Organometallics **1998,** *17,* 5927−5930

New Bis-biphosphole−Transition-Metal Complexes: Spontaneous Isomerization of *trans-meso-* into *cis*-(±)-[Ru(trifluoroacetate)$_2$(1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole)$_2$]

Olivier Tissot, Maryse Gouygou,*,† Jean-Claude Daran, and
Gilbert G. A. Balavoine*,‡

*Laboratoire de Chimie de Coordination du CNRS, 205 Route de Narbonne,
31077 Toulouse Cedex, France*

Received August 3, 1998

*Summary: The reaction of [Ru$_2$(O$_2$CCF$_3$)$_2$(μ-O$_2$CCF$_3$)$_2$(COD)$_2$(μ-H$_2$O)] with 1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole (**1**) provides trans-meso-[Ru(trifluoroacetate)$_2$(1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole)$_2$] complex **3**, which spontaneously isomerizes in solution into cis-(±)-[Ru(trifluoroacetate)$_2$(1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole)$_2$] complex **4**. These new bis-biphosphole−ruthenium complexes have been characterized by X-ray diffraction.*

The structural characterization of 1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole[1] (**1**) (BIPHOS) led to a renewed interest in the coordination chemistry of this C_2-symmetric bidentate ligand, first described by Mathey.[2] Recently, we have synthesized and fully characterized new nickel, palladium, and platinum complexes [MX$_2$(BIPHOS)].[3] With Pd(II) and Rh(I), we obtained the first bis-biphosphole complexes,[3] proving that BIPHOS is a rather good ligand for transition metals. A similar palladium complex was later described by Matsuda and co-workers.[4] We report here the synthesis, spectroscopic characterization and X-ray structural analysis of new ruthenium(II) bis-biphosphole complexes.

[Ru$_2$(O$_2$CCF$_3$)$_2$(μ-O$_2$CCF$_3$)$_2$(COD)$_2$(μ-H$_2$O)][5] (**2**) is a good precursor for the preparation of diphosphine dicarboxylato ruthenium complexes [Ru(O$_2$CCF$_3$)$_2$(P−P)].[6] Surprisingly, the reaction of biphosphole **1**, prepared according to the previously described method,[7] with complex **2** in dichloromethane at 30 °C gives in moderate yield a bis-biphosphole−ruthenium complex **3** (Scheme 1), as indicated by elemental analysis and mass spectroscopy. Crystals of complex **3**, suitable for X-ray analysis, were obtained by slow evaporation from a dichloromethane solution.

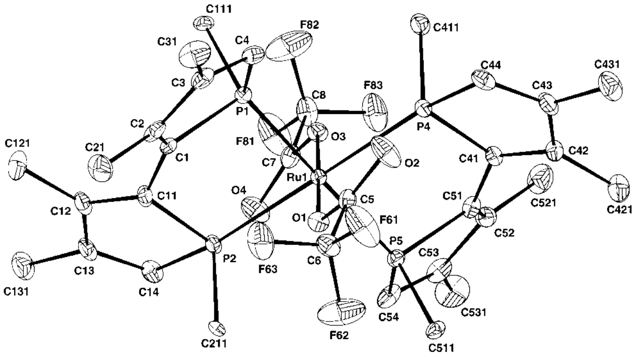
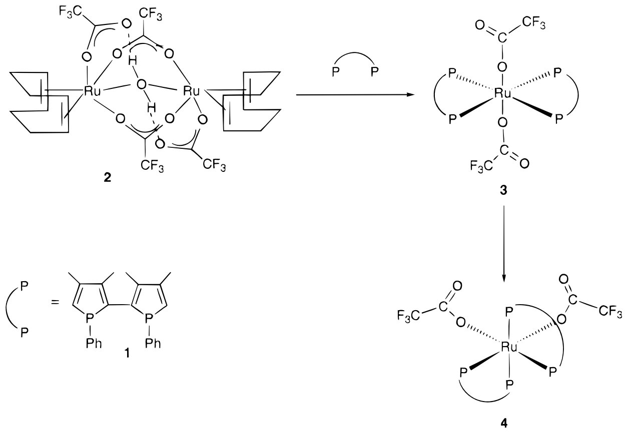


Figure 1. Molecular view of complex **3**. The ellipsoids are drawn at 30% probability. Phenyl carbons are omitted for clarity.

Scheme 1



The CAMERON[8] plot given in Figure 1 shows a near-octahedral geometry for ruthenium and mutually *trans*-ligated monodentate trifluoroacetate groups. X-ray structural analysis confirms the formation of [Ru(O$_2$CCF$_3$)$_2$(BIPHOS)$_2$] as complex **3**. This complex contains the S_{RR} and R_{SS} absolute configurations of the biphosphole **1** (Figure 2), and it is then the *meso* diastereomer as already observed in the [Pd(BIPHOS)$_2$](BF$_4$)$_2$ complex.[3] Surprisingly this compound **3** crystallized in the polar enantiomorphous $P2_1$ space group. This non-centrosymmetry might be induced by the packing arrangement of the complex with the occurrence of four solvent molecules. Indeed, it is worth noting that crystals of the

---

[†] E-mail: gouygou@lcc-toulouse.fr.

[‡] E-mail: balavoin@lcc-toulouse.fr.

[1] Tissot, O.; Gouygou, M.; Daran, J.-C.; Balavoine, G. G. A. *J. Chem. Soc., Chem. Commun.* **1996**, 2288.

[2] Mercier, F.; Holand, S.; F. Mathey, F. *J Organomet Chem.* **1986**, *316*, 271.

[3] Gouygou, M.; Tissot, O.; Daran, J.-C.; Balavoine, G. G. A. *Organometallics* **1997**, *5*, 1008.

[4] Kojima, T. K.; Saeki, K.; Ono, K.; Ohda, M.; Matsuda, Y. *J. Chem. Soc., Chem. Commun.* **1997**, 1679; **1998**, 521.

[5] Albers, M. O.; Liles, D. C.; Singleton, E.; Yates, J. E. *J Organomet Chem.* **1984**, *272*, C62.

[6] Heiser, B.; Broger, E. A.; Crameri, Y. *Tetrahedron: Asymmetry* **1991**, *2*, 51.

[7] Deschamps, E.; Mathey, F. *Bull. Soc. Chim. Fr.* **1992**, *29*, 486.

[8] Watkin, D. J.; Prout, C. K.; Pearce, L. J. *CAMERON*; Chemical Crystallography Laboratory, University of Oxford: Oxford, 1996.

10.1021/om980667i CCC: $15.00 © 1998 American Chemical Society
Publication on Web 12/01/1998

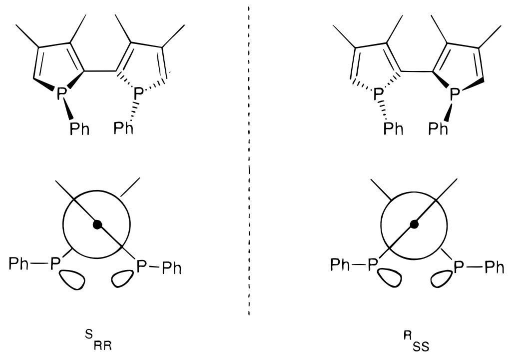


Figure 2. Configuration of the 2,2′-biphosphole ligand in complex **3**. The projection is along the axis of the C−C bond linking the phosphole rings. Superscript refers to axial chirality generated by the biphosphole framework; subscript refers to phosphorus central chirality.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) with esd's in Parentheses for Compounds 3 and 3′

molecule **3**		molecule **3′**	
Ru(1)−P(1)	2.359(1)	Ru(1)−P(1)	2.358(4)
Ru(1)−P(2)	2.388(1)	Ru(1)−P(2)	2.392(4)
Ru(1)−P(5)	2.379(1)	Ru(1)−P(5)	2.372(4)
Ru(1)−P(4)	2.396(1)	Ru(1)−P(4)	2.375(3)
Ru(1)−O(1)	2.125(3)	Ru(1)−O(1)	2.106(9)
Ru(1)−O(3)	2.129(3)	Ru(1)−O(3)	2.112(8)
P(1)−Ru(1)−P(2)	83.75(5)	P(1)−Ru(1)−P(2)	83.4(1)
P(1)−Ru(1)−P(5)	179.17(6)	P(1)−Ru(1)−P(5)	178.7(1)
P(2)−Ru(1)−P(5)	97.06(5)	P(2)−Ru(1)−P(5)	97.3(1)
P(1)−Ru(1)−P(4)	95.38(5)	P(1)−Ru(1)−P(4)	95.8(1)
P(2)−Ru(1)−P(4)	178.89(6)	P(2)−Ru(1)−P(4)	179.1(1)
P(5)−Ru(1)−P(4)	83.80(5)	P(5)−Ru(1)−P(4)	83.5(1)
P(1)−Ru(1)−O(1)	83.3(1)	P(1)−Ru(1)−O(1)	84.8(3)
P(2)−Ru(1)−O(1)	81.8(1)	P(2)−Ru(1)−O(1)	82.5(3)
P(5)−Ru(1)−O(1)	96.7(1)	P(5)−Ru(1)−O(1)	96.3(3)
P(4)−Ru(1)−O(1)	97.5(1)	P(4)−Ru(1)−O(1)	96.9(3)
P(1)−Ru(1)−O(3)	96.4(1)	P(1)−Ru(1)−O(3)	95.7(3)
P(2)−Ru(1)−O(3)	97.5(1)	P(2)−Ru(1)−O(3)	98.2(2)
P(5)−Ru(1)−O(3)	83.7(1)	P(5)−Ru(1)−O(3)	83.1(3)
P(4)−Ru(1)−O(3)	83.3(1)	P(4)−Ru(1)−O(3)	82.5(2)
O(1)−Ru(1)−O(3)	179.2(2)	O(1)−Ru(1)−O(3)	179.2(3)

same *meso* form having only two CH_2Cl_2 solvent molecules, compound **3′**, belong to the centrosymmetric space group $P2_1/c$. Although unexpected, the monodentate coordination mode of the trifluoroacetate groups is not unprecedented, and there are many examples of a such bonding mode for the trifluoroacetate.[9] The four Ru−P bond distances lie in the range 2.32−2.42 Å found for related ruthenium(II) bisphosphine *trans*-disubstituted complexes[10] (cf. Table 1).

This *meso*-Ru complex **3** is stereochemically less stable in dichloromethane solution than the *meso*-palladium complex $[Pd(BIPHOS)_2](BF_4)_2$.[3] Transformation of complex **3** was observed in solution, leading to the formation of a new complex **4** (Scheme 1). By following the course of this conversion by ^{31}P NMR spectroscopy, we observed the disappearance of the singlet at $\delta = 54.5$ corresponding to four equivalent phosphorus nuclei in complex **3** concomitant with the appearance of an ABCD system corresponding to four nonequivalent phosphorus nuclei in complex **4**. Elemental analysis, mass spectroscopy, and ^1H NMR spectroscopy confirmed the formation of a bis-biphosphole−ruthenium complex **4**. The molecular structure determined by X-ray analysis and represented in Figure 3 shows a chiral near-octahedral geometry for ruthenium. As in **3**, this complex **4** contains the pair of enantiomers of biphosphole **1** with S_{RR} and R_{SS} absolute configurations but with two *cis* monodentate trifluoroacetate groups leading to a chiral arrangement around the metal atom. The two Ru−P bond lengths corresponding to the P atoms *trans* to each other, 2.358(4) and 2.394(4) Å, are similar to those observed for **3**, whereas for the two P atoms *trans* to the trifluoroacetate the Ru−P distances are much shorter, 2.275(3) and 2.296(4) Å, as also observed in related complexes[11] (cf. Table 2). This large difference could be the consequence of a strong *trans* influence of the trifluoroacetate ligands. We assume that the formation of the kinetic product **3** is

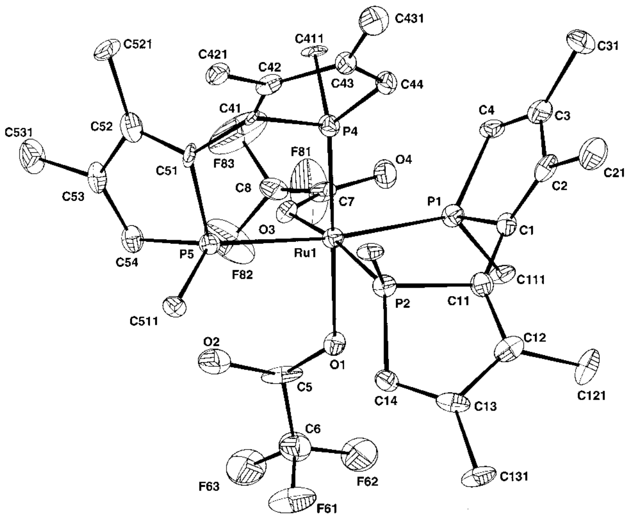


Figure 3. Molecular view of complex **4**. The ellipsoids are drawn at 30% probability.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) with esd's in Parentheses for Compounds 4

Ru(1)−P(1)	2.358(4)	Ru(1)−P(2)	2.296(4)
Ru(1)−P(4)	2.275(3)	Ru(1)−P(5)	2.394(4)
Ru(1)−O(1)	2.173(9)	Ru(1)−O(3)	2.130(9)
P(4)−Ru(1)−P(2)	94.2(1)	O(3)−Ru(1)−O(1)	82.8(3)
P(4)−Ru(1)−P(1)	88.6(1)	O(3)−Ru(1)−P(4)	95.9(2)
P(2)−Ru(1)−P(1)	84.3(1)	O(1)−Ru(1)−P(4)	178.6(3)
O(3)−Ru(1)−P(5)	82.8(2)	O(3)−Ru(1)−P(2)	169.9(2)
O(1)−Ru(1)−P(5)	95.0(3)	O(1)−Ru(1)−P(2)	87.1(2)
P(4)−Ru(1)−P(5)	84.2(1)	O(3)−Ru(1)−P(1)	95.6(2)
P(2)−Ru(1)−P(5)	98.6(1)	O(1)−Ru(1)−P(1)	92.1(3)
P(1)−Ru(1)−P(5)	172.4(1)		

---

[9] (a) Fachinetti, G.; Funaioli, T.; Lecci, L.; Marchetti, F. *Inorg. Chem.* **1996**, *35*, 7217; (b) Wong, W.-K.; Lai, K.-K.; Tse, M.-S.; Tse, M.-C.; Gao, J.-X.; Wong, W.-T.; Chan, S. *Polyhedron* **1994**, *13*, 2751; (c) Nishiyama, H.; Itoh, Y.; Sugawara, Y.; Matsumoto, H.; Aoki, K.; Itoh, K. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1247; (d) Zanetti, N. C.; Spindler, F.; Spencer, J.; Togni, A.; Rihs, G. *Organometallics* **1996**, *15*, 860.

[10] (a)Touchard, D.; Morice, C.; Cadierno, V.; Haquette, P.; Toupet, L.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1994**, 859. (b) Field, L. D.; Hambley, T. W.; Yau, B. C. K. *Inorg. Chem.* **1994**, *33*, 2009. (c) Hockless, D. C. R.; Wild, S. B.; McDonagh, A. M.; Whittall, I. R.; Humphrey, M. G. *Acta Crystallogr., Sect. C* **1996**, *52*, 1639. (d) Faulkner, C. W.; Ingham, S. L.; Khan, M. S.; Lewis, J.; Long, N. J.; Raithby, P. R. *J. Organomet. Chem.* **1994**, *482*, 139. (e) Buys, I. E.; Field, L. D.; George, A. V.; Hambley, T. W.; Purches, G. R. *Aust. J. Chem.* **1995**, *48*, 27. (f) Szczepura, L. F.; Giambra, J.; See, R. F.; Lawson, H.; Janik, T. S.; Jircitano, A. J.; Churchill, M. R.; Takeuchi, K. J. *Inorg. Chim. Acta* **1995**, *239*, 77.

[11] (a) Dobson, A.; Moore, D. S.; Robinson, S. D.; Hurthouse, M. B.; New, L. *Polyhedron* **1985**, *4*, 1119. (b) Albers, M. O.; Liles, D. C.; Singleton, E. *Acta Crystallogr., Sect. C* **1987**, *43*, 860.

Table 3. Crystal Data

	3	**3′**	**4**
formula	$C_{52}H_{48}F_6O_4P_4Ru$, $(CH_2Cl_2)_4$	$C_{52}H_{48}F_6O_4P_4Ru$, $(CH_2Cl_2)_2$	$C_{52}H_{48}F_6O_4P_4Ru$, C_5H_{12}, $CH_3CO_2C_2$
fw	1415.6	1245.8	1155.98
cryst size, mm	0.58 × 0.45 × 0.30	0.8 × 0.3 × 0.3	0.38 × 0.08 × 0.05
cryst system	monoclinic	monoclinic	orthorhombic
space gp	$P2_1$	$P2_1/c$	$Pcab$
a, Å	11.120(2)	22.416(5)	20.652(2)
b, Å	23.012(3)	11.144(2)	21.906(3)
c, Å	12.145(2)	22.628(2)	24.229(3)
β, deg	96.38(2)	104.58(2)	
V, Å^3	3088.6(8)	5493(8)	10961(2)
Z	2	4	8
D_{calcd}, g cm^{-3}	1.522	1.501	1.401
μ(Mo Kα), cm^{-1}	7.650	6.511	4.70
no. of rflns collected	17 973	3937	33 608
no. of unique rflns (R_{int})	9373(0.055)	3789(0.026)	5777(0.212)
refinement method	full-matrix on F	full-matrix on F	full-matrix on F^2
no. of data/restraints/params	8095/0/714	2343/0/389	5777/0/644
R ($I > 2\sigma(I)$)[a]	0.0476	0.0676	0.0847
R_w[a]	0.0555	0.0796	
wR^2 (all data)[a]			0.1749
goodness of fit	1.070	1.170	1.068

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma(|F_o|)$, $R_w = \{\Sigma[w(|F_o| - |F_c|)]^2/\Sigma[w(F_o)^2\}^{1/2}$, $wR^2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o)^2]\}^{1/2}$.

probably controlled by steric factors. Indeed, the molecular structures reveal that steric constraints between the two enantiomers of **1** seem to be lower in the *trans-meso*-**3** than in the *cis*-(±)-**4**. On the other hand, we assume that the isomerization of the *trans-meso*-**3** into the thermodynamic product *cis*-(±)-**4** is triggered by the *trans* influence of the monodentate trifluoroacetate ligands. We may consider that this *trans* influence facilitates a decoordination−recoordination process of one of the trifluoroacetate ligands eventually assisted by the formation of an intermediate with a trihapto coordination of the other.

Experimental Section

General Procedures. All reactions were conducted under an inert atmosphere of dry argon by using Schlenk glassware and vacuum line techniques. Solvents were freshly distilled from standard drying agents.

^1H, $^{13}C\{^1H, ^{31}P\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on the Bruker WMX 400 instrument operating at 400, 162, and 100 MHz, respectively. Chemical shifts are reported in parts per million (ppm) relative to Me_4Si (^1H and ^{13}C) or 85% H_3PO_4 (^{31}P).

Elemental analyses were performed by the “Service d’Analyse du Laboratoire de Chimie de Coordination” at Toulouse, France.

Mass spectra were obtained on a Mermag R10-10 instrument.

Synthesis of [Ru(O_2CCF_3)$_2$(BIPHOS)$_2$], 3. To a solution of 31 mg of $[Ru_2(O_2CCF_3)_2(\mu\text{-}O_2CCF_3)_2(COD)_2(\mu\text{-}H_2O)]$ (0.033 mmol) in 2 mL of dichloromethane was added a solution of 52 mg of biphosphole **1** (0.13 mmol, 4 equiv) in 1 mL of dichloromethane. The yellow mixture was stirred for 3 h at 30 °C. After removal of the solvent the resulting orange solid was washed two times with 1 mL of diethyl ether at 0 °C and then dried in vacuo. Orange blocks of **3** were isolated after crystallization in a CH_2Cl_2 solution. Yield: 30 mg (40%). Mp: 197 °C (decomp). Anal. Calcd for $C_{52}H_{48}P_4O_4F_6Ru$: C, 58.05; H, 4.49. Found: C, 57.86; H, 4.28. MS (FAB, MNBA matrix), *m/z*: 1077 (M^+, 27); 963 ($[M - O_2CCF_3]^+$, 100); 849 ($[M - 2(O_2CCF_3)]^+$, 56). ^1H NMR (CD_2Cl_2): δ 1.99 (s, 12H, Me21,121,321,421), 2.08 (d, 12H, $^4J_{HH}$ 1.0 Hz, Me31,131,321,421), 6.79 (m, 4H, =CH−P), 6.91−7.15 (m, 20H, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 54.5. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 161.11 (q, $^2J_{CF}$ 38.2 Hz, O_2CCF_3), 151.74 (s, C3,13,43,53), 142.43 (t, J_{CP} 6.9 Hz, C2,12,52,42), 138.89 (t, J_{CP} 19.0 Hz, C1,11,41,51), 128.12 (t, J_{CP} 20.8 Hz, C4,14,44,54), 112.29 (q, J_{CF} 293.4 Hz, O_2CCF_3), 17.37 (t, J_{CP} 2.5 Hz, C31,131,431,531), 15.02 (t, J_{CP} 1.7 Hz, C21,121,421,521).

Synthesis of [Ru(O_2CCF_3)$_2$(BIPHOS)$_2$], 4. Complex **4** was quantitatively obtained by slow evolution of **3** in a dichloromethane solution within 8 days at room temperature. **4** crystallizes from an ethyl acetate solution by slow diffusion with pentane as yellow plates. Mp: 203 °C (decomp). Anal. Calcd for $C_{52}H_{48}P_4O_4F_6Ru$: C, 58.05; H, 4.49. Found: C, 58.35; H, 4.54. MS (FAB, MNBA matrix), *m/z*: 963 ($[M - O_2CCF_3]^+$, 100); 849 ($[M - 2(O_2CCF_3)]^+$, 44). ^1H NMR (CD_2Cl_2): δ 1.38 (s, 3H), 1.91 (s, 3H), 2.11 (s, 3H), 2.32 (s, 3H) [Me21,121,321,421], 1.66 (s, br, 3H), 1.70 (d,$^4J_{HH}$ 1.8 Hz, 3H), 1.90 (s, br, 3H), 2.16 (d, $^4J_{HH}$ 2.7 Hz, 3H) [Me31,131,321,421], 5.61 (d, $^2J_{HP}$ 28.9 Hz, 1H), 6.17 (d, $^2J_{HP}$ 28.8 Hz, 1H), 6.71 (d, $^2J_{HP}$ 27.3 Hz, 1H), 7.03 (d, $^2J_{HP}$ 21.1 Hz, 1H) [=CH−P], 6.23−8.05 (m, 20H, Ph). $^{31}P\text{-}\{^1H\}$ NMR (CD_2Cl_2): δ 63.35 (m, P_A, P_B), 54.11 (m, P_C), 44.78 (m, P_D). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 153.23 (d, J_{CP} 8.7 Hz), 152.00 (m), 150.39 (m), 149.32 (m) [C3,13,43,53], 146.94 (t, J_{CP} 12.7 Hz), 142.47 (t, J_{CP} 13.0 Hz), 137.54 (s, br), 136.72 (d, J_{CP} 13.7 Hz) [C2,12,52,42], 145,12 (m), 140.13 (m), 139.69 (m), 137.16 (m) [C1,11,41,51], 133.92 (d, J_{CP} 39.5 Hz), 132.05 (m), 127.04 (d, J_{CP} 38.0 Hz), 121.25 (d, J_{CP} 46.0 Hz) [C4,14,44,54], 18.44 (d, J_{CP} 5.0 Hz), 17.53 (d, J_{CP} 10.8 Hz), 17.1 (d, J_{CP} 10.2 Hz), 16.96 (d, J_{CP} 9.7 Hz) [C31,131,431,531], 15.37 (d, J_{CP} 6.9 Hz), 15.21 (d, J_{CP} 7.1 Hz), 14.60 (d, J_{CP} 7.9 Hz), 14.40 (d, J_{CP} 9.6 Hz) [C21,121,421,521].

X-ray Structure Determination. For **3** and **4**, the data were collected on a Stoe IPDS (Imaging Plate Diffraction System) equipped with an Oxford Cryosystems cooler device, whereas for **3′** an Enraf-Nonius CAD4F was used. The final unit cell parameters were obtained by the least-squares refinement of 5000 reflections for **3** and **4** and based on 25 well-centered reflections for **3′**. Only statistical fluctuations were observed in the intensity monitors over the course of the data collection for **3** and **4**, but a decrease of 44% was observed in the case of **3′**.

The three structures were solved by direct methods (SIR92)[12] and refined by least-squares procedures. H atoms were introduced in calculation in idealized positions (d(CH) = 0.96 Å) and were treated as riding models with isotropic thermal parameters 20% higher than those of the carbon to which they

---

(12) Altomare, A.; Cascarano, G.; Giacovazzo, G.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *SIR92*−a program for automatic solution of crystal structures by direct methods. *J Appl. Crystallogr.* **1994**, *27*, 435.

are attached. Details of data collections and refinements are given in Table 3. In crystal **4**, there is apparently a disordered mixture of pentane and ethyl acetate solvents statistically distributed around inversion centers; however no correct models could be defined and all the residual electron densities were considered as C atoms. The calculations were carried out with the CRYSTALS package[13] or the SHELXL97 program[14] running on a PC. The drawing of the molecule was realized with the help of CAMERON.[8]

Selected bond lengths and bond angles are given in Tables 1 and 2.

Acknowledgment. We acknowledge the CNRS and Rhône-Poulenc for financial support and Professor F. Mathey for advice and fruitful discussions.

Supporting Information Available: The fractional atomic coordinates, full bond lengths and bond angles, anisotropic thermal parameters, and atomic coordinates for H atoms for **3**, **3′**, and **4** (20 pages). Ordering information is given on any current masthead page. This information has also been deposited at the Cambridge Crystallographic Data Centre.

OM980667I

---

(13) Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS Issue 10*; Chemical Crystallography Laboratory, University of Oxford: Oxford, 1996.

(14) Sheldrick, G. M. *SHELXL-97*, program for crystal structure refinement; University of Göttingen, 1997.