Complexes of Ruthenium(II) with Unsymmetrical Diphosphines and Diphosphinomethanides. A Way to Synthesize Chiral Metallodiphosphines

Marta E. G. Mosquera, Javier Ruiz,* and Víctor Riera

Departamento de Química Orgánica e Inorgánica, Universidad de Oviedo, 33071 Oviedo, Spain

Santiago Garcia-Granda and Miguel A. Salvadó

Departamento de Química Física y Analítica, Universidad de Oviedo, 33071 Oviedo, Spain

Received February 3, 2000

Summary: Ruthenium(II) complexes with the unsymmetrical diphosphinomethanide $[PPh_2CHP^tBu_2]^-$ containing isocyanides and chiral amines as ancillary ligands were prepared, and the molecular structure of $[Ru(CN^tBu)_4\{PPh_2CHP^tBu_2\}]^+$ was studied by X-ray crystallography. The reactivity of the coordinated methanide toward $[AuCl(PPh_3)]$ was investigated, leading to the stereoselective formation of the chiral metallodiphosphine $[PPh_2CH(AuPPh_3)P^tBu_2]$.

Introduction

Complexes of ruthenium(II) with diphosphines are of interest due to their potential applications in catalytic processes.[1] Those bearing chiral diphosphines are particularly efficient catalysts for asymmetric hydrogenation of olefinic substrates and have found applications in the fine chemicals industry.[2,3] The central work within our group has been focused on the transformation of the diphosphine dppm coordinated to group 7 and 8 metals into new functionalized diphosphines and metallodiphosphines.[4] These transformations are accomplished via electrophilic attack on the corresponding intermediate complexes containing the coordinated methanide ligand $[PPh_2CHPPh_2]^-$. We considered interesting the extension of these studies to the unsymmetrical diphosphinomethanide $[PPh_2CHP^tBu_2]^-$ coordinated to Ru(II). In this ligand the central carbon is a prochiral center, so its transformations by electrophilic attacks could lead to the formation of new chiral diphosphines or metallodiphosphines. The presence of a chiral auxiliary ligand coordinated to the metal would make these attacks stereoselective.

Here we report the synthesis of several Ru(II) derivatives with the unsymmetrical diphosphine $[PPh_2CH_2P^tBu_2]$, containing isocyanides and chiral amines as ancillary ligands, and their corresponding derivatives with the diphosphinomethanide ligand $[PPh_2CHP^tBu_2]^-$. Some promising results on the reactivity of this ligand toward electrophiles, which has led to the stereoselective formation of chiral metallodiphosphines, are also presented.

Results and Discussion

When the diphosphine $\{PPh_2CH_2P^tBu_2\}$[5] was refluxed with *trans*-$[Ru(Cl)_2(CN^tBu)_4]$[6] in toluene for 4 h, a mixture of three compounds was formed. These compounds were identified in the $^{31}P\{^1H\}$ NMR and IR spectra of the reaction mixture as *cis*,*trans*-$[Ru(Cl)_2(CN^tBu)_2\{PPh_2CH_2P^tBu_2\}]$ (**1a**) and two isomers of *mer*-$[Ru(Cl)(CN^tBu)_3\{PPh_2CH_2P^tBu_2\}]Cl$ (**1b**,**c**) (Scheme 1). The chemical shift values in the phosphorus NMR spectra allowed us to distinguish the different species formed, since the presence of a chloride or an isocyanide ligand trans to the phosphine promotes opposite displacement of the chemical shift in comparison with the uncoordinated ligand, as observed in related dppm−isocyanide complexes.[7] Derivatives **1a**−**c** follow this behavior, showing the chemical shift of the phosphorus trans to a chloride moved more than 30 ppm toward low field (in relation to the free phosphine), whereas in the case of the isocyanide the shift is only about 5 ppm toward high field (see Table 1). A careful choice of the reaction conditions allowed the selective synthesis of the derivative *mer*-$[Ru(Cl)(CN^tBu)_3\{PPh_2CH_2P^tBu_2\}](Cl)$ (**1c**), where the Cl ligand is trans to the P^tBu_2 group.

(1) (a) McAulife, C. A. In *Comprehensive Coordination Chemistry;* Wilkinson, G., Gillard, R. D., McCleverty, J., Eds.; Pergamon: Oxford, 1987; Vol. 2, p 989. (b) Schroder, M.; Stephenson, T. A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J., Eds.; Pergamon: Oxford, 1987; Vol. 4, p 366.

(2) (a) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*; John Wiley: New York, 1992; pp 36−39. (b) Takaya, H.; Ohta, T.; Mashima, K. In *Homogeneous Transition Metal Catalyzed Reactions*; Moser, W. R., Slocum, D. W., Eds.; Advances in Chemistry Series 230; ACS: Washington, 1992; pp 123−142.

(3) (a) Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345. (b) Noyori, R. *Chem. Soc. Rev.* **1989**, *18*, 187. (c) Noyori, R. *Tetrahedron* **1994**, *50*, 4259. (d) Ojima, I.; Clos, N.; Bastos, C. *Tetrahedron* **1989**, *45*, 6901. (e) Znetti, N. C.; Spindler, F.; Spencer, J.; Togni, A.; Grety, R. *Organometallics* **1996**, *15*, 860. (f) Wiles, J. A.; Lee, C. E.; McDonald, R.; Bergens, S. H. *Organometallics* **1996**, *15*, 3782. (g) Mikami, K.; Korenaga, T.; Terada, M.; Ohkuma, T.; Pham, T.; Noyori, R. *Angew. Chem., Int. Ed.* **1999**, *38*, 495.

(4) (a) Ruiz, J.; Riera, V.; Vivanco, M.; Lafranchi, M.; Tiripicchio, A. *Organometallics* **1998**, *17*, 3835. (b) Ruiz, J.; Mosquera, M. E. G.; Riera, V.; Vivanco, M.; Bois, C. *Organometallics* **1997**, *16*, 3388. (c) Ruiz, J.; Riera, V.; Vivanco, M.; Garcia-Granda, S. *Organometallics* **1996**, *15*, 1080. (d) Ruiz, J.; Riera, V.; Vivanco, M.; Lafranchi, M.; Tiripicchio, A. *Organometallics* **1996**, *15*, 1082. (e) Ruiz, J.; Arauz, R.; Riera, V.; Vivanco, M.; García-Granda, S.; Perez-Carreño, A. *J. Chem. Soc., Chem. Commun.* **1993**, 740.

(5) Grim, S. O.; Smith, P. H.; Colquhoun, I. J.; MacFarlane, W. *Inorg. Chem.* **1980**, *19*, 3195.

(6) Bassett, J. M.; Berry, D. E.; Barker, G. K.; Green, M.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1979**, 1003.

(7) (a) Ruiz, J.; Riera, V.; Vivanco, M. *J. Chem. Soc., Dalton Trans.* **1995**, 1069. (b) Mosquera, M. E. G.; Ruiz, J.; Riera, V. *J. Organomet. Chem.* **1997**, *527*, 35.

10.1021/om000097y CCC: $19.00
Publication on Web 11/15/2000

Scheme 1

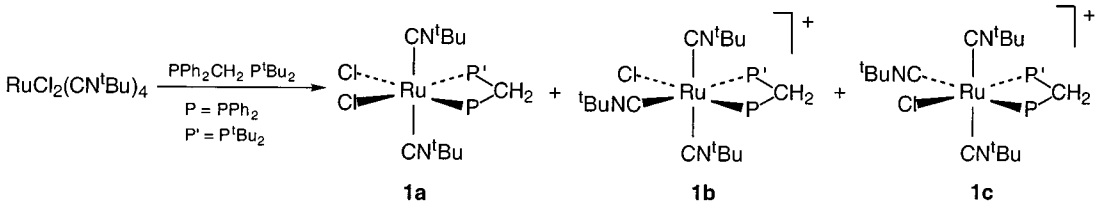


Table 1. IR and $^{31}P\{^1H\}$ NMR Data for Compounds 1−4 and $\{PPh_2CH_2P^tBu_2\}$

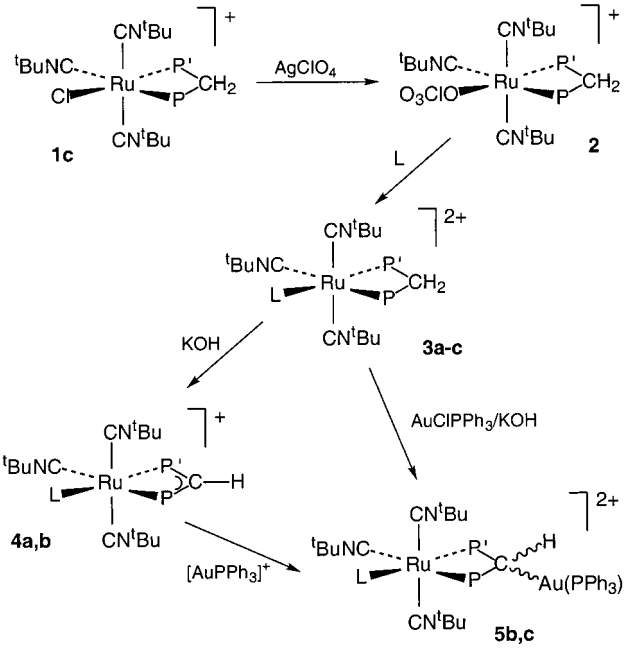
		$^{31}P\{^1H\}$ NMR, (δ, ppm; J, Hz)[b]		
compound	ν(CN),[a] cm^{-1}	δ (P^tBu_2)	δ (PPh_2)	$^2J_{PP}$
$\{PPh_2CH_2P^tBu_2\}$		15.8 (d)	−15.0 (d)	138
1a		52.1 (d)	20.4 (d)	41
1b		11.7 (d)	17.0 (d)	37
1c	2201 (w), 2164 (s)	48.7 (d)	−22.7 (d)	43
2	2210 (w), 2175 (s)	58.6 (d)	−15.4 (d)	46[c]
3a	2216 (w), 2174 (s)	22.5 (d)	−15.3 (d)	39[c]
3b	2194 (w), 2156(s)	42.9 (d)	−16.7 (d)	36[c]
3c	2196 (w), 2159(s)	43.9 (d)	−16.2 (d)	37[c]
4a	2202 (w), 2153(s)	21.5 (d)	−29.7 (d)	9[c]
4b	2186 (w), 2148(s)[d]	35.9 (d)	−25.4 (d)	8[e]

[a] In CH_2Cl_2. Abbreviations: w = weak, s = strong. [b] In CH_2Cl_2 with D_2O capillary. Abbreviation: d = doublet. [c] In CD_2Cl_2. [d] In THF. [e] In THF with D_2O capillary.

In the next step of our work, we changed the chloride ligand in **1c** for a neutral ligand. We were particularly interested in coordinating a chiral group that could act as a chirality inductor in further reactions on the diphosphine. Therefore **1c** was first treated with $AgClO_4$ to give *mer*-$[Ru(OClO_3)(CN^tBu)_3\{PPh_2CH_2P^tBu_2\}]^+$ (**2**); second, **2** was reacted with an excess of the corresponding neutral ligand L, affording *mer*-$[Ru(L)(CN^tBu)_3\{PPh_2CH_2P^tBu_2\}](ClO_4)_2$ (**3a**, L = ^{t}BuCN; **3b**, L = (*S*)-CyCH(Me)NH_2; **3c**, L = (*S*)-PhCH(Me)NH_2). These new compounds were fully spectroscopically characterized (see Experimental Section). It is worth remarking that the presence of a chiral ligand in **3b**,**c** promotes a differentiating factor in the equatorial plane of the molecule. Thus the axial isocyanide groups that are equivalents in the achiral derivatives (**2** and **3a**) become diastereotopic in **3b**,**c**. This inequivalence is evidenced in the proton spectra by the presence of three different signals for the CN^tBu groups. Equally, the ^{t}Bu groups in the diphosphine are diastereotopic, appearing as two doublets with similar $^3J_{PH}$ values (in the achiral compounds the P^tBu_2 groups appear as a unique doublet).

The deprotonation reaction of *mer*-$[Ru(L)(CN^tBu)_3\{PPh_2CH_2P^tBu_2\}]^{2+}$ (**3a**,**b**) with KOH in CH_2Cl_2 or THF led to the formation of the new diphosphinomethanide species $[Ru(L)(CN^tBu)_3\{PPh_2CHP^tBu_2\}]^+$ (**4a**, L = ^{t}BuCN; **4b**, L = (*S*)-CyCH(Me)NH_2) (Scheme 2). Although a large number of diphosphinomethanides containing two equivalent phosphino groups are known,[8] compounds **4a**,**b** are, to our knowledge, the first examples where the coordinated diphosphinomethanide is unsymmetrical. This feature converts the central carbon atom in a prochiral center; hence its transformation into a quaternary atom would lead to the formation of chiral diphosphines or metallodiphosphines.

Scheme 2[a]



[a] **3a**,**4a**, L = CN^tBu; **3b**,**4b**,**5b**, L = CyCH(Me)NH_2; **3c**,**5c**, L = PhCH(Me)NH_2; P = PPh_2, P′ = P^tBu_2.

Only in the case of **4a** could suitable crystals for an X-ray structural determination be grown. The molecular structure of **4a** (Figure 1) shows the coordinated unsymmetrical ligand $\{PPh_2CHP^tBu_2\}^-$ with a coplanar Ru−P(1)−P(2)−C(9) skeleton. The P(1)−C(9) (1.723 (10) Å) and P(2)−C(9) (1.724 (10) Å) distances are very similar and fall between the usual values observed for single and double bonds, suggesting that the excess of electronic density on the carbon atom is equally shared by both phosphorus atoms. The Ru(1)−P(1) distance (2.369(3) Å) is similar to that observed in other diphosphino methanide complexes (2.35 Å on average).[4b] However the Ru(1)−P(2) bond length appears a bit longer, 2.464(4) Å, perhaps owing to the greater steric congestion around the donor atom in the P(2)R_3 group, as suggested in other ruthenium complexes with phosphines.[9]

Finally we studied the reactivity of the coordinated ligand $\{PPh_2CHP^tBu_2\}^-$ toward electrophiles, starting with the species $[AuCl(PPh_3)]$ since its behavior with other methanide complexes is well established.[4b] The reaction was generally carried out in a one-pot process by stirring a mixture of *mer*-$[Ru(L)(CN^tBu)_3\{PPh_2CH_2P^tBu_2\}](ClO_4)_2$ (**3b**,**c**), KOH, and $AuClPPh_3$. This

(8) (a) Puddhepatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99. (b) Karsch, H. H.; Richter, R.; Deubelly, B.; Schier, A.; Paul, M.; Heckel, M.; Angermeir, K.; Hiller, W. *Z. Naturforsch. B: Chem. Sci.* **1994**, *49*, 1798. (c) Balch, A. L.; Oram, D. E. *Organometallics* **1986**, *5*, 2159. (d) Karsch, H. H.; Ferazin, G.; Kooijman, H.; Steigelmann, O.; Hiller, W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1739. (e) Kasani, A.; McDonald, R.; Cavell R. G., *Organometallics* **1999**, *18*, 3775.

(9) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Chem. Soc., Chem Commun*, **1988**, 278.

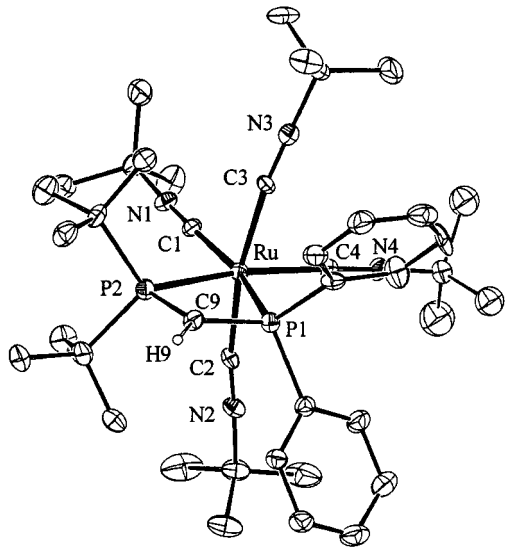


Figure 1. Molecular structure of the cationic complex in **4a** together with the atomic numbering system. Selected Bond lengths (Å) and Angles (deg): Ru−P(1) 2.369(3), Ru−P(2) 2.464(4), P(2)−C(9) 1.724(10), P(1)−C(9) 1.723(10), Ru−C(4) 2.000(10), Ru−C(3) 1.982(11), Ru−C(2) 1.995(11), Ru−C(1) 2.019(12), P(1)−C(9)−P(2) 102.4(4), P(1)−Ru−P(2) 67.5(2).

Table 2. Selected Spectroscopic Data for Complexes 5

			$^{31}P\{^1H\}$ NMR, (δ,ppm; J,Hz)[b]			
compound	ν(CN),[a] cm^{-1}	δ (P^tBu_2)	δ (AuP)	δ (PPh_2)	$^2J_{PP}$	$^3J_{PP}$
(*SS*/*SR*)**5b**	2189 (w), 2149 (s)					
major diastereomer	(86%)	63.0 (dd)	42.4 (t)	1.2 (dd)	40	7
minor diastereomer	(14%)	63.1 (dd)	42.7 (t)	1.4 (dd)	39	6
(*SS*/*SR*)**5c**	2190 (w), 2151 (s)					
major diastereomer	(82%)	63.9 (dd)	42.3 (t)	1.2 (dd)	33	7
minor diastereomer	(18%)	63.4 (dd)	42.8 (t)	2.4 (dd)	31	7

[a] In CH_2Cl_2. [b] In CH_2Cl_2 with D_2O capillary.

methodology allowed us to obtain the complexes *mer*-$[Ru(L)(CN^tBu)_3\{PPh_2CH(AuPPh_3)P^tBu_2\}]^{2+}$ (**5b**, L = (*S*)-CyCH(Me)NH_2; **5c**, L = (*S*)-PhCH(Me)NH_2) (Scheme 2), which contain a new chiral metallodiphosphine. As expected, the reaction was diastereoselective due to the presence of the chiral amine. In the $^{31}P\{^1H\}$ NMR spectra of **5b** and **5c** it is possible to clearly distinguish the signals due to each diastereomer with a major isomer observed in both cases, as summarized in Table 2.

It was not possible to resolve the diasteromeric mixture in **5b** and **5c** compounds, preventing the determination of the absolute configuration of the major and minor isomer. The de was estimated from the value of the NMR band integrals,[10] being 72 for **5b** and 64 in **5c**. The slightly better ability as a chirality inductor of the cyclohexylamine can be attributed to the major steric hindrance promoted by the cyclohexyl ring in relation to the phenyl ring. In this context, Morandini observed an increase of the diastereoslectivity in the electrophilic attack of CH_3X on the compounds [Rh(η^5-C_9H_7)(chiral diphosphine)] on changing the diphosphine from $PPh_2CH_2CH(Ph)PPh_2$ (phenphos) to PPh_2CH_2CH-(Cy)PPh_2 (cyphos).[11]

In conclusion we have prepared in this work some ruthenium(II) complexes with the unsymmetrical diphosphine $\{PPh_2CH_2P^tBu_2\}$ and the corresponding diphosphinomethanide $\{PPh_2CHP^tBu_2\}^-$, containing chiral amines as ancillary ligands. From these, the new chiral metallodiphosphine $\{PPh_2CH(AuPPh_3)P^tBu_2\}$ coordinated to ruthenium(II) can be synthesized in moderate diastereomeric excess. Unfortunately, the extension of this reactivity to organic electrophiles, such as RX, RC≡C−X, or RC(O)X (R = alkyl or aryl, X = halogen) has not been successful so far, precluding practical application in enantioselective synthesis of chiral diphosphines. Nonetheless, this study establishes the potential of unsymmetrical diphosphinomethanides, coordinated to transition metal complexes with chiral ancillary ligands, for the diastereoselective transformation of coordinated diphosphines.

Experimental Section

General Considerations. For the general experimental procedure see ref 4b. The compounds $\{PPh_2CH_2P^tBu_2\}$[5] and $[Ru(Cl)_2(CN^tBu)_4]$[6] were prepared as described elsewhere.

***mer*-[(Ru(Cl)(CN^{t}Bu)$_3${PPh$_2$CH$_2$P^{t}Bu$_2$}]Cl (1c).** A solution in 7 mL of toluene of *trans*-$[Ru(Cl)_2(CN^tBu)_4]$ (0.15 g, 0.29 mmol) and the diphosphine $\{PPh_2CH_2P^tBu_2\}$ (0.15 g, 0.43 mmol) was refluxed for 3 h. In the reaction mixture white crystals appeared corresponding to **1c**. These crystals were washed with ether three times to eliminate the excess of diphosphine and other minor products and dried in the vacuum line. Yield: 0.19 g (85%). Anal. Calcd for $RuCl_2P_2N_3C_{36}H_{57}$: C, 56.46; H, 7.50; N, 5.49. Found: C, 55.96; H, 7.33; N, 5.03. ^1H NMR (CD_2Cl_2): δ 8.13−7.41 (10H, Ph); 4.14 (t, 2H, $^2J_{HP}$ = 10, CH_2); 1.54 (s, 9H, CN^t*Bu*); 1.29 (s, 18H, CN^t*Bu*); 1.25 (d, 18H, $^3J_{PH}$ = 15, P^t*Bu*$_2$). ^{13}C NMR (CD_2Cl_2): δ 147.2 (br, *C*N^{t}Bu); 135.3−126.2 (Ph); 58.5 (s, CN*C*(CH$_3$)$_3$); 58.3 (s, CN*C*(CH$_3$)$_3$); 37.6 (d, $^1J_{PC}$ = 13, P*C*(CH$_3$)$_3$); 36.6 (dd, $^1J_{PC}$ = 26, $^1J_{PC}$ = 17, P$_2$*C*H$_2$); 31.1 (s, CNC(*C*H$_3$)$_3$); 30.2 (d, $^2J_{PC}$ = 3, PC(*C*H$_3$)$_3$); 30.1 (s, CNC(*C*H$_3$)$_3$).

***mer*-[Ru(OClO$_3$)(CN^{t}Bu)$_3${PPh$_2$CH$_2$P^{t}Bu$_2$}](ClO$_4$) (2).** A 76 mg (0.1 mmol) sample of the compound *mer*-[Ru(Cl)(CN^{t}Bu)$_3${PPh$_2$CH$_2$P^{t}Bu$_2$}](Cl) was reacted with 40 mg (0.2 mmol) of $AgClO_4$ in 10 mL of CH_2Cl_2. After being stirring for 1 h, the solution was filtered and the filtrate reduced under vacuum. The white solid obtained was washed with hexane and dried under vacuum. Yield: 79 mg (89%). Anal. Calcd for $RuO_8Cl_2P_2N_3C_{36}H_{57}$: C, 48.38; H, 6.43; N, 4.90. Found: C, 47.85; H, 6.67; N, 4.24. ^1H NMR (CD_2Cl_2): δ 7.89−7.43 (10H, Ph); 4.02 (t, 2H, $^2J_{HP}$ = 10, CH_2); 1.57 (s, 9H, CN^t*Bu*); 1.34 (s, 18H, CN^t*Bu*); 1.26 (d, 18H, $^3J_{PH}$ = 15, P^t*Bu*$_2$). ^{13}C NMR (CD_2Cl_2): δ 144.1 (br, *C*N^{t}Bu); 134.1−129.3 (Ph); 59.4 (s, CN*C*(CH$_3$)$_3$); 59.1 (s, CN*C*(CH$_3$)$_3$); 37.8 (dd, $^1J_{PC}$ = 15, $^3J_{PC}$ = 3, P*C*(CH$_3$)$_3$); 35.3 (dd, $^1J_{PC}$ = 26, $^1J_{PC}$ = 17, P$_2$*C*H$_2$); 30.6 (s, CNC(*C*H$_3$)$_3$); 29.9 (d, $^2J_{PC}$ = 3, PC(*C*H$_3$)$_3$); 29.7 (s, CNC(*C*H$_3$)$_3$).

Synthesis of Compounds [Ru(L)(CN^{t}Bu)$_3${PPh$_2$CH$_2$P^{t}Bu$_2$}](ClO$_4$)$_2$ (3). In a general procedure, compound **2** (0.1 g, 0.11 mmol) was dissolved in 10 mL of CH_2Cl_2, and to this solution 0.04 mL (0.33 mmol) of ^{t}BuNC was added. The mixture was stirred for 10 h at room temperature. The solvent was reduced under vacuum, and a white solid corresponding to **3a** precipitated by the addition of 20 mL of hexane. The solid was washed with hexane and dried in a vacuum. Yield:

(10) (a) Staubach, B.; Buddrus, J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1344. (b) Nelson, J. H. *Coord. Chem. Rev.* **1995**, *139*, 245.

(11) Morandini, F.; Pilloni, G.; Consiglio, G.; Sironi, A.; Moret, M. *Organometallics* **1993**, *12*, 3495.

100 mg (93%). Anal. Calcd for $RuO_8Cl_2P_2N_4C_{41}H_{66}$: C, 50.41; H, 6.81; N, 5.73. Found: C, 49.93; H, 6.77; N, 5.57. ^{1}H NMR (CD_2Cl_2): δ 7.81−7.39 (10H, Ph); 4.28 (dd, 2H, $^2J_{HP}$ = 11, $^2J_{HP}$ = 9, CH_2); 1.68 (s, 9H, CN^t*Bu*); 1.59 (s, 9H, CN^t*Bu*); 1.33 (s, 18H, CN^t*Bu*); 1.31 (d, 18H, $^3J_{PH}$ = 15, P^t*Bu*$_2$). ^{13}C NMR (CD_2Cl_2): δ 148.3 (br, *C*N^{t}Bu); 132.9−129.1 (Ph); 60.8 (s, CN*C*(CH$_3$)$_3$); 60.2 (s, CN*C*(CH$_3$)$_3$); 37.3 (dd, $^1J_{PC}$ = 12, $^3J_{PC}$ = 4, P*C*(CH$_3$)$_3$); 34.6 (dd, $^1J_{PC}$ = 29, $^1J_{PC}$ = 18, P$_2$*C*H$_2$); 30.7 (s, C(*C*H$_3$)$_3$); 30.6 (s, C(*C*H$_3$)$_3$); 29.8 (s, C(*C*H$_3$)$_3$).

***mer*-[Ru{*S*-CH$_3$CH(C$_6$H$_{11}$)NH$_2$}(CN^{t}Bu)$_3${PPh$_2$CH$_2$P^{t}Bu$_2$}](ClO$_4$)$_2$ (3b)** was obtained from **2** (0.1 g, 0.11 mmol) and *S*-CH$_3$CH(C$_6$H$_{11}$)NH$_2$ (17 μL, 0.12 mmol) as a white solid. Yield: 103 mg (92%). Anal. Calcd for $RuO_8Cl_2P_2N_4C_{44}H_{74}$: C, 51.76; H, 7.30; N, 5.49. Found: C, 51.51; H, 7.31; N, 5.60. $[\alpha]^{20}_D$ −1.1° (*c* = 0.002 gr/mL; CH_2Cl_2). ^{1}H NMR (CD_2Cl_2): δ 7.94−7.38 (10H, Ph); 4.03 (t, 2H, $^2J_{HP}$ = 10, P$_2$CH_2); 3.67 (m, H, C*H*); 2.89 (m, H, C*H*NH$_2$); 1.57 (s, 9H, CN^t*Bu*); 1.53 (s, 9H, CN^t*Bu*); 1.32 (s, 2H, NH_2); 1.27 (s, 9H, CN^t*Bu*); 1.38 (d, 9H, P^t*Bu*$_2$, $^3J_{PH}$ = 15); 1.23 (d, 9H, P^t*Bu*$_2$, $^3J_{PH}$ = 15); 2.38−0.84 (CH_2 and CH_3). ^{13}C NMR (CD_2Cl_2): δ 134−128 (Ph); 62.3 (s, *C*(H)NH$_2$); 60.5 (s, CN*C*(CH$_3$)$_3$); 60.4 (s, CN*C*(CH$_3$)$_3$); 59.8 (s, CN*C*(CH$_3$)$_3$); 44.1 (s, CH, Cy); 37.8 (dd, $^1J_{PC}$ = 14, $^3J_{PC}$ = 6, P*C*(CH$_3$)$_3$); 37.0 (d, P*C*(CH$_3$)$_3$, $^1J_{PC}$ = 15); 35.5 (dd, $^1J_{PC}$ = 28, $^1J_{PC}$ = 16, P$_2$*C*H$_2$); 31.2, 29.1, 26.6, 26.3, 26.2 (*C*H$_2$, Cy); 30.7 (s, CNC(*C*H$_3$)$_3$); 30.1 (s, CNC(*C*H$_3$)$_3$); 30.0 (s, CNC(*C*H$_3$)$_3$); 30.4 (d, $^2J_{PC}$ = 3, PC(*C*H$_3$)$_3$); 29.9 (d, $^2J_{PC}$ = 3, PC(*C*H$_3$)$_3$); 17.8 (s, *Me*C(H)NH$_2$). Obviously, by using (*R*)-CH$_3$CH(C$_6$H$_{11}$)NH$_2$ it was possible to prepare the *R* enantiomer, whose spectroscopic data are identical to **3b**.

***mer*-[Ru{*S*-CH$_3$CH(Ph)NH$_2$}(CN^{t}Bu)$_3${PPh$_2$CH$_2$P^{t}Bu$_2$}](ClO$_4$)$_2$ (3c)** was obtained from **2** (0.1 g, 0.11 mmol) and (*S*)-CH$_3$CH(C$_6$H$_5$)NH$_2$ (15 μL, 0.12 mmol) as a white solid. Yield: 102 mg (91%). Anal. Calcd for $RuO_8Cl_2P_2N_4C_{44}H_{68}$: C, 52.07; H, 6.75; N, 5.52. Found: C, 51.99; H, 6.82; N, 5.16. $[\alpha]^{20}_D$ −21.8° (*c* = 0.01 gr/mL; CH_2Cl_2). ^{1}H NMR (CD_2Cl_2): δ 7.90−7.19 (15H, Ph); 4.74 (m, C*H*); 4.01 (m, 2H, P$_2$CH_2); 1.61 (s, 9H, CN^t*Bu*); 1.56 (s, 9H, CN^t*Bu*); 1.04 (s, 9H, CN^t*Bu*); 1.39 (d, 9H, $^3J_{PH}$ = 15, P^t*Bu*$_2$); 1.23 (d, 9H, $^3J_{PH}$ = 15, P^t*Bu*$_2$); 1.27 (s, NH$_2$). Using (*R*)-CH$_3$CH(C$_6$H$_5$)NH$_2$ it is possible to prepare the *R* enantiomer, whose spectroscopic data are identical to **3c**.

[Ru(CN^{t}Bu)$_4${PPh$_2$CHP^{t}Bu$_2$}](ClO$_4$) (4a). To a solution of **3a** (80 mg, 0.08 mmol) in 10 mL of CH_2Cl_2 was added 1.25 g of KOH. The reaction mixture was stirred for 1 h. The solution was then filtered and 20 mL of ether carefully added to the filtrate. Slow diffusion of the solvents afforded crystals of **4a**. Yield: 43 mg (60%). Anal. Calcd for $RuO_4ClP_2N_4C_{41}H_{65}$: C, 56.19; H, 7.47; N, 6.39. Found: C, 56.35; H, 7.22; N, 6.01. ^{1}H NMR (CD_2Cl_2): δ 7.74−7.21 (10H, Ph); 1.86 (t, H, $^2J_{PH}$ = 3, C*H*); 1.67 (s, 9H, CN^t*Bu*); 1.51 (s, 9H, CN^t*Bu*); 1.22 (d, 18H, $^3J_{PH}$ = 14, P^t*Bu*$_2$); 1.15 (s, 18H, CN^t*Bu*). ^{13}C NMR (CD_2Cl_2): δ 145.2 (br, *C*N^{t}Bu); 143.7 (d, *C*N^{t}Bu, $^2J_{CP}$ = 5); 143.1 (br, C, *C*N^{t}Bu); 58.6 (s, CN*C*(CH$_3$)$_3$); 58.2 (s, CN*C*(CH$_3$)$_3$); 57.7 (s, CN*C*(CH$_3$)$_3$); 38.4 (dd, $^1J_{PC}$ = 16, $^3J_{PC}$ = 5, P*C*(CH$_3$)$_3$); 31.1 (s, C(*C*H$_3$)$_3$); 30.8 (s, C(*C*H$_3$)$_3$); 30.6 (s, C(*C*H$_3$)$_3$); 29.9 (s, C(*C*H$_3$)$_3$); 14.2 (dd, $^1J_{PC}$ = 66, $^1J_{PC}$ = 47, P$_2$CH).

***mer*-[Ru{*S*-CH$_3$CH(C$_6$H$_{11}$)NH$_2$}(CN^{t}Bu)$_3${PPh$_2$CHP^{t}Bu$_2$}](ClO$_4$) (4b).** Following a similar procedure as above, using THF as a solvent, **4b** was isolated as a yellow solid. Yield: 65%. Anal. Calcd for $RuO_4ClP_2N_4C_{44}H_{73}$: C, 57.41; H, 7.99; N, 6.09. Found: C, 56.97; H, 7.57; N, 5.98.

Synthesis of *mer*-[Ru{*S*-(CH$_3$CH(R)NH$_2$}(CN^{t}Bu)$_3$-{PPh$_2$CH{Au(PPh$_3$)}P^{t}Bu$_2$}](ClO$_4$)$_2$ (R = C$_6$H$_{11}$(5b), R = Ph (5c)). To a solution of the derivative **3b** or **3c** (75 mg, 0.07 mmol) in 10 mL of CH_2Cl_2 were added 35 mg (0.07 mmol) of AuCl(PPh$_3$) and 1.25 g of KOH. The reaction mixture was stirred for 10 min and then filtered. A 20 mL sample of ether was added to the filtrate, and a white solid was formed. This solid constitutes a mixture of the *SR* and *SS* isomers of **5**.

***(SS/SR)*5b.** Yield: 95 mg (64%). Anal. Calcd for $RuAuO_8Cl_2P_3N_4C_{62}H_{88}$: C, 50.34; H, 6.00; N, 3.79. Found: C, 50.03; H, 5.93; N, 3.74; de 72. ^{1}H NMR (major isomer) (CD_2Cl_2): δ 8.38−7.05 (25H, Ph); 3.63 (td, H, $^2J_{HP}$ = 13, $^3J_{HP}$ = 10, P$_2$C*H*); 3.84 (m, H, C*H*); 2.58 (m, H, C*H*NH$_2$); 1.67 (s, 9H, CN^t*Bu*); 1.58 (s, 9H, CN^t*Bu*); 1.32 (s, 2H, NH_2); 1.19 (s, 9H, CN^t*Bu*); 1.46 (d, 9H, P^t*Bu*$_2$, $^3J_{PH}$ = 14); 1.33 (d, 9H, P^t*Bu*$_2$, $^3J_{PH}$ = 12); 2.38−0.84 (CH_2 and CH_3). ^{13}C NMR (major isomer) (CD_2Cl_2): δ 134.4−128.9 (Ph); 62.3 (s, *C*(H)NH$_2$); 61.2 (s, CN*C*(CH$_3$)$_3$); 59.7 (s, CN*C*(CH$_3$)$_3$); 59.3 (s, CN*C*(CH$_3$)$_3$); 45.1 (s, CH, Cy); 38.0 (m, P*C*(CH$_3$)$_3$); 36.6 (d, P*C*(CH$_3$)$_3$, $^1J_{PC}$ = 16); 51.6 (dd, $^1J_{PC}$ = 19, $^1J_{PC}$ = 10, P$_2$*C*H); 31.1−26.2 (*C*H$_2$ and *C*H$_3$); 17.7 (s, *Me*C(H)NH$_2$).

***(SS/SR)*5c.** Yield: 69 mg (67%). Anal. Calcd for $RuAuO_8Cl_2P_3N_4C_{62}H_{82}$: C, 50.55; H, 5.61; N, 3.80. Found: C, 50.30; H, 5.53; N, 3.74; de 64. ^{1}H NMR (major isomer) (CD_2Cl_2): δ 8.36−7.08 (30H, Ph); 4.04 (m, C*H*); 3.62 (td, H, $^2J_{HP}$ = 13, $^3J_{HP}$ = 11, P$_2$C*H*); 1.67 (s, 9H, CN^t*Bu*); 1.57 (s, 9H, CN^t*Bu*); 1.17 (s, 9H, CN^t*Bu*); 1.30 (s, 2H, NH$_2$); 1.44 (d, 9H, $^3J_{PH}$ = 14, P^t*Bu*$_2$); 1.31 (d, 9H, $^3J_{PH}$ = 11, P^t*Bu*$_2$). In a similar way it was possible to prepare the mixture of the *RS* and *RR* isomers, using as starting materials the corresponding *R* enantiomers of **3b** and **3c**, whose spectroscopic data are identical to the *SR*/*SS* mixture.

X-ray Crystallography. Crystal data for **4a**: $[C_{41}H_{65}RuN_4P_2][ClO_4]\cdot CH_2Cl_2$, M_r = 961.36, orthorhombic, space group $P2_12_12_1$, a = 12.76(1) Å, b = 16.30(2) Å, c = 24.71(9) Å, V = 5140(20) Å^3, Z = 4, ρ_{calc} = 1.24 Mg m^{-3}, F(000) = 2016, λ(Mo Kα) = 0.71073 Å, μ = 5.62 cm^{-1}, T = 200 K; yellow crystals (0.30 × 0.26 × 0.23 mm); Nonius CAD4 diffractometer; $\omega-2\theta$ scan technique; 3984 reflections measured ($0° < \theta < 23°$), all used in refinement. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 procedures: R = 0.050 (for 3044 $I > 2\sigma(I)$), and wR2 = 0.134 (for all reflections), $w = 1.0/[\sigma^2(F_o)^2 + (0.071P)^2 + 3.8P]$ where $P = (\max(F_o^2,0) + 2F_c^2)/3$; total number of parameters 507; residual electron density less than 0.70 e Å^{-3}. Absolute configuration was checked (Flack parameter c = 0.00(7)). The plot in Figure 1 was made by the EUCLID package.[12] Additional crystallographic data are available in the Supporting Information.

Acknowledgment. We gratefully acknowledge the Ministerio de Educación y Ciencia for financial assistance (Project DGE-96-PB-0317) and for a research grant (M.E.G.M.).

Supporting Information Available: Tables of bond distances, angles, positional parameters, anisotropic thermal parameters, and hydrogen atom coordinates of **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000097Y

(12) Spek, A. L. In *Computational Crystallography*; Sayre, D., Ed.; Clarendon Press: Oxford, U.K., 1982; p 528.