b″**. These exchange crosspeaks are drawn with a single contour, whereas the NOE crosspeaks appear in solid black. b) ^{31}*P-EXSY Spectrum showing interchanging P spins of* **2b′** *and* **2b″**.

cent of those in the cationic complexes **1a** and **1b**. However, the NMR data for **2a** and **2b** (see *Table 6*) are significantly different from those of the corresponding $CF_3SO_3^-$ or PF_6^- salts **1a** and **1b** (see *Table 3*). The predominant formation of an uncharged compound and only minor dissociation of the Cl-ligand is also suggested by conductivity measurements performed on 10^{-3} M solutions: In $CHCl_3$, a value of 1.3 Ω^{-1} cm mol^{-1} is found for **2a**, whereas the reference compound Ph_4PCl and the cationic complex **1a** give 3.8 and 3.9 Ω^{-1} cm mol^{-1}, respectively, in agreement with the presence of a 1:1 electrolyte in this solvent. Cl-Dissociation in this solvent leads to the formation of some four-coordinate complex [Ir(cod){(−)-norphos}]$^+$, which can act as an intermediate in the exchange of the two diastereoisomers of **2b**. Neglecting solvent effects on the ^{31}P-chemical shifts, one can roughly estimate the percentage of Cl-dissociation: The weight-averaged chemical shifts of P–C(2) and P–C(3) in **2b′** and **2b″** are −3.7 and 0.7 ppm, respectively, which are to high field of the dynamically averaged shifts as observed in $CDCl_3$ (0.3 and 3.9 ppm). These data are reasonably interpreted in terms of *ca.* 20% dissociation and fast Cl-exchange in the chlorinated-hydrocarbon medium.

Conclusions. – It was shown that there exists a close relationship between the structures of the square-planar four-coordinate complexes [Ir(bisphosphine)(cod)]$^+$ in the solid state and the solution. The five-coordinate compounds [IrCl(bisphosphine)(cod)] show two recognizable types of dynamic processes: One involves Cl-dissociation, which is slow in toluene and fast in chloroform solution. The use of the non-symmetrical bisphosphine (−)-norphos, leading to two diastereoisomers of [IrCl(cod){(−)-norphos}], proved invaluable for its recognition. The second process involves fast rotation of the cyclooctadiene fragment with respect to the [IrCl(bisphosphine)] fragment. As such a rotational process is of degenerate nature (giving back the same complex), only limited information on its mechanism can be obtained. This is particularly true, because equivalence resulting from non-rigid behaviour is difficult to distinguish from accidental overlap of resonances. The use of suitably substituted diolefins would lead to distinguishable diastereoisomers which should allow one to describe these dynamics in more detail. Such a study is in progress in this laboratory.

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REFERENCES

[1] a) R. Noyori, M. Kitamura, in 'Modern Synthetic Methods', Ed. R. Scheffold, Verlag Sauerländer, Aarau, 1989, Vol. 5, p. 115; b) R. Noyori, *Science (Washington)* **1990,** *248,* 1194; c) R. Noyori, M. Kitamura, *Angew. Chem.* **1991,** *103,* 34.

[2] M. D. Fryzuk, B. Bosnich, *J. Am. Chem. Soc.* **1977,** *99,* 6262.

[3] H. B. Kagan, T.-P. Dang, *J. Am. Chem. Soc.* **1972,** *94,* 6429.

[4] a) H. Brunner, W. Pieronczyk, *Angew. Chem.* **1979,** *91,* 655; b) H. Brunner, W. Pieronczyk, B. Schönhammer, K. Streng, I. Bernal, J. Korp, *Chem. Ber.* **1981,** *114,* 1137.

[5] U. Nagel, B. Rieger, *Organometallics* **1989,** *8,* 1534.

[6] a) H. Rüegger, R. W. Kunz, C. J. Ammann, P. S. Pregosin, *Magn. Reson. Chem.* **1991,** *29,* 197; b) C. J. Ammann, P. S. Pregosin, H. Rüegger, A. Albinati, F. Lianza, R. W. Kunz, *J. Organomet. Chem.* **1992,** *423,* 415.

[7] a) G. Szalontai, P. Sandor, J. Bakos, *Magn. Reson. Chem.* **1991,** *29,* 449; b) P.S. Pregosin, C. Ammann, *Pure Appl. Chem.* **1989,** *61,* 1771; c) A. Albinati, R.W. Kunz, C.J. Ammann, P.S. Pregosin, *Organometallics* **1991,** *10,* 1800.

[8] a) A. Albinati, C. Ammann, P.S. Pregosin, H. Rüegger, *Organometallics* **1990,** *9,* 1826; b) A. Albinati, R.W. Kunz, C.J. Ammann, P.S. Pregosin, *ibid.* **1991,** *10,* 1800.

[9] R.H. Crabtree, J.M. Quirk, H. Felkin, T. Fillebeen-Khan, *Synth. React. Inorg. Met.-Org. Chem.* **1982,** *12,* 407.

[10] T.G. Schenck, J.M. Downes, C.R.C. Milne, P.B. MacKenzie, H. Boucher, J. Whelan, B. Bosnich, *Inorg. Chem.* **1985,** *24,* 2334.

[11] A.J. Shaka, J. Keeler, T. Frenkiel, R. Freeman, *J. Magn. Reson.* **1983,** *52,* 335.

[12] M. Rance, O.W. Sørensen, G. Bodenhausen, G. Wagner, R.R. Ernst, K. Wüthrich, *Biochem. Biophys. Res. Commun.* **1983,** *117,* 479.

[13] J. Jeener, B.H. Meier, P. Bachmann, R.R. Ernst, *J. Chem. Phys.* **1979,** *71,* 4546.

[14] A. Bax, S. Subramanian, *J. Magn. Reson.* **1986,** *67,* 565.

[15] A. Bax, D. Marion, *J. Magn. Reson.* **1988,** *78,* 186.

[16] V. Sklenár, H. Miyashiro, G. Zon, H.T. Miles, A. Bax, *FEBS Lett.* **1986,** *208,* 94.

[17] D. Marion, K. Wüthrich, *Biochem. Biophys. Res. Commun.* **1983,** *113,* 967.

[18] A.R. Sanger, K.G. Tan, *Inorg. Chim. Acta* **1978,** *31,* L439.

[19] S. Brunie, J. Mazan, N. Langlois, H.B. Kagan, *J. Organomet. Chem.* **1976,** *114,* 225.

[20] a) R.G. Ball, N.C. Payne, *Inorg. Chem.* **1977,** *16,* 1187; b) M.R. Churchill, S.A. Bezman, *ibid.* **1972,** *11,* 2243; c) M.R. Churchill, S.A. Bezman, *ibid.* **1973,** *12,* 260; d) M.R. Churchill, S.A. Bezman, *ibid.* **1973,** *12,* 531; e) K. Onuma, A. Nakamura, *Bull. Chem. Soc. Jpn.* **1981,** *54,* 761; f) T. Hayashi, M. Tanaka, I. Ogata, T. Kodama, T. Takahashi, Y. Uchida, T. Uchida, *ibid.* **1983,** *56,* 1780; g) M.P. Anderson, L.H. Pignolet, *Inorg. Chem.* **1981,** *20,* 4101; h) E. Cesarotti, A. Chiesa, G. Ciani, A. Sironi, *J. Organomet. Chem.* **1983,** *251,* 79; i) J. Bakos, I. Tóth, B. Heil, G. Szalontia, L. Párkányi, V. Fülöp, *ibid.* **1989,** *370,* 263; j) Y. Ohga, Y. Iitaka, K. Achiwa, *Chem. Lett.* **1980,** 861; k) U. Nagel, B. Rieger, *Chem. Ber.* **1988,** *121,* 1123.

[21] a) E.P. Kyba, R.E. Davis, P.N. Juri, K.R. Shirley, *Inorg. Chem.* **1981,** *20,* 3616; b) R.E. Davis, B.B. Meyer, K.L. Hassett, P.N. Juri, E.P. Kyba, *Acta Crystallogr., Sect. C* **1984,** *40,* 21; c) H. Brunner. G. Vitulli, W. Porzio, M. Zocchi, *Inorg. Chim Acta* **1985,** *96,* 67; d) H. Brunner, A.F.M.M. Rahman, I. Bernal, *ibid.* **1984,** *83,* L93; e) H. Nishiyama, H. Brunner, P.G. Jones, *J. Organomet. Chem.* **1991,** *405,* 247.

[22] L.M. Haines, E. Singleton, *J. Chem. Soc., Dalton Trans.* **1972,** 1891.

[23] H.C. Volger, K. Vrieze, A.P. Praat, *J. Organomet. Chem.* **1968,** *14,* 429.

[24] a) M. Karplus, *J. Chem. Phys.* **1959,** *30,* 11; b) C.A.G. Haasnoot, F.A.A.M. de Leeuw, C. Altona, *Tetrahedron* **1980,** *36,* 2783.

[25] H. Kessler, H. Oschkinat, C. Griesinger, W. Bermel, *J. Magn. Reson.* **1986,** *70,* 106.

[26] H. Kessler, A. Müller, H. Oschkinat, *Magn. Reson. Chem.* **1985,** *23,* 844.

[27] H.C. Clark, M.J. Hampden-Smith, *Coord. Chem. Rev.* **1987,** *79,* 229.

[28] J.R. Shapley, J.A. Osborn, *J. Am. Chem. Soc.* **1970,** *92,* 6976.

[29] R.S. Berry, *J. Chem. Phys.* **1960,** *32,* 933.

[30] a) H. Rüegger, P.S. Pregosin, *Inorg. Chem.* **1987,** *26,* 2912; b) M.J. Hampden-Smith, H. Rüegger, *Magn. Reson. Chem.* **1989,** *27,* 1107.