Synthesis, Separation, and Stereochemical Studies of Chiral-at-Metal Rhodium(III) Complexes. Crystal Structure of (S_{Rh},R_C)-$[(\eta^5\text{-}C_5Me_5)RhCl\{Ph_2PCH(Me)CH_2PPh_2\}]BF_4$

Daniel Carmona,* Fernando J. Lahoz, and Luis A. Oro

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas, 50009 Zaragoza, Spain

María Pilar Lamata, Fernando Viguri, and Emilio San José

Departamento de Química Inorgánica, Escuela Universitaria de Ingeniería Técnica e Industrial, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza, Corona de Aragón 35, 50009 Zaragoza, Spain

Received February 26, 1996[⊗]

The synthesis of chiral-at-metal $[(\eta^5\text{-}C_5Me_5)RhX(prophos)]X$ (prophos = (*R*)-1,2-propanediylbis(diphenylphosphine); X = Cl (**2a**, **2a′**), I (**4a**)) complexes from $[\{(\eta^5\text{-}C_5Me_5)RhX\}_2(\mu\text{-}X)_2]$ in methanol is reported (de = 54 and ≥98, respectively). The rhodium center is configurationally stable in the iodo complex, but the chloro analogue epimerizes in polar solvents. Complexes **2** and **4** are formed through the dinuclear intermediates $[\{(\eta^5\text{-}C_5Me_5)RhX_2\}_2(\mu\text{-prophos})]$ and the monodentate diphosphine complexes $[(\eta^5\text{-}C_5Me_5)RhX_2(prophos)]$ with high stereoselectivity. The determination of the absolute configuration of **2a** and **2a′** complexes comes from the X-ray diffraction study of $[(\eta^5\text{-}C_5Me_5)RhCl(prophos)]BF_4$ (**2b**) obtained from mixtures of **2a** and **2a′** by anion exchange. In **2b** the chiral metal exhibits an *S* absolute configuration.

Introduction

Chiral-at-metal, pseudo-octahedral, three-legged "piano stool" complexes are excellent templates for stoichiometric asymmetric synthesis and have therefore been extensively studied.[1] In addition, the investigation of the stereochemical course of simple reactions that provides detailed information regarding the identification and definition of catalytic cycles appears more facile when these compounds are used.[1c,d,2] In some of these complexes, the metal is the unique center of chirality, while, in other species, optically active ligands such as α-amino acids,[3] Schiff bases,[4] or diphosphines[2c] are also present. Especially relevant are the stereochemical studies performed by Consiglio *et al.* on ruthenium complexes of the type $[(\eta^5\text{-}C_5H_5)RuX(prophos)]^{n+}$ (prophos = (*R*)-1,2-propanediylbis(diphenylphosphine) ($Ph_2PCH(Me)CH_2PPh_2$)),[2c] as well as the catalytic studies, reported by Noyori *et al.*, on (arene)ruthenium compounds of the type $[(\eta^6\text{-arene})Ru(binap)X]^+$ (binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl).[5]

Direct reaction between diphosphines and $[\{(\eta^5\text{-}C_5Me_5)MCl\}_2(\mu\text{-}Cl)_2]$ (M = Rh, Ir) or $[\{(\eta^6\text{-arene})RuCl\}_2(\mu\text{-}Cl)_2]$ dimers has proven to be an excellent preparative method for the synthesis of binuclear neutral diphosphino-bridged $[\{(\eta\text{-ring})MCl_2\}_2(\mu\text{-diphosphine})]$ compounds[6] although, in some cases, neutral mononuclear complexes with monodentate diphosphine ligands have been prepared instead.[7] However, the preparation of related cationic compounds of formula $[(\eta\text{-ring})MCl(diphosphine)]Cl$ has been rarely achieved by this route due to the contamination of the desired products by the

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1996.

(1) (a) Davies, S. G. *Pure Appl. Chem.* **1988**, *60*, 40. (b) Davies, S. G. *Aldrichim. Acta* **1990**, *23*, 31. (c) Brunner, H. *Adv. Organomet. Chem.* **1980**, *18*, 151. (d) *Organometallic Compounds and Optical Activity. J. Organomet. Chem.* **1989**, 370 (Brunner, H., Vol. Ed.). (e) Faller, J. W.; Mazzieri, M. R.; Nguyen, J. T.; Parr, J.; Tokunaga, M. *Pure Appl. Chem.* **1994**, *66*, 1463.

(2) See for example: (a) Meyer, O.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1995**, *14*, 1844 and references therein. (b) Johnson, T. J.; Alvey, L. J.; Brady, M.; Mayne, C. L.; Arif, A. M.; Gladysz, J. A. *Chem. Eur. J.* **1995**, *1*, 294 and references therein. (c) Consiglio, G.; Morandini, F. *Chem. Rev.* **1987**, *87*, 761.

(3) (a) Dersnah, D. F.; Baird, M. C. *J. Organomet. Chem.* **1977**, *127*, C55. (b) Sheldrick, W. S.; Heeb, S. *J. Organomet. Chem.* **1989**, *377*, 357. (c) Sheldrick, W. S.; Heeb, S. *Inorg. Chim. Acta* **1990**, *168*, 93. (d) Sheldrick, W. S.; Gleichmann, A. *J. Organomet. Chem.* **1994**, *470*, 183. (e) Krämer, R.; Polborn, K.; Wanjek, H.; Zahn, I.; Beck, W. *Chem. Ber.* **1990**, *123*, 767. (f) Zahn, I.; Wagner, B.; Polborn, K.; Beck, W. *J. Organomet. Chem.* **1990**, *394*, 601. (g) Zahn, I.; Polborn, K.; Wagner, B.; Beck, W. *Chem. Ber.* **1991**, *124*, 1065. (h) Krämer, R.; Polborn, K.; Robl, C.; Beck, W. *Inorg. Chim Acta* **1992**, *198-200*, 415. (i) Krämer, R.; Maurus, M.; Bergs, R.; Polborn, K.; Sünkel, K.; Wagner, B.; Beck, W. *Chem. Ber.* **1993**, *126*, 1969. (j) Werner, H.; Daniel, T.; Nürnberg, O.; Knaup, W.; Meyer, U. *J. Organomet. Chem.* **1993**, *445*, 229. (k) Carmona, D.; Mendoza, A.; Lahoz, F. J.; Oro, L. A.; Lamata, M. P.; San José, E. *J. Organomet. Chem.* **1990**, *396*, C17. (l) Carmona, D.; Lahoz, F. J.; Atencio, R.; Oro, L. A.; Lamata, M. P.; San José, E. *Tetrahedron: Asymmetry* **1993**, *4*, 1425.

(4) (a) Mandal, S. K.; Chakravarty, A. R. *J. Organomet. Chem.* **1991**, *417*, C59. (b) Mandal, S. K.; Chakravarty, A. R. *J. Chem. Soc., Dalton Trans.* **1992**, 1627. (c) Mandal, S. K.; Chakravarty, A. R. *Inorg. Chem.* **1993**, *32*, 3851. (d) Brunner, H.; Oeschey, R.; Nuber, B. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 866. (e) Brunner, H.; Oeschey, R.; Nuber, B. *Inorg. Chem.* **1995**, *34*, 3349.

(5) Noyori, R. In *Asymmetric Catalysis in Organic Synthesis*; John Wiley and Sons: New York, 1994; Chapters 2 and 3.

(6) (a) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970. (b) Keim, W.; Kraneburg, P.; Dahmen, G.; Deckers, G.; Englert, U.; Linn, K.; Spaniol, T. P.; Raabe, G.; Krüger, C. *Organometallics* **1994**, *13*, 3085.

(7) (a) Coleman, A. W.; Jones, D. F.; Dixneuf, P. H.; Brisson, C.; Bonnet, J.-J.; Lavigne, G. *Inorg. Chem.* **1984**, *23*, 952. (b) Coleman, A. W.; Zhang, H.; Bott, S. G.; Dixneuf, P. H. *J. Coord. Chem.* **1987**, *16*, 9.

S0276-7333(96)00134-3 CCC: $12.00

diphosphino-bridged species, as well as mononuclear bis(diphosphine) compounds formed by loss of the η-ring ligand.[8] As an alternative route, the oxidative addition reaction of MeI to rhodium(I) compounds, has been exploited as a preparative method for a variety of related cationic mononuclear rhodium(III) compounds of stoichiometry [(η^5-ring)Rh(Me)(diphosphine)]I (ring = cyclopentadienyl, indenyl).[9] Additionally, it has been very recently reported that the treatment of [{(η^5-C_5Me_5)RhCl}$_2$(μ-Cl)$_2$] with the diphosphine bis(bis(pentafluorophenyl)phosphino)ethane (dfppe) afforded the cationic mononuclear complex [{η^5-C_5Me_3[$CH_2C_6F_4$P(C_6F_5)CH_2]$_2$-1,3}RhCl]Cl in which one *ortho* C−F bond of one of the pentafluorophenyl rings and one C−H bond of the methyl groups have been cleaved and two C−C bonds have been formed, with concomitant displacement of two HF molecules.[10]

We report herein a simple procedure which leads to optically pure cationic complexes [(η^5-C_5Me_5)RhX(prophos)]$^+$ (X = Cl, I) in high chemical yield. The binuclear diphosphino-bridged [{(η^5-C_5Me_5)RhX$_2$}$_2$(μ-prophos)] and the mononuclear [(η^5-C_5Me_5)RhX$_2${Ph_2PCH$_2$CH(Me)PPh_2}] and [(η^5-C_5Me_5)RhX$_2${Ph_2PCH(Me)-CH_2PPh_2}] are characterized as intermediates for this preparative route. In order to assign the absolute configuration of the metal, the molecular structure of the cationic complex [(η^5-C_5Me_5)RhCl(prophos)]BF_4 has been determined by diffractometry. The cationic compounds undergo epimerization processes at the metal which are also discussed.

Results and Discussion

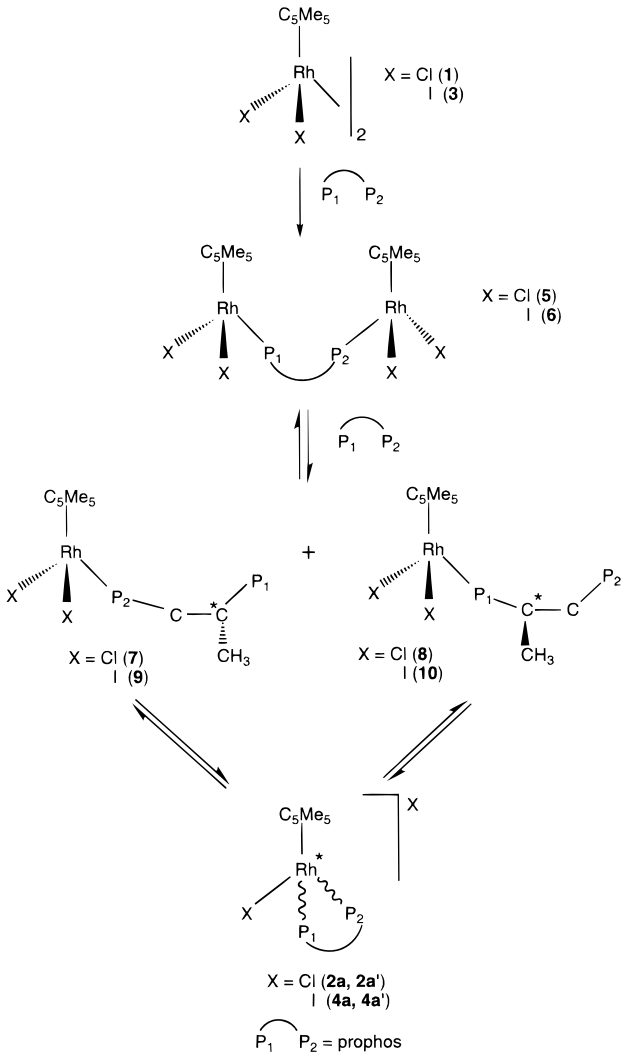
The reaction of the dinuclear chloride complex [{(η^5-C_5Me_5)RhCl}$_2$(μ-Cl)$_2$] (**1**) with 1 equiv of prophos in methanol-d_4 afforded two diastereomers of the cationic compound [(η^5-C_5Me_5)RhCl(prophos)]Cl, **2a** and **2a′**, that differ in the configuration at the metal (eq 1). The

$$\frac{1}{2}[\{(\eta^5\text{-}C_5Me_5)RhX\}_2(\mu\text{-}X)_2] + \text{prophos} \rightarrow \underset{X = Cl\ (\mathbf{1}),\ I\ (\mathbf{3})}{} \quad (SR,RR)\text{-}[(\eta^5\text{-}C_5Me_5)RhX(\text{prophos})]X \quad (1)$$
$$X = Cl\ (\mathbf{2a},\ \mathbf{2a'}),\ I\ (\mathbf{4a})$$

reaction was monitored by ^{31}P NMR, and this technique showed that (i) it was completed after 5 min, (ii) **2a** and **2a′** were the only detectable reaction products, and (iii) diastereomer **2a** was predominantly formed (molar ratio 77:23 for **2a**:**2a′**).[11] The analogous reaction with the iodine derivative [{(η^5-C_5Me_5)RhI}$_2$(μ-I)$_2$] (**3**) is completely stereoselective, with only one of the diastereomers of the complex [(η^5-C_5Me_5)RhI(prophos)]I (**4a**, de ≥ 98%) being obtained.

Diastereomerically pure samples of the tetrafluoroborate derivatives [(η^5-C_5Me_5)RhX(prophos)]BF_4 (X = Cl (**2b**), I (**4b**)) can be prepared by adding, in methanol, equimolecular amounts of $NaBF_4$ to 77:23 mixtures of **2a**:**2a′** (60% chemical yield) or pure **4a** (95% chemical yield). From the mother liquors of the former, a 19:81 mixture of **2b**:**2b′** could be isolated.

Scheme 1



Kinetic control of the asymmetric induction in organotransition-metal complexes is a focus of current interest.[12] In order to gain some insight into the process of formation of the cationic complexes **2a**, **2a′**, and **4a**, we have carried out reaction 1 in chloroform (Scheme 1). Addition of prophos to a chloroform solution of the dimers **1** or **3** (1:1 molar ratio) afforded the binuclear complexes [{(η^5-C_5Me_5)RhX$_2$}$_2$(μ-prophos)] (X = Cl (**5**), I (**6**)) in quantitative yield. Subsequently, complexes **5** and **6** reacted with an additional 1 mol of prophos to yield a mixture of the neutral species [(η^5-C_5Me_5)RhX$_2$-{Ph_2PCH$_2$CH(Me)PPh_2}] (X = Cl (**7**), I (**9**)) and [(η^5-C_5-Me_5)RhX$_2${Ph_2PCH(Me)CH_2PPh_2}] (X = Cl (**8**), I (**10**)), in which the diphosphine acts as a monodentate ligand, along with the corresponding cationic diastereomers **2a**, **2a′**, **4a**, and **4a′**. Complexes **5**−**7** and **9** were fluxional. The variable-temperature ^{31}P{^{1}H} NMR spectra of these complexes could be accounted for by assuming that, at room temperature or above, there is free rotation around the Rh−P_2 bonds (see Scheme 1). Below room temperature this process was slowed down, and the low-limiting temperature spectrum has been achieved, in all cases, at −50 °C. Conversely, the ^{31}P{^{1}H} NMR

(8) Fogg, D. E.; James, B. R. *J. Organomet. Chem.* **1993**, *462*, C21.
(9) (a) Morandini, F.; Consiglio, G. *J. Chem. Soc., Chem. Commun.* **1991**, 676. (b) Morandini, F.; Pilloni, G.; Consiglio, G.; Sironi, A.; Moret, M. *Organometallics* **1993**, *12*, 3495.
(10) Atherton, M. J.; Fawcett, J.; Holloway, J. H.; Hope, E. G.; Karaçar, A.; Rusell, D. R.; Saunders, G. C. *J. Chem. Soc., Chem. Commun.* **1995**, 191.
(11) Ratios were determined from ^{31}P NMR measurements. Error limits on each integer are estimated as ±2.
(12) See for example: Peng, T.-S.; Arif, A. M.; Gladysz, J. A. *J. Chem. Soc., Dalton Trans.* **1995**, 1857 and references therein.

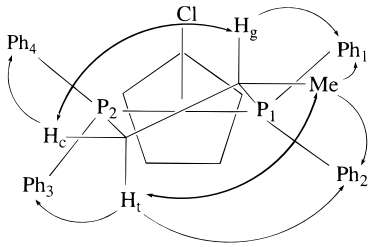


Figure 1. Schematic view of the prophos ligand in complex **2b** projected onto the C_5Me_5 ring (methyls omitted for clarity). Some selected NOE effects are shown.

spectra of complexes **8** and **10** were not temperature dependent from −50 to 60 °C and showed that the compounds were stereochemically rigid. Most probably the rotation around the Rh−P_1 bond is hindered by the presence of the *geminal* to phosphorus methyl group. Additionally, the formation of **2a**, **2a′**, **4a**, and **4a′** from the corresponding **7**−**10** was highly stereoselective.

The new complexes have been characterized by a combination of elemental analysis and spectroscopic methods (see Experimental Section). The $^{31}P\{^1H\}$ NMR spectrum of **2b** consisted of two double doublets centered at 74.9 and 45.5 ppm. Its $^{31}P\{^1H\}-^1H$ correlation spectrum allowed us to assign the resonance at 74.9 ppm to the phosphorus nucleus nearer to the asymmetric carbon atom. Besides the C_5Me_5 peak and the phenyl resonances, its ^1H NMR spectrum showed three multiplets at 2.13, 2.87, and 3.54 ppm due to the CH_2 and CH protons and a double doublet at 1.23 ppm attributed to the methyl group of the diphosphine ligand (see Figure 1). An $^1H-^1H$ COSY experiment permitted us to assign the signal at 3.54 ppm to H_g. The signals centered at 2.13 and 2.87 ppm were attributed to H_t and H_c on the basis of their relative NOE effects with the H_g hydrogen and the methyl diphosphine group. The assignment of the *ortho* proton resonances for the four phenyl groups was made through inspection of their NOE effects with H_g, H_c, H_t, and the Me group of the diphosphine ligand. Moreover, these latter NOE effects supported an equatorial disposition for the methyl group with a λ conformation for the Rh(prophos) metallacycle.[13]

The assignments of the NMR resonances of the **2b′** were done in a similar way. The NMR data for this complex are collected in the Experimental Section. As in **2b**, all the data were consistent with a λ conformation for the Rh(prophos) metallacycle.

Although the spectral data allowed us to assign the conformation of the metallacycle in solution for complexes **2b** and **2b′**, they were not conclusive for the assignment of the metal absolute configuration. In order to accomplish this point, an X-ray structural analysis of complex **2b** was undertaken. A molecular representation of the complex cation is shown in Figure 2. Bond parameters and atomic coordinates are reported in Table 1 and the Supporting Information, respectively. The coordination around the rhodium is pseudo-octahedral. An η^5-C_5Me_5 group occupies three *fac* coordination positions, and the chelate diphosphine and one chlorine ligand complete the coordination sphere of the metal. The rhodium center displays an *S* configuration.[14] The Rh(prophos) metallacycle has a λ conformation (C(37) is equatorially disposed)[13] with a negative torsion angle[15] P(2)−C(35)−C(36)−P(1) of −52.7(5)°. The cyclopentadienyl ring is roughly planar with slightly different C−C [range 1.418(8)−1.459(8) Å] and Rh−C [range 2.217(5)−2.253(6) Å] bond lengths, as a consequence of the asymmetry of coordination around the metal. The rhodium atom lies 1.873(1) Å apart from the least-squares plane through the five-membered carbocyclic ring. The methyl substituents are bent away from the rhodium, the largest displacements from the plane through the carbocyclic ring corresponding to carbons C(6), C(7), and C(10), 0.225(7), 0.219(8), and 0.221(7) Å, respectively. The two Rh−P bond distances are slightly different from each other: the Rh−P(1) value, 2.314(1) Å, is close to those found for the related Rh(III) complex[16] $[(\eta^5\text{-}C_5Me_5)RhH(PPh_3)_2]PF_6$, 2.309(4) and 2.306(5) Å, while the Rh−P(2) bond distance, 2.335-

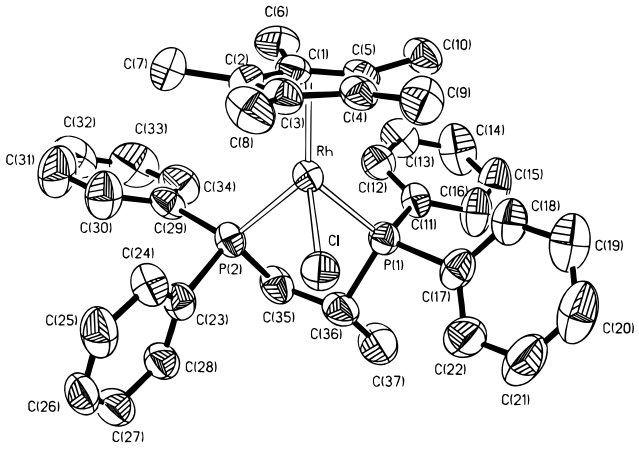


Figure 2. Molecular view of the cation of the complex $[(\eta^5\text{-}C_5Me_5)RhCl(prophos)]BF_4$ (**2b**).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex 2b[a]

Rh−Cl	2.393(1)	P(2)−C(35)	1.832(5)
Rh−P(1)	2.314(1)	C(1)−C(2)	1.427(8)
Rh−P(2)	2.335(1)	C(1)−C(5)	1.455(7)
Rh−C(1)	2.217(5)	C(1)−C(6)	1.482(8)
Rh−C(2)	2.236(6)	C(2)−C(3)	1.420(8)
Rh−C(3)	2.253(5)	C(2)−C(7)	1.513(8)
Rh−C(4)	2.229(5)	C(3)−C(4)	1.459(8)
Rh−C(5)	2.244(5)	C(3)−C(8)	1.472(9)
Rh−G	1.873(2)	C(4)−C(5)	1.418(8)
P(1)−C(11)	1.826(6)	C(4)−C(9)	1.477(8)
P(1)−C(17)	1.821(6)	C(5)−C(10)	1.485(8)
P(1)−C(36)	1.841(6)	C(35)−C(36)	1.528(8)
P(2)−C(23)	1.825(6)	C(36)−C(37)	1.537(10)
P(2)−C(29)	1.826(6)		
Cl−Rh−P(1)	83.0(1)	Rh−P(1)−C(36)	107.1(2)
Cl−Rh−P(2)	89.3(1)	Rh−P(2)−C(23)	115.2(2)
Cl−Rh−G	120.0(1)	Rh−P(2)−C(29)	123.1(2)
P(1)−Rh−P(2)	84.8(1)	Rh−P(2)−C(35)	106.8(2)
P(1)−Rh−G	131.7(1)	P(2)−C(35)−C(36)	110.8(4)
P(2)−Rh−G	132.3(1)	P(1)−C(36)−C(35)	107.4(4)
Rh−P(1)−C(11)	117.6(2)	P(1)−C(36)−C(37)	113.8(5)
Rh−P(1)−C(17)	113.5(2)	C(35)−C(36)−C(37)	113.0(5)

[a] G represents the centroid of the C_5Me_5 group.

(13) Fryzuk, M. D.; Bosnich, B. *J. Am. Chem. Soc.* **1978**, *100*, 5491.

(14) (a) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598. (b) Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1. (c) The absolute configuration of complexes **2a**, **2b**, and **4a′** is $S_{Rh}R_C$, while **2a′**, **2b′**, **4a**, and **4b** are the corresponding $R_{Rh}R_C$ epimers.

(15) (a) Hall, M. C.; Kilburn, B. T.; Taylor, K. A. *J. Chem. Soc.* **1970**, 2539. (b) Commission on the Nomenclature of Inorganic Chemistry of the IUPAC. *Inorg. Chem.* **1970**, *9*, 1.

(16) Mingos, D. M. P.; Minshall, P. C.; Hursthouse, M. B.; Malik, K. M. A.; Willoughby, S. D. *J. Organomet. Chem.* **1979**, *181*, 169.

(2) Å, compares well with those found for[17] [(η^5-C_5Me_5)RhCl($PPh_2CH_2CH_2NEt_2$)$_2$]BPh_4, 2.338(2) and 2.358(2) Å. The Rh−Cl distance, 2.393(1) Å, is not significantly different from those found in complexes [(η^5-C_5Me_5)RhCl(dimethylglyoxime)]Cl,[18] 2.389(1) Å, [(η^5-C_5Me_5)RhCl(1,10-phenanthroline)]ClO_4,[19] 2.386(1) Å, and [(η^5-C_5Me_5)RhCl($PPh_2CH_2CH_2NEt_2$)$_2$]BPh_4,[17] 2.393(2) Å. The angles around the rhodium atom are in the sequence P(2)−Rh−G, 132.3(1) > P(1)−Rh−G, 131.7(1) > Cl−Rh−G, 120.0(1) > Cl−Rh−P(2), 89.3(1) > P(1)−Rh−P(2), 84.8(1) > Cl−Rh−P(1), 83.0(1)°, with the chlorine ligand bent toward the P(1) atom.

The crystallographic determination of the absolute configuration of **2b** permitted us to assign the configuration $R_{Rh}R_C$ to the less stable diastereomer **2b′** and the configurations $S_{Rh}R_C$ and $R_{Rh}R_C$ to the related complexes **2a** and **2a′**, respectively.[14c] Moreover, Consiglio *et al*. have reported that in compounds of stoichiometry [(η^5-C_5Me_5)RuL(prophos)]X diastereomers having the $S_{Ru}R_C$ configuration exhibit differences in the ^{31}P chemical shifts for the two phosphorus atoms which are always larger than those for the $R_{Ru}R_C$ diastereomers. Furthermore, the chemical shifts of the $R_{Ru}R_C$ diastereomers usually fall between those for the $S_{Ru}R_C$ ones.[2c] In keeping with these empirical criteria, which also apply to related ruthenium and iron compounds,[20] the rhodium atom in the iodo complexes **4a**,**b** should display an *R* absolute configuration.[21] From NOEDIFF experiments, a λ conformation, in solution, was assigned to complex **4b**.

At room temperature, in solution, the rhodium center in complexes **2** and **4** is configurationally stable. Thus, for example, a 77:23 mixture of **2a**:**2a′** remained unchanged after 30 days in methanol-d_4. Even at 55 °C, in chloroform, a 19:81 mixture of **2b**:**2b′** retained its composition after 13 h, and we have not detected the formation of **4b′** by refluxing **4b**, in methanol, during 21 days. However, epimerization of complex **2** at rhodium takes place on heating it in polar solvents such as methanol, cyclopentanol, or dimethyl sulfoxide. We have measured the equilibrium constant for the process **2b** ⇌ **2b′**, in refluxing methanol, as 0.041, approaching it from both directions. Starting with **2b** (3.9×10^{-3} M) the ratio [**2b′**]/[**2b**] was 0.041 after 14 days. Starting with a solution 3.9×10^{-3} M in a 19:81 mixture of **2b**:**2b′**, the ratio [**2b′**]/[**2b**] was also 0.041 after 24 h. An identical ratio [**2a′**]/[**2a**] of 0.041 was achieved by refluxing, in methanol, a 77:23 mixture of **2a**:**2a′**. This composition remained unchanged during 7 days.

Next, epimerization of complex **2b′** was monitored by ^{31}P NMR spectroscopy, in methanol-d_4. At 55 °C, the process showed an induction period of *ca*. 3 h that decreased to 1 h, at 62 °C. At 55 °C, addition of chloride ions (1:1 molar ratio) reduced the induction period to 30 min. In dimethyl sulfoxide-d_6, at 85 °C, a simple first-order rate law was obeyed ($k = 6.18 \times 10^{-5}$ s^{-1}); the performance of the isomerization process in the same conditions, but in the presence of a 10-fold excess of Cl^-, increased significantly the rate of epimerization ($k_{obs} = 1.25 \times 10^{-4}$ s^{-1}). Complex **2b′** did not epimerize, at 55 °C, in chloroform, in the presence of a 10-fold excess of chloride ions. Although more experiments would be necessary to elucidate definitely the mechanism of this process, the observed results seems to suggest an associative mechanism that probably involves a transient intermediate species such as [(η^5-C_5Me_5)$RhCl_2$(prophos)], related to the previously reported 1,2-bis(diphenylphosphino) complex [(η^5-C_5Me_5)$RhCl_2$(diphos)].[6a]

Additionally, it should be pointed out that only relative small differences were observed in the circular dichroism spectra of epimers ($S_{Rh}R_C$)-**2b** and ($R_{Rh}R_C$)-**2b′**. The absorptions should be mainly due to the prophos conformation, and consequently, this technique was not diagnostic. An analogous situation has been described for the related diastereomeric complexes (*SR*,*RR*)-[(η^5-C_5Me_5)RuX(prophos)] (X = Cl, $SnCl_3$), which only differ in the configuration at the metal but showed very similar chiroptical properties.[2c]

Concluding Remarks

The reaction of the chiral diphosphine prophos with rhodium dimers [{(η^5-C_5Me_5)RhX}$_2$(μ-X)$_2$] in methanol is a highly stereoselective process kinetically controlled. The new chiral metal center is configurationally stable in solution at room temperature and in chloroform at 55 °C, but it epimerizes on heating the complex in methanol, cyclopentanol, or dimethyl sulfoxide. In dimethyl sulfoxide a first-order approach to the epimerization equilibrium **2b** ⇌ **2b′** takes place. The rate of epimerization, in this solvent, increases in the presence of chloride ions, suggesting that the reaction goes through an associative mechanism. High stereoselectivity in the formation of the cationic complexes **2a**, **2a′**, **4a,** and **4a′** is achieved.

Experimental Section

General Comments. All solvents were dried over appropriate drying agents, distilled under nitrogen, and degassed prior to being used. All preparations have been carried out under a nitrogen atmosphere. ^{1}H and ^{31}P NMR spectra were recorded on a Varian UNITY 300 [121.4 (^{31}P) and 299.9 (^{1}H) MHz], and a Bruker 300 ARX [121.5 (^{31}P) and 300.1 (^{1}H) MHz]. Chemical shifts are expressed in ppm upfield from $SiMe_4$ (^{1}H) or 85% H_3PO_4 (^{31}P). CD spectra were determined in $CHCl_3$ (10^{-4}−10^{-3} M solutions) in a 0.1-cm path length cell by using a Jasco-710 apparatus.

Preparation of [(η^5-C_5Me_5)RhCl(prophos)]Cl (2a, 2a′). A mixture of **1** (500.0 mg, 0.809 mmol) and prophos (667.3 mg, 1.618 mmol) in 20 mL of methanol was stirred for 2 h. A mixture of the two orange complexes was isolated by partial vacuum-evaporation and subsequent addition of diethyl ether. Yield: 95%; molar ratio **2a**:**2a′**, 77:23. Anal.[22] Calcd for $C_{37}H_{41}Cl_2P_2Rh$: C, 61.60; H, 5.72. Found: C, 59.80; H, 5.51. **2a**: ^{31}P{^{1}H} NMR ($CDCl_3$) δ 75.4 (dd, $^1J_{RhP_1} = 129$ Hz, $^2J_{P_2P_1} = 39$ Hz, P_1), 46.1 (dd, $^1J_{RhP_2} = 134$ Hz, P_2); ^{1}H NMR ($CDCl_3$) δ 1.41 (pt, $^4J_{PH} = 3.3$ Hz, 15 H, C_5Me_5), 1.18 (dd, $^3J_{P_1H} = 13.0$ Hz, $^3J_{H_gH} = 7.0$ Hz, 3 H, Me), 3.50 (m, 1 H, H_g), 2.08 (m, 1 H, H_t), 2.84 (m, $^3J_{P_1H_c} = 49.0$ Hz, 1 H, H_c), 7.0−7.9 (m, 20 H, Ph). **2a′**: ^{31}P{^{1}H} NMR ($CDCl_3$) δ 63.9 (dd, $^1J_{RhP_1} = 132$ Hz, $^2J_{P_2P_1} = 33$ Hz, P_1), 57.0 (dd, $^1J_{RhP_2} = 128$ Hz, P_2).

(17) Stoppioni, P.; di Vaira, M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1982**, 1147.
(18) Koelle, U.; Raabe, E.; Kruger, C.; Rotzinger, F. P. *Chem. Ber.* **1987**, *120*, 979.
(19) Voninon, T.; Ziessel, R. *J. Organomet. Chem.* **1989**, *363*, 197.
(20) Nelson, J. H. *Coord. Chem. Rev.* **1995**, *139*, 245.
(21) Note that the priority order is I > η^5-C_5Me_5 > P_1 > P_2[14] and, consequently, a stereochemical disposition such as those found in **2a** or **2b** is denoted with an opposite descriptor.

(22) Satisfactory microanalytical data could not be obtained for **2a** + **2a′** due to the presence of crystallization water, which we have not been able to efficiently remove.

Preparation of [(η^5-C_5Me_5)RhI(prophos)]I (4a). A mixture of **3** (59.6 mg, 0.060 mmol) and prophos (50.0 mg, 0.121 mmol) in 20 mL of methanol was stirred for 4 h. The resulting solution was concentrated under reduced pressure. Slow addition of diethyl ether gave an orange microcrystalline solid, which was separated by filtration. Yield: 95%. Anal. Calcd for $C_{37}H_{41}I_2P_2Rh$: C, 49.13; H, 4.56. Found: C, 48.69; H, 4.50. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 73.5 (dd, $^1J_{RhP_1}$ = 133 Hz, $^2J_{P_2P_1}$ = 34 Hz, P_1), 42.6 (dd, $^1J_{RhP_2}$ = 137 Hz, P_2). ^1H NMR ($CDCl_3$): δ 1.69 (pt, $^4J_{PH}$ = 3.1 Hz, 15 H, C_5Me_5), 1.22 (dd, $^3J_{P_1H}$ = 12.6 Hz, $^3J_{H_gH}$ = 6.5 Hz, 3 H, Me), 3.83 (m, 1 H, H_g), 2.01 (m, 1 H, H_t), 3.00 (m, $J_{P_1H_c}$ = 49.2 Hz, 1 H, H_c), 7.1−7.8 (m, 20 H, Ph).

Preparation of [(η^5-C_5Me_5)RhCl(prophos)]BF_4 (2b). To a solution of a 77:23 mixture of **2a**:**2a′** (200.0 mg, 0.277 mmol) in 15 mL of methanol was added $NaBF_4$ (31.0 mg, 0.277 mmol). The mixture was stirred for 7 h, and the orange-yellow compound which precipitated was filtered off and washed with water and diethyl ether. Yield: 60%. The mother liquors were vacuum-evaporated to dryness, the residue was extracted with dichloromethane, and the resulting solution was vacuum-evaporated to dryness. By successive recrystallizations from methanol−diethyl ether a 19:81 **2b**:**2b′** mixture was obtained. Yield: 10%. Anal. Calcd for $C_{37}H_{41}BClF_4P_2Rh$: C, 57.50; H, 5.34. Found: C, 57.75; H, 5.52. **2b**: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 74.9 (dd, $^1J_{RhP_1}$ = 130 Hz, $^2J_{P_2P_1}$ = 39 Hz, P_1), 45.5 (dd, $^1J_{RhP_2}$ = 134 Hz, P_2); ^1H NMR ($CDCl_3$) δ 1.46 (pt, $^4J_{PH}$ = 3.4 Hz, 15 H, C_5Me_5), 1.23 (dd, $^3J_{P_1H}$ = 12.6 Hz, $^3J_{H_gH}$ = 6.8 Hz, 3 H, Me), 3.54 (m, 1 H, H_g), 2.87 (m, $J_{P_1H_c}$ = 48.7 Hz, 1 H, H_c), 2.13 (m, 1 H, H_t), 7.0−7.9 ((m, 20 H, Ph), *o*-Ph_1 = 7.60, *o*-Ph_2 = 7.43, *o*-Ph_3 = 7.15, *o*-Ph_4 = 7.65). **2b′**: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 63.4 (dd, $^1J_{RhP_1}$ = 132 Hz, $^2J_{P_2P_1}$ = 33 Hz, P_1), 56.3 (dd, $^1J_{RhP_2}$ = 128 Hz, P_2); ^1H NMR ($CDCl_3$) δ 1.47 (pt, $^4J_{PH}$ = 2.8 Hz, 15 H, C_5Me_5), 1.31 (dd, $^3J_{P_1H}$ = 12.9 Hz, $^3J_{H_gH}$ = 6.4 Hz, 3 H, Me), 2.88 (m, 2 H, H_g and H_c), 3.40 (m, 1 H, H_t), 6.8−7.9 ((m, 20 H, Ph), *o*-Ph_1 = 7.71, *o*-Ph_2 = 6.91, *o*-Ph_3 = 7.24, *o*-Ph_4 = 7.55).

Complex **4b** was similarly prepared but starting from **4a**. Yield: 95%. Anal. Calcd for $C_{37}H_{41}BF_4IP_2Rh$: C, 51.41; H, 4.78. Found: C, 51.38; H, 4.91. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 73.1 (dd, $^1J_{RhP_1}$ = 133 Hz, $^2J_{P_2P_1}$ = 35 Hz, P_1), 42.3 (dd, $^1J_{RhP_2}$ = 137 Hz, P_2). ^1H NMR ($CDCl_3$): δ 1.67 (pt, $^4J_{PH}$ = 3.0 Hz, 15 H, C_5Me_5), 1.22 (dd, $^3J_{P_1H}$ = 12.4 Hz, $^3J_{H_gH}$ = 6.5 Hz, 3 H, Me), 1.83 (m, 1 H, H_g), 2.01 (m, 1 H, H_t), 3.00 (m, $J_{P_1H_c}$ = 49.2 Hz, 1 H, H_c), 7.1−7.8 (m, 20 H, Ph).

Preparation of [{(η^5-C_5Me_5)$RhCl_2$}$_2$(μ-prophos)] (5). To a suspension of **1** (74.9 mg, 0.121 mmol) in 20 mL of chloroform was added 50.0 mg (0.121 mmol) of prophos. The resulting solution was stirred during 30 min and vacuum-concentrated to *ca*. 2 mL. The addition of *n*-hexane gave an orange solid, which was separated by filtration. Yield: 85%. Anal. Calcd for $C_{47}H_{56}Cl_4P_2Rh_2$: C, 54.78; H, 5.48. Found: C, 54.93; H, 5.62. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 223 K): δ 38.3 (dd, $^1J_{RhP_1}$ = 145 Hz, $^3J_{P_2P_1}$ = 18 Hz, P_1), 30.5 (dd, $^1J_{RhP_2}$ = 143 Hz, P_2). ^1H NMR ($CDCl_3$, 293 K): δ 1.22 (d, $^4J_{PH}$ = 3.4 Hz, 15 H, C_5Me_5), 1.11 (d, $^4J_{PH}$ = 3.4 Hz, 15 H, C_5Me_5), 0.71 (dd, $^3J_{P_1H}$ = 19.9 Hz, $^3J_{H_gH}$ = 6.7 Hz, 3 H, Me), 2.8 m, 3.3 m ($CHCH_2$), 7.0−8.2 (m, 20 H, Ph).

Complex [{(η^5-C_5Me_5)RhI_2}$_2$(μ-prophos)] (**6**) was similarly prepared starting from **3**. Yield: 85%. Anal. Calcd for $C_{47}H_{56}I_4P_2Rh_2$: C, 40.42; H, 4.04. Found: C, 40.32; H, 4.54. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 39.9 (dd, $^1J_{RhP_1}$ = 151 Hz, $^3J_{P_2P_1}$ = 15 Hz, P_1), 30.8 (dd, $^1J_{RhP_2}$ = 149 Hz, P_2). ^1H NMR ($CDCl_3$): δ 1.55 (d, $^4J_{PH}$ = 3.4 Hz, 15 H, C_5Me_5), 1.45 (d, $^4J_{PH}$ = 3.2 Hz, 15 H, C_5Me_5), 0.87 (dd, $^3J_{P_1H}$ = 20.4 Hz, $^3J_{H_gH}$ = 6.5 Hz, 3 H, Me), 3.3 m, 3.5 m ($CHCH_2$), 7.0−8.2 (m, 20 H, Ph).

Reaction of 5 with prophos in Chloroform. A mixture of **5** (124.9 mg, 0.121 mmol) and prophos (50.0 mg, 0.121 mmol) in 20 mL of chloroform was stirred for 2 h. Complexes **2a**, **2a′**, **5**, [(η^5-C_5Me_5)$RhCl_2${$Ph_2PCH_2CH(Me)PPh_2$}] (**7**), and [(η^5-C_5Me_5)$RhCl_2${$Ph_2PCH(Me)CH_2PPh_2$}] (**8**) in *ca*. 49, 14, 31, 4, and 2% yield, respectively, were detected by ^{31}P NMR spectroscopy. **7**: $^{31}P\{^1H\}$ NMR ($CDCl_3$, 223 K) δ 29.7 (dd, $^1J_{RhP_2}$ = 142 Hz, $^3J_{P_1P_2}$ = 30 Hz, P_2), 4.6 (d, P_1). **8**: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 34.7 (dd, $^1J_{RhP_1}$ = 141 Hz, $^3J_{P_2P_1}$ = 25 Hz, P_1), −16.4 (d, P_2).

Starting from **3** and prophos, complexes **4a**, **4a′**, **6**, [(η^5-C_5Me_5)RhI_2{$Ph_2PCH_2CH(Me)PPh_2$}] (**9**), and [(η^5-C_5Me_5)RhI_2{$Ph_2PCH(Me)CH_2PPh_2$}] (**10**) in *ca*. 13, 4, 50, 30, and 3% yield, respectively, were detected. **4a′**: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 66.3 (dd, $^1J_{RhP_1}$ = 139 Hz, $^3J_{P_2P_1}$ = 36 Hz, P_1), 55.0 (dd, $^1J_{RhP_2}$ = 128, P_2). **9**: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 27.3 (dd, $^1J_{RhP_2}$ = 148 Hz, $^3J_{P_1P_2}$ = 38 Hz, P_2), 5.4 (d, P_1). **10**: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 36.5 (dd, $^1J_{RhP_1}$ = 150 Hz, $^3J_{P_2P_1}$ = 19 Hz, P_1), −17.3 (d, P_2).

Epimerization of Complexes 2. (i) Complexes 2a and 2a′. A 5 mm NMR tube was charged with a mixture of **1** (12.0 mg, 0.019 mmol), prophos (16.1 mg, 0.039 mmol), and 2 mL of CD_3OD under inert atmosphere and periodically monitored by ^{31}P NMR spectroscopy. The **2a**:**2a′** molar ratio, which was 77:23 after 5 min of reaction, was the same 30 days later. Starting from a 77:23 mixture, a 96:4 **2a**:**2a′** molar ratio was achieved after refluxing in methanol for 7 days.

(ii) Complexes 2b and 2b′. A solution of complex **2b** (30.1 mg, 0.039 mmol) in 10 mL of methanol was monitored by ^{31}P NMR spectroscopy. At room temperature, no **2b′** was detected after 24 h. After the solution was refluxed for 14 days, the composition was 96:4 **2b**:**2b′**. A 19:81 mixture of **2b**:**2b′** (30.1 mg) in 10 mL of methanol was refluxed for 24 h. The $^{31}P\{^1H\}$ NMR spectrum showed a molar ratio for **2b**:**2b′** of 96:4. A 19:81 mixture of **2b**:**2b′** (50.0 mg) in 10 mL of cyclopentanol was heated at 80 °C for 2 h. The $^{31}P\{^1H\}$ NMR spectrum showed a molar ratio for **2b**:**2b′** of 96:4.

Rate of Epimerization of 2b′. Method i. A 19:81 mixture of **2b**:**2b′** (15.0 mg) was dissolved in 0.6 mL of $(CD_3)_2SO$ in a 5 mm NMR tube and the probe heated to 85 °C. The concentrations of **2b** and **2b′** were assayed by integration of the 75.3 and 46.0 (**2b**) or 63.8 and 56.9 ppm (**2b′**) ^{31}P NMR resonances.

Method ii. In a similar way a 19:81 mixture of **2b**:**2b′** (15.0 mg, 0.019 mmol), NEt_4Cl (32.2 mg, 0.190 mmol), and 0.6 mL of $(CD_3)_2SO$ at 85 °C was monitored by ^{31}P NMR spectroscopy. Concentration *vs* time data were fitted by conventional linear regression methods.

X-ray Structure Analysis of 2b. Collection and Reduction of Data. Crystals of **2b** suitable for the X-ray study were obtained from a chloroform/diethyl ether solution as

Table 2. Crystallographic Data for 2b

Crystal Data	
formula	$C_{37}H_{41}BClF_4P_2Rh$
mol wt	772.84
color and habit	orange, transparent, prismatic block
cryst size, mm	0.110 × 0.186 × 0.443
cryst syst	orthorhombic
space group	$C222_1$ (No. 20)
a, Å	9.2171(5)
b, Å	22.643(2)
c, Å	33.990(3)
V, Å^3; *Z*	7094(1); 8
D_{calcd}, g cm^{-3}	1.447
Data Collection and Refinement	
diffractometer	4-circle Siemens AED
λ(Mo Kα radiation), Å; technique	0.710 73; bisecting geometry
monochromator	graphite oriented
μ, cm^{-1}	6.83
max, min corr factors	0.855, 1.089
scan type	$\omega/2\theta$
2θ range, deg	3−50
no. of data collcd	7755 ($-10 \le h \le 10$; $0 \le k \le 26$; $0 \le l \le 40$)
no. of unique data	6253
unique obsd data	5368, $F_o \ge 6\sigma(F_o)$
no. of params refined	415
R, R_w[a]	0.0402, 0.0456

[a] $w^{-1} = \sigma^2(F_o) + 0.003243F_o^2$

orange prisms. A prismatic crystal was glued on a glass fiber and mounted on a Siemens AED-2 diffractometer. A summary of crystal data, intensity collection procedures, and refinement data is reported in Table 2. Cell parameters were obtained from the least-squares fit of the setting angles of 51 reflections in the range $20 \leq 2\theta \leq 42°$. The 7755 recorded reflections were corrected for Lorentz and polarization effects. Three orientation and intensity standards were monitored every 55 min of measuring time; no intensity decay was observed. An empirical method was used to correct the data for absorption effects.[23]

Structure Solution and Refinement. The structure was solved by Patterson (Rh atom) and conventional Fourier techniques. Refinement was carried out by full-matrix least squares with initial isotropic thermal parameters. Further refinement was performed with anisotropic thermal parameters for all non-hydrogen atoms of the cationic complex. At this stage of the refinement, the BF_4^- anion was observed highly disordered; it was modeled on the base of five different BF_4 groups with occupancy factors assigned according to their relative electronic density to complete one independent molecule (0.5 for B(1), B(2); 0.4 for F(11), F(12); 0.6 for F(13), F(14); 0.4 for F(21), F(22), F(23), F(24); 0.2 for F(25), F(26)). Hydrogen atoms were included in calculated positions and refined riding on carbon atoms with a common isotropic thermal parameter. The function minimized was $\sum([F_o] - [F_c])^2$ with the weight defined as $w^{-1} = \sigma^2(F_o) + 0.003243F_o^2$. Atomic scattering factors, corrected for anomalous dispersion for Rh, P, and Cl, were taken from ref 24. The chirality of the molecule was checked using the Rogers method.[25] Final R and R_w values were 0.0402 and 0.0456, respectively. All calculations were performed by use of the SHELXTL-PLUS system of computer programs.[26]

Acknowledgment. We thank the Dirección General de Investigación Científica y Técnica for financial support (Grant 92-0019). E.S.J. thanks the Ministerio de Educación y Ciencia of Spain for a fellowship.

Supporting Information Available: Tables of anisotropic thermal parameters, complete atomic coordinates and U values, experimental details of the X-ray study, bond distances and angles, selected least-squares planes, and interatomic distances (15 pages). Ordering information is given on any current masthead page.

OM960134E

(23) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(24) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.

(25) Rogers, D. *Acta Crystallogr.* **1981**, *A37*, 734.

(26) SHELXTL PLUS Program for Crystal Structure Determinations, Siemens Analytical X-Ray Instruments, Madison, WI, 1990.