An Easy Entry to Dimers [{RuX(μ-X)(CO)(P⌒P)}$_2$] (X = Cl, Br; P⌒P = 1,1′-Bis(diphenylphosphino)ferrocene, 1,1′-Bis(diisopropylphosphino)ferrocene) from η^3-Allylruthenium(II) Derivatives [RuX(η^3-2-C$_3$H$_4$R)(CO)(P⌒P)] (R = H, Me): Efficient Catalyst Precursors in Transfer Hydrogenation of Ketones§

Victorio Cadierno,*,† Pascale Crochet, Josefina Díez, Sergio E. García-Garrido, and José Gimeno*,‡

Departamento de Química Orgánica e Inorgánica, Instituto Universitario de Química Organometálica "Enrique Moles" (Unidad Asociada al CSIC), Facultad de Química, Universidad de Oviedo, E-33071 Oviedo, Spain

Santiago García-Granda

Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, E-33071 Oviedo, Spain

Received July 9, 2003

Complexes [RuX(η^3-2-C$_3$H$_4$R)(CO)(P⌒P)] (X = Cl, Br; R = H, Me; P⌒P = dppf, dippf) (**2a**−**d** and **3a**−**d**) have been prepared by reaction of the η^3-allylruthenium(II) derivatives [RuX(η^3-2-C$_3$H$_4$R)(CO)$_3$] (**1a**−**d**) with 1 equiv of the appropriate diphosphine. Treatment of **2a**−**d** and **3a**−**d** with HX allows the high-yield preparation of the dimeric compounds [{RuX(μ-X)(CO)(P⌒P)}$_2$] (P⌒P = dppf, X = Cl (**4a**), Br (**4b**); P⌒P = dippf, X = Cl (**5a**), Br (**5b**)). Complex [{RuCl(μ-Cl)(CO)(dppf)}$_2$] reacts with neutral ligands, via chloride bridge cleavage, affording the mononuclear derivatives [RuCl$_2$(CO)(L)(dppf)] (L = CO (**6a**), BzNC (**6b**), Py (**6c**), PhNH$_2$ (**6d**)). The structures of compounds [RuCl(η^3-C$_3$H$_5$)(CO)(dppf)] (**2a**), [{RuCl(μ-Cl)(CO)(dppf)}$_2$] (**4a**), and [RuCl$_2$(CO)(Py)(dppf)] (**6c**) have been confirmed by X-ray crystallography. The catalytic activity of dimers **4a**,**b** and **5a**,**b** in transfer hydrogenation of ketones by propan-2-ol has also been studied.

Introduction

The chemistry of carbonyl-halide-phosphine complexes of ruthenium(II) has been largely explored.[1] A wide series of six-coordinate mononuclear compounds of general formula [RuX$_2$(CO)$_2$(PR$_3$)$_2$] and [RuX$_2$(CO)(PR$_3$)$_3$] (several stereoisomers have been described for each of them) belong to this type of derivatives.[1] In contrast, only a limited number of five-coordinate 16-electron complexes [RuX$_2$(CO)(PR$_3$)$_2$] or their halide-bridged dimers [{RuX(μ-X)(CO)(PR$_3$)$_2$}$_2$] are known.[2,3] The competitive formation of [RuX$_2$(CO)(PR$_3$)$_2$] versus [{RuX(μ-X)(CO)(PR$_3$)$_2$}$_2$] is apparently influenced by the steric and electronic properties of the phosphine ligands. Thus, the bulky and electron-rich phosphines PCy$_3$, P^{t}Bu$_2$Me, and P^{i}Pr$_3$ appear to favor the formation of unsaturated monomers,[2] while the dimeric species contain relatively less sterically demanding monodentate phosphines, i.e., PPh$_3$, PMePh$_2$, and PMe$_2$Ph among others.[3] To the best of our knowledge, no five-coordinate complexes containing chelate diphosphines have been reported, and only three dimers, namely, [{RuCl(μ-Cl)(CO)(*o*-C$_6$H$_4$(PMePh)$_2$)}$_2$],[4] [{RuCl(μ-Cl)(CO)(t^{t}Bu$_2$P(CH$_2$)$_2$P^{t}Bu$_2$)}$_2$],[5] and [{RuCl(μ-Cl)(CO)(Cy$_2$P(CH$_2$)$_4$PCy$_2$)}$_2$],[6] have been described to date. Due to this fact, along with the scarce catalytic studies involving this type of derivatives,[7] we believed it of interest to prepare novel dimeric species and to explore their catalytic activity in transfer hydrogenation of ketones.

§ Dedicated to Prof. José Vicente on the occasion of his 60th birthday.

† E-mail: vcm@sauron.quimica.uniovi.es.
‡ E-mail: jgh@sauron.quimica.uniovi.es.

(1) (a) Seddon, E. A.; Seddon, K. R. In *The Chemistry of Ruthenium*; Elsevier: Amsterdam, 1984. (b) Schröder, M.; Stephenson, T. A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1987; Vol. 4, p 277. (c) Hill, A. F. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 7, p 299.

(2) For references dealing with the chemistry of five-coordinate complexes [RuX$_2$(CO)(PR$_3$)$_2$] see: (a) Moers, F. G.; Ten Hoedt, R. W. M.; Langhout, J. P. *J. Organomet. Chem.* **1974**, *65*, 93. (b) Moers, F. G.; Langhout, J. P. *J. Inorg. Nucl. Chem.* **1977**, *39*, 591. (c) Moers, F. G.; Buerskens, P. T.; Noordik, J. H. *Cryst. Struct. Commun.* **1982**, *11*, 1655. (d) Gaffney, T. R.; Ibers, J. A. *Inorg. Chem.* **1982**, *21*, 2062. (e) Moers, F. G. *J. Coord. Chem.* **1984**, *13*, 215. (f) Werner, H.; Tena, M. A.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1995**, *128*, 41. (g) Huang, D.; Folting, K.; Caulton, K. G. *Inorg. Chem.* **1996**, *35*, 7035. (h) Huang, D.; Heyn, R. H.; Bollinger, J. C.; Caulton, K. G. *Organometallics* **1997**, *16*, 292. (i) Huang, D.; Streib, W. E.; Bollinger, J. C.; Caulton, K. G.; Winter, R. F.; Scheiring, T. *J. Am. Chem. Soc.* **1999**, *121*, 8087. (j) Katayama, H.; Tanaguchi, K.; Kobayashi, M.; Sagawa, T.; Minami, T.; Ozawa, F. *J. Organomet. Chem.* **2002**, *645*, 192. (k) Werner, H.; Gruenwald, C.; Stueer, W.; Wolf, J. *Organometallics* **2003**, *22*, 1558. (l) Katayama, H.; Nagao, M.; Moriguchi, R.; Ozawa, F. *J. Organomet. Chem.* **2003**, *676*, 49.

10.1021/om030530e CCC: $25.00
Publication on Web 11/11/2003

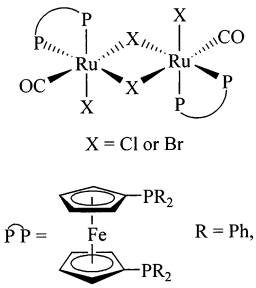


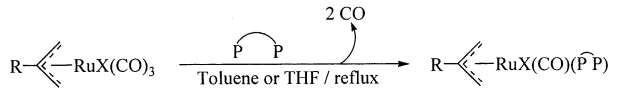
Figure 1. Structure of dimers [{RuX(μ-X)(CO)(P⌒P)}$_2$] reported in this paper.

Thus, in the present work we report the systematic synthesis of the ruthenium(II) dimers [{RuX(μ-X)(CO)(P⌒P)}$_2$] (X = Cl, Br; see Figure 1) containing the chelate diphosphine ligands 1,1′-bis(diphenylphosphino)ferrocene (dppf) and 1,1′-bis(diisopropylphosphino)ferrocene (dippf).[8] They have been prepared starting from the η^3-allyl complexes [RuX(η^3-2-C$_3$H$_4$R)(CO)(P⌒P)] (X = Cl, Br; R = H, Me; P⌒P = dppf, dippf), which readily undergo the releasing of the allyl units in the presence of the corresponding hydrogen halide. This unprecedented synthetic methodology allows an easy and efficient entry to the scarcely known dimeric carbonyl-halide-diphosphine ruthenium(II) complexes. Some of these species are shown to be highly efficient catalysts in transfer hydrogenation of ketones by propan-2-ol.

Results and Discussion

The most general synthetic approaches to [RuX$_2$(CO)(PR$_3$)$_2$] in their monomeric and dimeric forms are (i) the thermal or photochemical decarbonylation of [RuX$_2$(CO)$_2$(PR$_3$)$_2$] species[3e,f,i,m] and (ii) the treatment of alcoholic solutions of RuCl$_3$·*n*H$_2$O with carbon monoxide and the appropriate phosphine.[2a,f,3i,n] Although the former procedure was effective in the preparation of compounds [{RuCl(μ-Cl)(CO)(*o*-C$_6$H$_4$(PMePh)$_2$)}$_2$][4] and [{RuCl(μ-Cl)(CO)(^{t}Bu$_2$P(CH$_2$)$_2$P^{t}Bu$_2$)}$_2$],[5] attempts to prepare [{RuCl(μ-Cl)(CO)(Cy$_2$P(CH$_2$)$_4$PCy$_2$)}$_2$] by decarbonylation of [RuCl$_2$(CO)$_2$(Cy$_2$P(CH$_2$)$_4$PCy$_2$)] proved unsuccessful, being instead obtained by reaction of [RuCl$_2$(CO)(PPh$_3$)$_2$(DMF)] with Cy$_2$P(CH$_2$)$_4$PCy$_2$.[6]

Scheme 1



R = H, X = Cl (**1a**), Br (**1b**)
R = Me, X = Cl (**1c**), Br (**1d**)

P⌒P = dppf, R = H, X = Cl (**2a**), Br (**2b**)
P⌒P = dppf, R = Me, X = Cl (**2c**), Br (**2d**)
P⌒P = dippf, R = H, X = Cl (**3a**), Br (**3b**)
P⌒P = dippf, R = Me, X = Cl (**3c**), Br (**3d**)

We have designed an alternative synthetic approach that allows us to check the ability of the relatively bulky diphosphines dppf and dippf to stabilize halide-bridged dimeric derivatives [{RuX(μ-X)(CO)(P⌒P)}$_2$]. These complexes can be accessible from the readily available species [RuX(η^3-allyl)(CO)(P⌒P)] (X = Cl, Br; P⌒P = dppf, dippf) by releasing of the η^3-allyl fragment in the presence of the corresponding hydrogen halide. The role of η^3-allyl groups to act as labile ligands generating free coordination sites in acidic media is well-documented.[9]

Synthesis of the Precursor Complexes [RuX(η^3-2-C$_3$H$_4$R)(CO)(P⌒P)] (X = Cl, Br; R = H, Me; P⌒P = dppf, dippf). Treatment of tricarbonyl complexes [RuX(η^3-2-C$_3$H$_4$R)(CO)$_3$] (R = H, Me; X = Cl, Br; **1a**−**d**)[10] with 1 equiv of the appropriate diphosphine in refluxing toluene (**2a**,**b** and **3a**,**b**) or tetrahydrofuran (**2c**,**d** and **3c**,**d**) generates the monocarbonyl derivatives [RuX(η^3-2-C$_3$H$_4$R)(CO)(P⌒P)] (R = H, Me; X = Cl, Br; P⌒P = dppf, dippf; **2a**−**d** and **3a**−**d**), which have been isolated as yellow-orange air-stable solids in 69−82% yield (Scheme 1).

Spectroscopic data (IR and ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR) and elemental analyses for complexes **2a**−**d** and **3a**−**d** are in agreement with the proposed formulations (details are given in the Experimental Section). Relevant spectroscopic features are the following: (i) (IR) the presence of a strong ν(CO) absorption band in the range 1907−1926 cm^{-1}, (ii) (^{31}P{^{1}H} NMR) the appearance of a singlet signal at ca. 35 (**2a**−**d**) or 41 (**3a**−**d**) ppm, (iii) (^{1}H NMR) typical resonances for the *syn*- and *anti*-H of the η^3-allyl ligands (δ 3.57−3.72 and 2.07−2.47 ppm, respectively) as well as for the central hydrogen (**2a**,**b**, **3a**,**b**) or methyl (**2c**,**d**, **3c**,**d**) substituents (δ 4.69−4.91 and 2.05−2.12 ppm, respectively), and (iv) (^{13}C{^{1}H} NMR) a characteristic downfield signal (δ 202.98−205.78 ppm) for the carbonyl ligand which appears as a triplet ($^2J_{CP}$ = 14.3−16.1 Hz) due to the coupling with the two equivalent phosphorus nuclei of the ferrocenyl ligands. Since allyl groups in complexes **2a**−**d** and **3a**−**d** may adopt an *endo* or *exo* arrangement (see Figure 2), the observation of only one set of

(3) For references dealing with the chemistry of dimers [{RuX(μ-X)(CO)(PR$_3$)$_2$}$_2$] see: (a) Prince, R. H.; Raspin, K. A. *J. Chem. Soc. (A)* **1969**, 612. (b) Ruiz-Ramírez, L.; Stephenson, T. A.; Switkes, E. S. *J. Organomet. Chem.* **1973**, *49*, C77. (c) Ruiz-Ramírez, L.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1974**, 1640. (d) Armit, P. W.; Stephenson, T. A. *J. Organomet. Chem.* **1974**, *73*, C33. (e) Barnard, C. F. J.; Daniels, J. A.; Jeffery, J.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1976**, 953. (f) Barnard, C. F. J.; Daniels, J. A.; Holland, P. R.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1980**, 2418. (g) Paz-Sandoval, M. A.; Powell, P. *J. Organomet. Chem.* **1983**, *252*, 205. (h) Sánchez-Delgado, R. A.; Thewalt, U.; Valencia, N.; Andriollo, A.; Márquez-Silva, R. L.; Puga, J.; Schöllhorn, H.; Klein, H. P.; Fontal, B. *Inorg. Chem.* **1986**, *25*, 1097. (i) Krassowski, D. W.; Nelson, J. H.; Brower, K. R.; Hauenstein, D.; Jacobson, R. A. *Inorg. Chem.* **1988**, *27*, 4294. (j) Krassowski, D. W.; Nelson, J. H. *J. Organomet. Chem.* **1988**, *356*, 93. (k) Vac, R.; Nelson, J. H.; Milosavljević, E. B.; Solujić, L. *Inorg. Chem.* **1989**, *28*, 3831. (l) Pandey, K. K.; Tewari, S. K. *Polyhedron* **1989**, *8*, 1149. (m) Sun, Y.; Taylor, N. J.; Carty, A. J. *Inorg. Chem.* **1993**, *32*, 4457. (n) Bustelo, E.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Chem. Soc., Dalton Trans.* **1999**, 2399. (o) Marchenko, A. V.; Huffman, J. C.; Valerga, P.; Jiménez-Tenorio, M.; Puerta, M. C.; Caulton, K. G. *Inorg. Chem.* **2001**, *40*, 6444.

(4) Grocott, S. C.; Wild, S. B. *Inorg. Chem.* **1982**, *21*, 3535.

(5) Gottschalk-Gaudig, T.; Folting, K.; Caulton, K. G. *Inorg. Chem.* **1999**, *38*, 5241.

(6) Drouin, S. D.; Amoroso, D.; Yap, G. P. A.; Fogg, D. E. *Organometallics* **2002**, *21*, 1042.

(7) Hydrosilylation of alkynes: see refs 2j and 2l. Hydrogenation of olefins: see refs 3j and 3k. Hydrogenation of ketones and *ortho*-olefination of arenes (Murai catalysis): see ref 6.

(8) For reviews on the chemistry of ferrocenyl-phosphines see: (a) Gan, K. S.; Hor, T. S. A. In *Ferrocenes: Homogeneous Catalysis, Organic Synthesis and Material Science*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, 1995; p 3. (b) Bandoli, G.; Dolmella, A. *Coord. Chem. Rev.* **2000**, *209*, 161. (c) Colacot, T. J. *Platinum Metals Rev.* **2001**, *45*, 22.

(9) See for example: (a) Braterman, P. S. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum Press: New York, 1986; Vol. 1, p 103. (b) Ratovelomanana-Vidal, V.; Genêt, J. P. *J. Organomet. Chem.* **1998**, *567*, 163, and references therein. (c) Katayama, H.; Ozawa, F. *Organometallics* **1998**, *17*, 5190.

(10) (a) Sbrana, G.; Braca, G.; Piacenti, F.; Pino, P. *J. Organomet. Chem.* **1968**, *13*, 240. (b) Kondo, T.; Ono, H.; Satake, N.; Mitsudo, T.; Watanabe, Y. *Organometallics* **1995**, *14*, 1945.

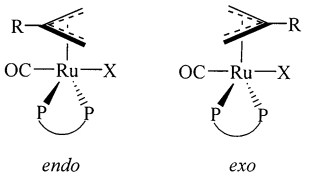


Figure 2. *Exo* and *endo* isomers of complexes [RuX(η^3-2-C_3H_4R)$(CO)_3$] (**1a**−**d**).

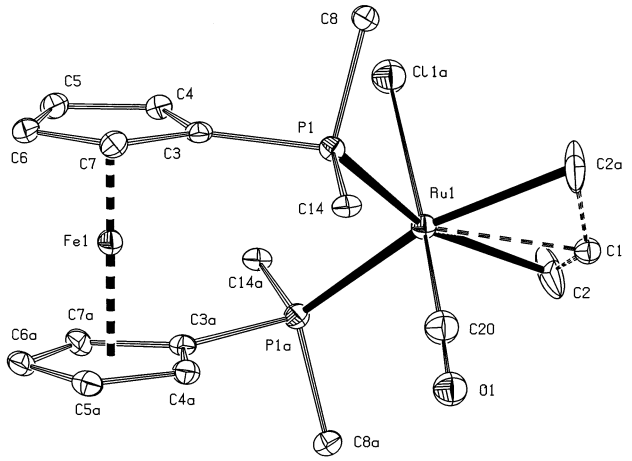
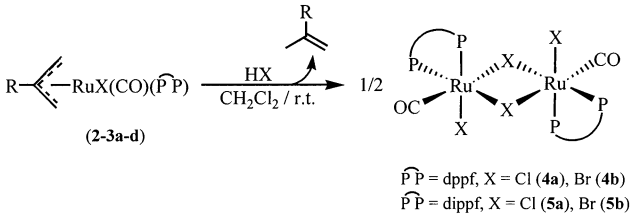


Figure 3. ORTEP-type view of the structure of [RuCl(η^3-C_3H_5)(CO)(dppf)] (**2a**) showing the crystallographic labeling scheme. Atoms labeled with an "a" are related to those indicated by a crystallographic 2-fold symmetry axis. Hydrogen atoms are omitted for clarity, and only the *ipso*-carbons of the phenyl rings of the Ph_2P groups are shown. Thermal ellipsoids are drawn at 20% probability level. Selected bond distances (Å) and angles (deg): Ru−C(1′) = 2.22(3); Ru−C(2) = 2.267(7); Ru−P(1) = 2.387(1); Ru−Cl(1a) = 2.532(5); Ru−C(20) = 1.744(15); C(1′)-C(2) = 1.31(2); C(20)−O(1) = 1.028(19); Fe−C* = 1.641(1); P(1)−Ru−P(1a) = 103.11(7); P(1)−Ru−Cl(1a) = 88.64(14); P(1)−Ru−C(20) = 87.5(4); P(1)−Ru−C(2) = 161.78(19); P(1)−Ru−C(2a) = 95.06(19); C(2)−Ru−Cl(1a) = 90.3(3); C(2)−Ru−C(20) = 93.6(5); C(2)−Ru−C(2a) = 66.8(4); C(2)−Ru−C(1′) = 33.9(6); C(2)−C(1′)−C(2a) = 132.0(2); C(20)−Ru−Cl(1a) = 176.1(4); Ru−C(20)−O(1) = 177.2(14). C* = centroid of the cyclopentadienyl ring (C(3), C(4), C(5), C(6), C(7)).

resonances for both the proton and carbon nuclei of the η^3-allyl units seems to indicate that in solution only one isomer is present.[11]

Although a single-crystal X-ray diffraction study on [RuCl(η^3-C_3H_5)(CO)(dppf)] (**2a**) was carried out, no *endo*/*exo* structural elucidation was achieved since the carbonyl, chloride, and allyl ligands are disordered in ca. 50/50 as a consequence of the opposite orientations adopted by the molecules in the crystal lattice. An ORTEP view is shown in Figure 3 (selected bond distances and angles are listed in the caption). This disorder is clearly reflected by the appearance of a crystallographic 2-fold symmetry axis that contains the ruthenium and iron atoms (in Figure 3 only one disposition of the mutually *trans* CO and Cl ligands is shown;

Scheme 2



for the η^3-C_3H_5 unit the average position for the terminal carbons C(2) and C(2a) is shown, while for the central carbon C(1′) one of the two possible positions is represented). The molecular structure shows a pseudooctahedron geometry around the ruthenium atom with the η^3-allyl fragment formally occupying two coordination sites. Interligand angles around ruthenium, in the range 67−104°, reveal the distortions caused by the geometric restrictions of the allyl ligand. The Ru−C(1′) and Ru−C(2) bond lengths of 2.22(3) and 2.267(7) Å, respectively, are consistent with the η^3-coordination mode of the allyl group. These values, together with the C(1′)−C(2) distance (1.31(2) Å) and the internal C(2)−C(1′)−C(2a) angle (132.0(2)°), compare well to those reported in the literature for other (η^3-allyl)-ruthenium(II) complexes.[10b,12]

Synthesis of Halide-Bridged Dimers [{RuX(μ-X)(CO)(P⌒P)}$_2$] (X = Cl, Br; P⌒P = dppf, dippf). In accordance with the well-known lability of the η^3-allyl groups in acidic media,[9] we have found that the treatment of complexes [RuX(η^3-C_3H_5)(CO)(P⌒P)] (P⌒P = dppf, X = Cl (**2a**), Br (**2b**); P⌒P = dippf, X = Cl (**3a**), Br (**3b**)) with a slight excess (ca. 1.5 equiv) of the appropriate HX acid, in dichloromethane at room temperature, affords the dimeric species [{RuX(μ-X)(CO)(P⌒P)}$_2$] (P⌒P = dppf, X = Cl (**4a**), Br (**4b**); P⌒P = dippf, X = Cl (**5a**), Br (**5b**)), via propene releasing (83−88% yield; Scheme 2). Alternatively, these compounds can also be obtained in similar yield starting from the corresponding (η^3-2-methylallyl)-ruthenium(II) complexes [RuX(η^3-2-C_3H_4Me)(CO)(P⌒P)] (P⌒P = dppf, X = Cl (**2c**), Br (**2d**); P⌒P = dippf, X = Cl (**3c**), Br (**3d**)).

Compounds **4a**,**b** and **5a**,**b** have been isolated as air-stable yellow-orange solids. They have been characterized by elemental analyses and IR and NMR spectroscopy, which confirm the releasing of the allyl groups (see the Experimental Section for details). $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR data are useful for the structural elucidation. In particular, the carbonyl resonances in the $^{13}C\{^1H\}$ NMR spectra (δ 200.07−202.10 ppm), which appear as a doublet of doublets signal with $^2J_{CP}$ values in the range 15.4−17.1 Hz, reveal a *cis* arrangement of the carbonyl groups with respect to both phosphorus nuclei of the diphosphines. The $^{31}P\{^1H\}$ NMR spectra, which

(11) It has been reported that complexes [RuX(η^3-C_3H_5)$(CO)_3$] (X = Cl, Br) exist in solution in a conformational equilibrium between *endo* and *exo* isomers: Wrighton, M. S.; Wuu, Y. M. *Organometallics* **1988**, *7*, 1839. Variable-temperature $^{31}P\{^1H\}$ and ^1H NMR experiments (from −60 to 60 °C) were carried out with a THF-d_8 solution of complex [RuCl(η^3-C_3H_5)(CO)(dppf)] (**2a**). No changes were observed in the NMR spectra, discarding the possibility of a dynamic equilibrium between *endo* and *exo* species in solution.

(12) See for example: (a) Smith, A. E. *Inorg. Chem.* **1972**, *11*, 2306. (b) Schoonover, M. W.; Eisenberg, R. *J. Am. Chem. Soc.* **1977**, *99*, 8371. (c) Hsu, L. Y.; Nordman, E.; Gibson, D. H.; Hsu, W. L. *Organometallics* **1989**, *8*, 241. (d) Braun, T.; Gevert, O.; Werner, H. *J. Am. Chem. Soc.* **1995**, *117*, 7291. (e) Esteruelas, M. A.; Liu, F.; Oñate, E.; Sola, E.; Zeier, B. *Organometallics* **1997**, *16*, 2919. (f) MacFralane, K. S.; Rettig, S. J.; Liu, Z.; James, B. R. *J. Organomet. Chem.* **1998**, *557*, 213. (g) Six, C.; Gabor, B.; Görls, H.; Mynott, R.; Philipps, P.; Leitner, W. *Organometallics* **1999**, *18*, 3316. (h) Nakanishi, S.; Sasake, H.; Takata, T. *Chem. Lett.* **2000**, 1058. (i) Older, C. M.; Stryker, J. M. *Organometallics* **2000**, *19*, 2661. (j) Smith, D. C.; Cadoret, J.; Jafarpour, L.; Stevens, E. D.; Nolan, S. P. *Can. J. Chem.* **2001**, *79*, 626. (k) Sasabe, H.; Nakanishi, S.; Takata, T. *Inorg. Chem. Commun.* **2002**, *5*, 177.

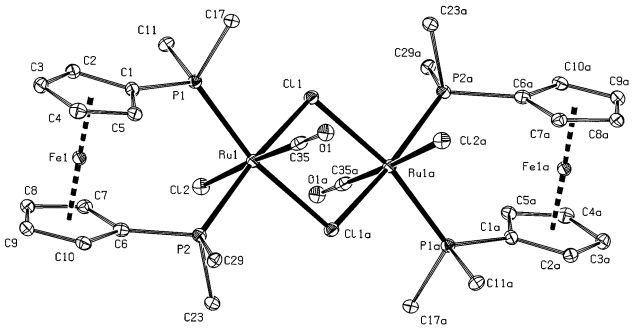


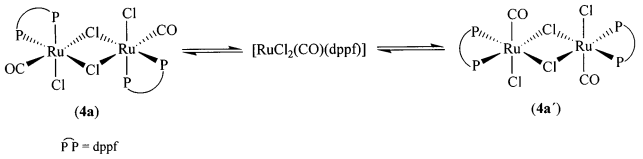
Figure 4. ORTEP-type view of the structure of [{RuCl(μ-Cl)(CO)(dppf)}$_2$] (**4a′**) showing the crystallographic labeling scheme. Atoms labeled with an "a" are related to those indicated by a crystallographic center of symmetry. Hydrogen atoms are omitted for clarity, and only the *ipso*-carbons of the phenyl rings of the Ph_2P groups are shown. Thermal ellipsoids are drawn at 20% probability level. Selected bond distances (Å) and angles (deg): Ru−Cl(1) = 2.446(1); Ru−Cl(1a) = 2.489(1); Ru−Cl(2) = 2.446(1); Ru−P(1) = 2.319(1); Ru−P(2) = 2.355(1); Ru−C(35) = 1.892(5); C(35)−O(1) = 1.047(5); Fe−C* = 1.640(1); Fe−C** = 1.643(1); P(1)−Ru−Cl(1) = 86.93(3); P(1)−Ru−Cl(2) = 94.06(3); P(1)−Ru−C(35) = 89.70(12); P(1)−Ru−P(2) = 101.32(3); P(1)−Ru−Cl(1a) = 167.27(3); Cl(1)−Ru−C(35) = 91.74(12); Cl(1)−Ru−Cl(1a) = 80.80(3); Cl(1)−Ru−Cl(2) = 85.86(3); Cl(1)−Ru−P(2) = 168.45(3); P(2)−Ru−Cl(2) = 85.53(3); P(2)−Ru−C(35) = 96.30(12); P(2)−Ru−Cl(1a) = 91.29(3); Cl(2)−Ru−C(35) = 175.42(12); Ru−C(35)−O(1) = 177.7(4); C*−Fe−C** = 177.90(1). C* and C** = centroids of the cyclopentadienyl rings (C(1), C(2), C(3), C(4), C(5) and C(6), C(7), C(8), C(9), C(10), respectively).

display a typical AB pattern (δ 46.39−64.90 ppm; $^2J_{PP}$ = 16.6−24.9 Hz), are also fully consistent with the structural proposal.[13]

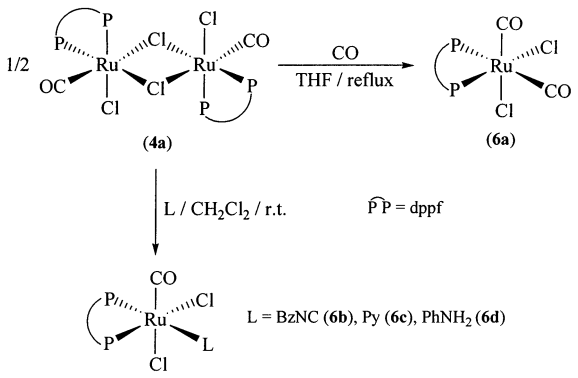
Moreover, the formation of dimeric species was unambiguously confirmed by a X-ray diffraction study of the complex [{RuCl(μ-Cl)(CO)(dppf)}$_2$] (**4a**). A drawing of the molecular structure is depicted in Figure 4. Selected bond distances and angles are listed in the caption; since they can be compared to those observed for other chlorocarbonyl derivatives, no further comments are deserved.[1−6]

The coordination geometry around each ruthenium center can be described as a distorted octahedron in which the carbonyl group and one chloride ligand occupy axial positions and the phosphorus atoms of the ferrocenyl-diphosphine and two bridging Cl ligands occupy the equatorial sites. The most relevant feature of this structure is the *anti* arrangement of the two metallic units (*transoid*-CO isomeric form). Since this dimeric structure has equivalent phosphorus nuclei, it cannot correspond to the initial products isolated, indicating that an isomerization has occurred during the crystallization process. To obtain information on this isomerization, we have examined the $^{31}P\{^1H\}$ NMR spectra of a crystalline sample of [{RuCl(μ-Cl)(CO)(dppf)}$_2$] (**4a′**) in CD_2Cl_2 at variable temperature. Thus, at −20 °C the spectrum shows a singlet signal at 45.65 ppm, as expected for the chemically equivalent phosphorus

Scheme 3



Scheme 4



nuclei of the diphosphine in **4a′**. Upon warming to room temperature, this signal gradually disappears while new signals of the AB spin system of **4a** (δ 46.39 and 53.69 ppm; d, $^2J_{PP}$ = 24.9 Hz) appear (ca. **4a′/4a** ratio 8:1, 1:1, and 1:4 at −10, 0, and 10 °C, respectively). After ca. 1 h at room temperature the spectrum displays only the AB pattern. In addition, starting from a solution of complex **4a** in CD_2Cl_2 at room temperature and then cooling to −20 °C the reverse transformation is observed. After a few minutes, the spectrum displays the signals both of the starting complex (**4a**) and of the singlet at 45.65 ppm due to the presence of the stereoisomer **4a′**, along with other minor unassigned resonances. These data are consistent with the existence in solution of an equilibrium between both stereoisomers (Scheme 3), which probably interconvert through a chloride bridge cleavage process, involving the formation of a transient five-coordinate species. A similar isomerization process has been recently described for the related dimeric species [{RuCl(μ-Cl)(CO)(P^{i}Pr$_2$Me)$_2$}$_2$] by Caulton, Puerta, and co-workers.[3o,14]

Reactivity of Halide-Bridged Dimer [{RuCl(μ-Cl)(CO)(dppf)}$_2$] (4a): Synthesis of Mononuclear Compounds [RuCl$_2$(CO)(L)(dppf)] (L = CO, BzNC, Py, PhNH$_2$). Complexes **4a** is prone to undergo addition of two electron donor ligands in accordance with the observed spontaneous cleavage of the chloride bridges. Thus, when carbon monoxide is bubbled through a refluxing THF solution of [{RuCl(μ-Cl)(CO)(dppf)}$_2$] (**4a**), the dicarbonyl complex *cis,cis,cis*-[RuCl$_2$(CO)$_2$(dppf)] (**6a**) is formed (89% yield; Scheme 4). IR and NMR spectroscopic data are consistent with a *cis* arrangement of the chloride and carbonyl ligands. Characteristic features are (a) the two strong ν(CO) absorption bands that appear at 2009 and 2070 cm^{-1} in the IR spectrum, (b) the AB pattern of the phosphorus resonances at δ 15.34 and 38.78 ppm; d, $^2J_{PP}$ = 25.3 Hz, and (c) the doublet of doublets carbonyl resonances at 189.15 (dd, $^2J_{CP}$ = 123.4 and 9.7 Hz) and 195.21 (dd, $^2J_{CP}$ = 13.8 and 11.8 Hz) ppm.[15]

Analogous *cis,cis*-[RuCl$_2$(CO)(L)(dppf)] complexes (L = BzNC (**6b**), Py (**6c**), PhNH$_2$ (**6d**)) have also been

(13) Although a monomeric five-coordinate structure [RuX$_2$(CO)(P⌒P)] could be also proposed for complexes **4a**,**b** and **5a**,**b**, it has been discarded on the basis of steric deshielding of the ruthenium atom. See ref 5.

obtained (85−95% yield) by treatment of [{RuCl(μ-Cl)(CO)(dppf)}$_2$] (**4a**) with an excess of benzyl isocyanide, pyridine, or aniline, respectively (Scheme 4). These compounds have been characterized by means of standard spectroscopic techniques (IR and ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR) and elemental analyses, all data being fully consistent with the proposed formulations (see the Experimental Section for details). Remarkable spectroscopic features are (i) (IR) the presence of one ν(CO) absorption band in the range 1944−1977 cm^{-1}, (ii) (^{31}P{^{1}H} NMR) the appearance of a pattern typical of the AB spin system (δ 17.35−47.11 ppm; $^2J_{PP}$ = 25.7−28.9 Hz), indicative of unequivalent phosphorus nuclei of the dppf ligand, and (iii) (^{13}C{^{1}H} NMR) a characteristic downfield signal (δ 198.23−201.76 ppm) for the carbonyl group that appears as a doublet of doublets with $^2J_{CP}$ values of 12.3−15.3 Hz. Moreover, the structure of the complex *cis,cis*-[RuCl$_2$(CO)(Py)(dppf)] (**6c**) has been unequivocally confirmed by a single-crystal X-ray diffraction study. An ORTEP view of the molecular structure is shown in Figure 5; bond distances and angles around the metal are listed in the caption, all of them being in the expected range.[1a]

Catalytic Transfer Hydrogenation of Ketones. Following our interest in ruthenium-catalyzed transfer hydrogenation of ketones by propan-2-ol,[16] we decided to explore the catalytic activity of the dimeric compounds [{RuX(μ-X)(CO)(P⌒P)}$_2$] (P⌒P = dppf, X = Cl (**4a**), Br (**4b**); P⌒P = dippf, X = Cl (**5a**), Br (**5b**)) in transfer hydrogenation of acetophenone (see Scheme 5).[17] Our present interest was mainly motivated by the recent observation that a hydride species obtained from the analogous dimeric compound [{RuCl(μ-Cl)(CO)(Cy$_2$P-(CH$_2$)$_4$PCy$_2$)}$_2$] is a highly active catalyst in the hydrogenation of ketones.[6] In addition, increasing activity was expected with respect to conventional octahedral chloride derivatives since the formation of transient five-coordinate species in solution can readily provide the required vacant site for coordination of the substrate. Thus, in a typical experiment, the ruthenium catalyst precursors **4a**,**b** and **5a**,**b** (0.2 mol %, i.e., 0.4 mol % of Ru) and NaOH (9.6 mol %) were added to a 0.1 M solution of acetophenone (5 mmol) in ^{i}PrOH at 82 °C, the reaction being monitored by gas chromatography.

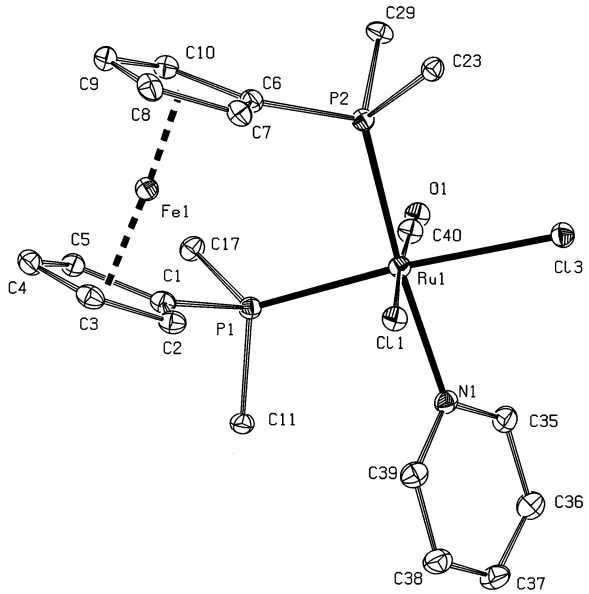
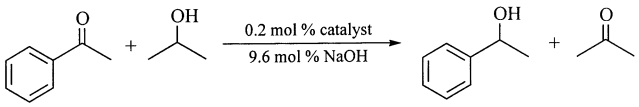


Figure 5. ORTEP-type view of the structure of *cis,cis*-[RuCl$_2$(CO)(py)(dppf)] (**6c**) showing the crystallographic labeling scheme. Only one disposition of the disordered and mutually *trans* CO and Cl ligands is shown. Hydrogen atoms are omitted for clarity, and only the *ipso*-carbons of the phenyl rings of the Ph$_2$P groups are shown. Thermal ellipsoids are drawn at 20% probability level. Selected bond distances (Å) and angles (deg): Ru−Cl(1) = 2.427(3); Ru−Cl(3) = 2.459(1); Ru−N(1) = 2.175(4); Ru−P(1) = 2.342-(1); Ru−P(2) = 2.359(1); Ru−C(40) = 1.795(11); C(40)−O(1) = 1.134(15); Fe−C* = 1.642(1); Fe−C** = 1.643(1); P(1)−Ru−P(2) = 95.47(4); P(1)−Ru−C(40) = 87.3(3); P(1)−Ru−Cl(3) = 172.34(4); P(1)−Ru−N(1) = 90.33(11); P(1)−Ru−Cl(1) = 95.41(6); P(2)−Ru−C(40) = 91.6(3); P(2)−Ru−Cl(3) = 90.48(4); P(2)−Ru−Cl(1) = 90.30(6); P(2)−Ru−N(1) = 172.94(11); Cl(1)−Ru−C(40) = 176.5(3); Cl(1)−Ru−Cl(3) = 89.35(6); Cl(1)−Ru−N(1) = 85.14(12); N(1)−Ru−C(40) = 92.7(3); N(1)−Ru−Cl(3) = 84.08(11); C(40)−Ru−Cl(3) = 87.7(3); Ru−C(40)−O(1) = 175.1(9); C*−Fe−C** = 176.77-(1). C* and C** = centroids of the cyclopentadienyl rings (C(1), C(2), C(3), C(4), C(5) and C(6), C(7), C(8), C(9), C(10), respectively).

Scheme 5



All the complexes have proven to be efficient catalysts, leading to nearly quantitative conversions of acetophenone into 1-phenylethanol within 10 h (Figure 6). The following features are worth noting: (i) the catalytic performances shown by dimers containing the bulkier and more basic dippf ligands **5a**,**b** are higher than those of their corresponding dppf counterparts **4a**,**b** (the nature of the halide bridges has little influence on the reaction rate), and (ii) the exceptional high activity of complexes [{RuX(μ-X)(CO)(dippf)}$_2$] (**5a**,**b**), which reach very good conversions within 5 min (97% (**5a**; X = Cl) and 86% (**5b**; X = Br)), is retained at lower catalyst loadings. As an example, using 0.05 mol % of **5a**, acetophenone (0.1 M solution in ^{i}PrOH; ketone/Ru/NaOH ratio: 1000/1/24) can be reduced in 97% yield within 5 h. It is interesting to note that initially the transformation is very rapid, giving rise to a yield of 73% in 1 min (TOF 43600 h^{-1}).

(14) A dimer/monomer equilibration has been also proposed by Caulton and Puerta for the isomerization of complex [{RuCl(μ-Cl)(CO)-(P^{i}Pr$_2$Me)$_2$}$_2$]. Other mechanisms for the **4a**/**4a′** stereochemical equilibration (involving halide or phosphine arm dissociation) cannot be totally discarded.

(15) As expected, complex **6a** undergoes a decarbonylation process in refluxing THF (ca. 3 h), regenerating the chloro-bridged dimer [{RuCl(μ-Cl)(CO)(dppf)}$_2$] (**4a**).

(16) (a) Crochet, P.; Gimeno, J.; García-Granda, S.; Borge, J. *Organometallics* **2001**, *20*, 4369. (b) Cadierno, V.; Crochet, P.; García-Álvarez, J.; García-Garrido, S. E.; Gimeno, J. *J. Organomet. Chem.* **2002**, *663*, 32. (c) Crochet, P.; Gimeno, J.; Borge, J.; García-Granda, S. *New J. Chem.* **2003**, *27*, 414. (d) Cadierno, V.; Crochet, P.; Díez, J.; García-Álvarez, J.; García-Garrido, S. E.; Gimeno, J.; García-Granda, S.; Rodríguez, M. A. *Inorg. Chem.* **2003**, *42*, 3293. (e) Cadierno, V.; Crochet, P.; Díez, J.; García-Álvarez, J.; García-Garrido, S. E.; García-Granda, S.; Gimeno, J.; Rodríguez, M. A. *Dalton Trans.* **2003**, 3240.

(17) For reviews on transition-metal-catalyzed transfer hydrogenation of ketones see: (a) Zassinovich, G.; Mestroni, G.; Gladiali, S. *Chem. Rev.* **1992**, *92*, 1051. (b) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97. (c) Palmer, M. J.; Wills, M. *Tetrahedron: Asymmetry* **1999**, *10*, 2045. (d) Noyori, R.; Yamakawa, M.; Hashiguchi, S. *J. Org. Chem.* **2001**, *66*, 7931. (e) Bäckvall, J. E. *J. Organomet. Chem.* **2002**, *652*, 105. (f) Carmona, D.; Lamata, M. P.; Oro, L. A. *Eur. J. Inorg. Chem.* **2002**, 2239. (g) Everaere, K.; Mortreux, A.; Carpentier, J. F. *Adv. Synth. Catal.* **2003**, *345*, 67.

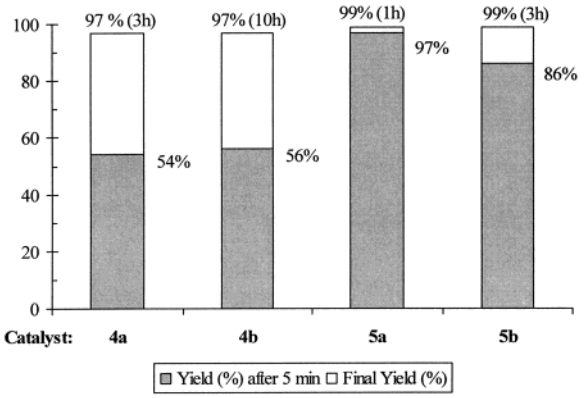
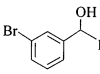
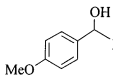
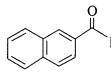
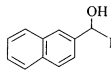


Figure 6. Catalytic transfer hydrogenation of acetophenone by dimers **4a**,**b** and **5a**,**b**. Conditions: reactions were carried out at 82 °C using 5 mmol of acetophenone (0.1 M in ^{i}PrOH). Ketone/Ru/NaOH ratio: 250/1/24. Yield of 1-phenylethanol determined by GC.

The most active complex, [{RuCl(μ-Cl)(CO)(dippf)}$_2$] (**5a**), has also been tested as catalyst in the hydride transfer hydrogenation of other ketones (see Table 1). Thus, it has shown to be very efficient in the reduction of dialkyl ketones (see entries 1−4), although the presence of bulky substituents in the ketone significantly reduces its catalytic activity (i.e., Me(Et)CO vs Me(^{t}Bu)CO; entry 3 vs 4). As observed for acetophenone, fast reductions have also been found for its *ortho*-, *meta*-, and *para*-substituted derivatives (see entries 5−11). Nevertheless, the catalytic performance of **5a** is reduced when an electron-donor group (OMe) is introduced at the *para* position of the aromatic ring (see entry 9).[18] Assuming that these catalytic transformations proceed through the well-established pathway in which the ketone coordinates on mononuclear hydride-ruthenium intermediates,[17,19] the observed effect seems to indicate that the hydride transfer from the metal to the coordinated ketone is the turnover-limiting step (rather than the ketone complexation) in the catalytic cycle.[20] The high catalytic efficiency of **5a** is also clearly shown in the transfer hydrogenation of α-tetralone (entry 12), 1-indanone (entry 13), and propiophenone (entry 14) since the reduction of such substrates is usually difficult.[17]

Table 1. Catalytic Transfer Hydrogenation of Ketones by Complex 5a[a]

entry	ketone	product	yield (%)[b]
1			99
2			99
3			99
4			10 (85)[c]
5			96 (99)[d]
6			99
7			99
8			97 (99)[d]
9			67 (94)[c]
10			99
11			96 (99)[d]
12			43 (89)[c]
13			77 (99)[c]
14			84 (99)[e]

[a] Conditions: reactions were carried out at 82 °C using 5 mmol of ketone (0.1 M in ^{i}PrOH). Ketone/Ru/NaOH ratio: 250/1/24. [b] Yield of the corresponding alcohol after 5 min. GC determined. [c] Yield after 24 h in parentheses. [d] Yield after 1 h in parentheses. [e] Yield after 3 h in parentheses.

Conclusions

A novel synthetic route to dimers [{RuX(μ-X)(CO)(P⌒P)}$_2$] (X = Cl, Br; P⌒P = 1,1′-bis(diphenylphosphino)ferrocene, 1,1′-bis(diisopropylphosphino)ferrocene), based on the HX-promoted releasing of the η^3-allyl units in complexes [RuX(η^3-2-C$_3$H$_4$R)(CO)(P⌒P)], has been discovered. These dimers provide synthetically valuable precursors not only to octahedral mononuclear ruthenium(II) derivatives but also to extremely active catalytic species for transfer hydrogenation reactions. In particular, [{RuCl(μ-Cl)(CO)(dippf)}$_2$] (**5a**) has proven to be a catalyst precursor comparable to the five- or six-coordinate ruthenium(II) species [RuCl$_2$(PPh$_3$)$_3$],[21] [RuCl$_2$(PPh$_3$)(P⌒N)] (P⌒N = iminophosphines, aminophosphines, oxazolinylferrocenylphosphine),[16a,c,22] [RuX(PPh$_3$)(P⌒C⌒P)] (X = Cl, CF$_3$SO$_3$; P⌒C⌒P = 2,6-C$_6$H$_3$(CH$_2$PPh$_2$)$_2$),[23] [RuCl$_2$(PPh$_3$)(P⌒N⌒O)] (P⌒N⌒O = 1-(diphenylphosphino)-2-ethoxy-1-(2-pyridyl)ethane),[24] [RuCl$_2$(PPh$_3$)(N⌒P⌒N)](N⌒P⌒N = bis(oxazolin-2-ylmethyl)phenylphosphine),[25] or [{RuCl(μ-Cl)(N⌒P⌒N)}$_2$] (N⌒P⌒N = bis(oxazolinyl)phenylphosphonite).[26] It is interesting to note that dimers **4a**,**b** and **5a**,**b** belong to

(18) Substrate reactivity is not attenuated when the methoxy substituent is introduced in *ortho* position (see entry 10). This rate enhancement can be attributed to chelate binding of *o*-methoxyacetophenone to the metal center. See for example: Evans, D. A.; Nelson, S. G.; Gagné, M. R.; Muci, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 9800.

(19) Attempts to isolate any catalytic intermediate by reacting **5a** with NaOH, in ^{i}PrOH and in the presence of acetophenone, have been unsuccessful.

(20) See for example: (a) Faller, J. W.; Lavoie, A. R. *Organometallics* **2001**, *20*, 5245. (b) Faller, J. W.; Lavoie, A. R. *Organometallics* **2002**, *21*, 3493.

(21) Chowdhury, R. L.; Bäckvall, J.-E. *J. Chem. Soc., Chem. Commun.* **1991**, 1063.

(22) Nishibayashi, Y.; Takei, I.; Uemura, S.; Hidai, M. *Organometallics* **1999**, *18*, 2291.

(23) Dani, P.; Karlen, T.; Gossage, R. A.; Gladiali, S.; van Koten, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 743.

(24) Yang, H.; Alvarez, M.; Lugan, N.; Mathieu, R. *J. Chem. Soc., Chem. Commun.* **1995**, 1721.

(25) Braunstein, P.; Fryzuk, M. D.; Naud, F.; Rettig, S. J. *J. Chem. Soc., Dalton Trans.* **1999**, 589.

the limited series of efficient catalysts containing ligands with no N-H functionalities. As it is well-known, the presence of an NH group is required to achieve efficient ketone transfer hydrogenations.[17b,d,f,g,27] The synthesis of related dimers containing optically active diphosphines to use in asymmetric catalysis is currently in progress.

Experimental Section

The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers and used without further purification with the exception of compounds [RuX(η^3-2-C_3H_4R)(CO)$_3$] (R = H, X = Cl (**1a**),[10a] Br (**1b**);[10a] R = Me, X = Cl (**1c**),[10a] Br (**1d**)[10b]) and [Fe(η^5-$C_5H_4PR_2$)$_2$] (R = Ph (dppf),[28] ^{i}Pr (dippf)[29]), which were prepared by following the methods reported in the literature. Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. The C, H, and N analyses were carried out with a Perkin-Elmer 2400 microanalyzer. NMR spectra were recorded on a Bruker DPX-300 instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P), or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standard. DEPT experiments have been carried out for all the compounds reported. Abbreviations used: s, singlet; br, broad singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet.

Synthesis of [RuX(η^3-C_3H_5)(CO)(P⌒P)] (P⌒P = dppf, X = Cl (2a), Br (2b); P⌒P = dippf, X = Cl (3a), Br (3b)). General Procedure. The corresponding diphosphine (1 mmol) was added at room temperature to a solution of [RuX(η^3-C_3H_5)(CO)$_3$] (**1a**,**b**) (1 mmol) in 30 mL of toluene. The reaction mixture was heated under reflux for 40 min (**3a**,**b**) or 3 h (**2a**,**b**) and then evaporated to dryness. The solid residue was dissolved in dichloromethane (ca. 3 mL) and the resulting solution transferred to an Al_2O_3 (neutral; activity grade I) chromatography column. Elution with methanol gave a yellow-orange band, from which complexes **2a**,**b** and **3a**,**b** were obtained by solvent removal. **2a**: yield 75% (0.570 g). Anal. Calcd for $FeRuC_{38}H_{33}P_2ClO$: C, 60.06; H, 4.38. Found: C, 59.85; H, 4.13. IR (KBr, cm^{-1}): ν 1926 (C≡O). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 34.31 (s) ppm. ^{1}H NMR (CD_2Cl_2): δ 2.09 (dd, 2H, $^3J_{HH}$ = 8.9 Hz, $^3J_{HP}$ = 5.0 Hz, CH$H_{(anti)}$), 3.69 (d, 2H, $^3J_{HH}$ = 5.8 Hz, CHH$_{(syn)}$), 4.20, 4.39, 4.55 and 5.40 (br, 2H each, C_5H_4), 4.91 (m, 1H, CH), 7.30−7.65 (m, 20H, Ph) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 58.80 (m, CH_2), 72.05, 72.34, 75.14, and 76.39 (br, CH of C_5H_4), 82.54 (d, $^1J_{CP}$ = 45.0 Hz, C of C_5H_4), 101.28 (s, CH), 127.25−138.55 (m, Ph), 202.98 (t, $^2J_{CP}$ = 14.3 Hz, CO) ppm. **2b**: yield 80% (0.644 g). Anal. Calcd for $FeRuC_{38}H_{33}P_2BrO$: C, 56.74; H, 4.13. Found: C, 56.41; H, 4.02. IR (KBr, cm^{-1}): ν 1926 (C≡O). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 34.55 (s) ppm. ^{1}H NMR (CD_2Cl_2): δ 2.07 (dd, 2H, $^3J_{HH}$ = 12.8 Hz, $^3J_{HP}$ = 5.1 Hz, CH$H_{(anti)}$), 3.69 (d, 2H, $^3J_{HH}$ = 7.4 Hz, CHH$_{(syn)}$), 4.18, 4.39, 4.55 and 5.39 (br, 2H each, C_5H_4), 4.90 (m, 1H, CH), 7.30−7.65 (m, 20H, Ph) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 58.75 (m, CH_2), 72.07, 72.35, 75.13, and 76.36 (br, CH of C_5H_4), 82.46 (d, $^1J_{CP}$ = 45.0 Hz, C of C_5H_4), 101.24 (s, CH), 127.25−138.50 (m, Ph), 202.99 (t, $^2J_{CP}$ = 14.3 Hz, CO) ppm. **3a**: yield 70% (0.437 g). Anal. Calcd for $FeRuC_{26}H_{41}P_2ClO$: C, 50.05; H, 6.62. Found: C, 50.12; H, 6.71. IR (KBr, cm^{-1}): ν 1913 (C≡O). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 41.03 (s) ppm. ^{1}H NMR (CD_2Cl_2): δ 1.31 (m, 24H, CH(CH_3)$_2$), 2.32 (dd, 2H, $^3J_{HH}$ = 12.2 Hz, $^3J_{HP}$ = 4.9 Hz, CH$H_{(anti)}$), 2.44 and 2.94 (m, 2H each, CH(CH$_3$)$_2$), 3.72 (d, 2H, $^3J_{HH}$ = 4.9 Hz, CHH$_{(syn)}$), 4.36 (br, 6H, C_5H_4), 4.69 (m, 1H, CH), 4.81 (br, 2H, C_5H_4) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 19.69, 20.25, 20.60, and 21.08 (s, CH(CH_3)$_2$), 30.21 and 30.52 (d, $^1J_{CP}$ = 19.3 Hz, CH(CH$_3$)$_2$), 55.62 (m, CH_2), 70.69, 71.69, 73.98, and 75.51 (br, CH of C_5H_4), 82.31 (d, $^1J_{CP}$ = 34.2 Hz, C of C_5H_4), 98.64 (s, CH), 204.45 (t, $^2J_{CP}$ = 15.3 Hz, CO) ppm. **3b**: yield 82% (0.548 g). Anal. Calcd for $FeRuC_{26}H_{41}P_2BrO$: C, 46.73; H, 6.18. Found: C, 46.51; H, 6.29. IR (KBr, cm^{-1}): ν 1911 (C≡O). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 40.74 (s) ppm. ^{1}H NMR (CD_2Cl_2): δ 1.32 (m, 24H, CH(CH_3)$_2$), 2.32 (dd, 2H, $^3J_{HH}$ = 12.5 Hz, $^3J_{HP}$ = 5.3 Hz, CH$H_{(anti)}$), 2.44 and 2.94 (m, 2H each, CH(CH$_3$)$_2$), 3.71 (dd, 2H, $^3J_{HH}$ = 5.3 Hz, $^3J_{HP}$ = 2.0 Hz, CHH$_{(syn)}$), 4.36 (br, 6H, C_5H_4), 4.69 (m, 1H, CH), 4.80 (br, 2H, C_5H_4) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 19.69, 20.25, 20.61, and 21.08 (s, CH(CH_3)$_2$), 30.21 and 30.51 (d, $^1J_{CP}$ = 19.5 Hz, CH(CH$_3$)$_2$), 55.62 (m, CH_2), 70.70, 71.09, 73.99, and 75.51 (br, CH of C_5H_4), 82.30 (d, $^1J_{CP}$ = 34.6 Hz, C of C_5H_4), 98.63 (s, CH), 204.45 (t, $^2J_{CP}$ = 15.3 Hz, CO) ppm.

Synthesis of [RuX(η^3-2-C_3H_4Me)(CO)(P⌒P)] (P⌒P = dppf, X = Cl (2c), Br (2d); P⌒P = dippf, X = Cl (3c), Br (3d)). General Procedure. The corresponding diphosphine (1 mmol) was added at room temperature to a solution of [RuX(η^3-2-C_3H_4Me)(CO)$_3$] (**1c**,**d**) (1 mmol) in 30 mL of tetrahydrofuran. The reaction mixture was heated under reflux for 2 h (**3c**,**d**) or 7 h (**2c**,**d**) and then evaporated to dryness. The solid residue was dissolved in dichloromethane (ca. 3 mL) and the resulting solution transferred to an Al_2O_3 (neutral; activity grade I) chromatography column. Elution with methanol gave a yellow-orange band, from which complexes **2c**,**d** and **3c**,**d** were obtained by solvent removal. **2c**: yield 75% (0.581 g). Anal. Calcd for $FeRuC_{39}H_{35}P_2ClO$: C, 60.52; H, 4.56. Found: C, 60.37; H, 4.43. IR (KBr, cm^{-1}) ν 1921 (C≡O). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 35.45 (s) ppm. ^{1}H NMR (CD_2Cl_2): δ 2.06 (s, 3H, CH_3), 2.11 (d, 2H, $^3J_{HP}$ = 5.1 Hz, CH$H_{(anti)}$), 3.57 (s, 2H, CHH$_{(syn)}$), 4.18, 4.39, 4.55 and 5.41 (br, 2H each, C_5H_4), 7.25−7.65 (m, 20H, Ph) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 26.19 (s, CH_3), 59.52 (m, CH_2), 72.06, 72.28, 75.08, and 76.32 (br, CH of C_5H_4), 82.51 (d, $^1J_{CP}$ = 45.1 Hz, C of C_5H_4), 118.94 (s, C), 127.15−138.40 (m, Ph), 204.55 (t, $^2J_{CP}$ = 15.0 Hz, CO) ppm. **2d**: yield 76% (0.622 g). Anal. Calcd for $FeRuC_{39}H_{35}P_2BrO$: C, 57.23; H, 4.31. Found: C, 57.42; H, 4.70. IR (KBr, cm^{-1}): ν 1920 (C≡O). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 35.27 (s) ppm. ^{1}H NMR (CD_2Cl_2): δ 2.12 (s, 3H, CH_3), 2.18 (d, 2H, $^3J_{HP}$ = 5.6 Hz, CH$H_{(anti)}$), 3.63 (s, 2H, CHH$_{(syn)}$), 4.24, 4.45, 4.61, and 5.47 (br, 2H each, C_5H_4), 7.30−7.70 (m, 20H, Ph) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 25.89 (s, CH_3), 59.23 (m, CH_2), 71.76, 71.99, 74.77, and 76.02 (br, CH of C_5H_4), 82.23 (d, $^1J_{CP}$ = 43.6 Hz, C of C_5H_4), 118.65 (s, C), 127.00−138.15 (m, Ph), 204.26 (t, $^2J_{CP}$ = 14.2 Hz, CO) ppm. **3c**: yield 69% (0.440 g). Anal. Calcd for $FeRuC_{27}H_{43}P_2ClO$: C, 50.83; H, 6.79. Found: C, 50.91; H, 6.87. IR (KBr, cm^{-1}): ν 1908 (C≡O). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 41.08 (s) ppm. ^{1}H NMR (CD_2Cl_2): δ 1.38 (m, 24H, CH(CH_3)$_2$), 2.05 (s, 3H, CH_3), 2.45 (m, 4H, CH$H_{(anti)}$ and CH(CH$_3$)$_2$), 3.04 (m, 2H, CH(CH$_3$)$_2$), 3.62 (s, 2H, CHH$_{(syn)}$), 4.36, 4.41, 4.45, and 4.83 (br, 2H each, C_5H_4) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 19.41, 20.12, 20.26, and 20.88 (s, CH(CH_3)$_2$), 25.45 (s, CH_3), 29.73 and 29.75 (d, $^1J_{CP}$ = 21.2 Hz, CH(CH$_3$)$_2$), 56.65 (m, CH_2), 70.43, 70.72, 73.38, and 75.26 (br, CH of C_5H_4), 82.27 (d, $^1J_{CP}$ = 34.1 Hz, C of C_5H_4), 115.06 (s, C), 205.78 (t, $^2J_{CP}$ = 16.1 Hz, CO) ppm. **3d**: yield 77% (0.525 g). Anal. Calcd for $FeRuC_{27}H_{43}P_2BrO$: C, 47.52; H, 6.35. Found: C, 47.21; H, 6.14. IR (KBr, cm^{-1}): ν 1907 (C≡O). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 41.04 (s) ppm. ^{1}H NMR (CD_2Cl_2): δ 1.36 (m, 24H, CH(CH_3)$_2$), 2.05 (s, 3H, CH_3), 2.47 (m, 4H, CH$H_{(anti)}$ and CH(CH$_3$)$_2$), 3.03 (m, 2H, CH(CH$_3$)$_2$), 3.61 (s, 2H, CHH$_{(syn)}$), 4.41, 4.45, 4.51, and 4.82 (br, 2H each, C_5H_4) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 19.40, 20.13, 20.25, and 20.88 (s, CH(CH_3)$_2$), 25.47 (s, CH_3), 29.72 and 29.74 (d, $^1J_{CP}$ = 21.8 Hz, CH(CH$_3$)$_2$), 56.64 (m, CH_2), 70.44,

(26) Braunstein, P.; Naud, F.; Pfaltz, A.; Rettig, S. J. *Organometallics* **2000**, *19*, 2676.
(27) Noyori, R.; Ohkuma, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 40.
(28) Bishop, J. J.; Davison, A.; Katcher, M. L.; Lichtenberg, D. W.; Merrill, R. E.; Smart, J. C. *J. Organomet. Chem.* **1971**, *27*, 241.
(29) Butler, I. R.; Cullen, W. R.; Kim, T. J. *Synth. React. Inorg. Met.-Org. Chem.* **1985**, *15*, 109.

70.72, 73.38, and 75.26 (br, CH of C_5H_4), 82.25 (d, $^1J_{CP}$ = 34.1 Hz, C of C_5H_4), 115.04 (s, C), 205.78 (t, $^2J_{CP}$ = 16.1 Hz, CO) ppm.

Synthesis of [{RuX(μ-X)(CO)(P⌒P)}$_2$] (P⌒P = dppf, X = Cl (4a), Br (4b); P⌒P = dippf, X = Cl (5a), Br (5b)). General Procedure. A solution of complexes [RuX(η^3-C_3H_5)(CO)(P⌒P)] (**2a**,**b** and **3a**,**b**) or [RuX(η^3-2-C_3H_4Me)(CO)(P⌒P)] (**2c**,**d** and **3c**,**d**) (1 mmol) in 50 mL of dichloromethane was treated at room temperature with the appropriate HX acid (1.5 mL of a 1.0 M solution in diethyl ether;[30] 1.5 mmol). The reaction mixture was stirred at room temperature for 30 min and then evaporated to dryness. The resulting yellow-orange solid residue was washed with diethyl ether (3 × 50 mL) and vacuum-dried. **4a**: yield 88% (0.664 g). Anal. Calcd for $Fe_2Ru_2C_{70}H_{56}Cl_4P_4O_2$: C, 55.73; H, 3.74. Found: C, 55.47; H, 3.51. IR (KBr, cm^{-1}): ν 1987 (C≡O). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 46.39 and 53.69 (d, $^2J_{PP}$ = 24.9 Hz) ppm. ^1H NMR (CD_2Cl_2): δ 4.30−4.55 (m, 16H, C_5H_4), 7.20−7.90 (m, 40H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 72.70, 73.15, 74.76, and 75.40 (d, $^2J_{CP}$ = 6.2 Hz, CH of C_5H_4), 76.10, 76.21, and 77.05 (d, $^3J_{CP}$ = 8.8 Hz, CH of C_5H_4), 77.67 and 79.01 (d, $^1J_{CP}$ = 55.9 Hz, C of C_5H_4), 126.90−135.60 (m, Ph), 200.07 (dd, $^2J_{CP}$ = 16.2 and 16.2 Hz, CO) ppm. **4b**: yield 86% (0.725 g). Anal. Calcd for $Fe_2Ru_2C_{70}H_{56}Br_4P_4O_2$: C, 49.85; H, 3.35. Found: C, 49.62; H, 3.21. IR (KBr, cm^{-1}): ν 1978 (C≡O). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 46.96 and 52.72 (d, $^2J_{PP}$ = 21.1 Hz) ppm. ^1H NMR (CD_2Cl_2): δ 4.05−4.80 (m, 16H, C_5H_4), 7.20−7.95 (m, 40H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 73.11, 73.72, 74.58, and 76.31 (d, $^2J_{CP}$ = 6.6 Hz, CH of C_5H_4), 75.96, 76.75, and 77.47 (d, $^3J_{CP}$ = 8.2 Hz, CH of C_5H_4), 78.45 and 79.49 (d, $^1J_{CP}$ = 54.8 Hz, C of C_5H_4), 127.35−136.40 (m, Ph), 201.09 (dd, $^2J_{CP}$ = 15.4 and 15.4 Hz, CO) ppm. **5a**: yield 87% (0.538 g). Anal. Calcd for $Fe_2Ru_2C_{46}H_{72}Cl_4P_4O_2$: C, 44.68; H, 5.87. Found: C, 44.51; H, 5.78. IR (KBr, cm^{-1}): ν 1959 (C≡O). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 63.40 and 64.90 (d, $^2J_{PP}$ = 18.1 Hz) ppm. ^1H NMR (CD_2Cl_2): δ 0.75−1.85 (m, 48H, CH(CH_3)$_2$), 2.56, 2.65, 2.92 and 3.46 (m, 2H each, CH(CH$_3$)$_2$), 4.35−4.95 (m, 16H, C_5H_4) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 17.39, 18.88, 19.34, 20.03, 20.33, 20.79, 21.65, and 22.19 (s, CH(*C*H$_3$)$_2$), 28.49 (d, $^1J_{CP}$ = 25.6 Hz, *C*H(CH$_3$)$_2$), 28.51 (d, $^1J_{CP}$ = 29.4 Hz, *C*H(CH$_3$)$_2$), 29.10 (d, $^1J_{CP}$ = 28.4 Hz, *C*H(CH$_3$)$_2$), 29.71 (d, $^1J_{CP}$ = 21.8 Hz, *C*H(CH$_3$)$_2$), 70.38, 70.63, 71.24, and 73.60 (d, $^2J_{CP}$ = 5.8 Hz, CH of C_5H_4), 70.83, 71.76, 74.91, and 75.35 (d, $^3J_{CP}$ = 8.5 Hz, CH of C_5H_4), 79.14 and 79.74 (d, $^1J_{CP}$ = 48.3 Hz, C of C_5H_4), 201.07 (dd, $^2J_{CP}$ = 17.1 and 17.1 Hz, CO) ppm. **5b**: yield 83% (0.587 g). Anal. Calcd for $Fe_2Ru_2C_{46}H_{72}Br_4P_4O_2$: C, 39.06; H, 5.13. Found: C, 39.14; H, 5.02. IR (KBr, cm^{-1}): ν 1965 (C≡O). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 62.69 and 63.68 (d, $^2J_{PP}$ = 16.6 Hz) ppm. ^1H NMR (CD_2Cl_2): δ 0.75−1.85 (m, 48H, CH(CH_3)$_2$), 2.68 (m, 4H, CH(CH$_3$)$_2$), 2.93 and 3.35 (m, 2H each, CH(CH$_3$)$_2$), 4.35−4.90 (m, 16H, C_5H_4) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 18.67, 18.74, 19.88, 19.96, 20.88, 21.55, 21.96, and 22.47 (s, CH(*C*H$_3$)$_2$), 29.73 (d, $^1J_{CP}$ = 26.6 Hz, *C*H(CH$_3$)$_2$), 30.11 (d, $^1J_{CP}$ = 29.7 Hz, *C*H(CH$_3$)$_2$), 30.49 (d, $^1J_{CP}$ = 28.7 Hz, *C*H(CH$_3$)$_2$), 31.35 (d, $^1J_{CP}$ = 21.5 Hz, *C*H(CH$_3$)$_2$), 71.91, 72.10, and 74.63 (d, $^2J_{CP}$ = 6.1 Hz, CH of C_5H_4), 72.63, 76.49, and 76.51 (d, $^3J_{CP}$ = 9.2 Hz, CH of C_5H_4), 79.76 and 79.81 (d, $^1J_{CP}$ = 48.1 Hz, C of C_5H_4), 202.10 (dd, $^2J_{CP}$ = 16.4 and 16.4 Hz, CO) ppm.

Synthesis of *cis,cis,cis*-[RuCl$_2$(CO)$_2$(dppf)] (6a). Carbon monoxide was bubbled through a solution of [{RuCl(μ-Cl)(CO)(dppf)}$_2$] (**4a**) (0.755 g, 0.5 mmol) in 70 mL of tetrahydrofuran at 65 °C for 5 h. After removing the solvent under reduced pressure, diethyl ether (50 mL) was added to the residue, yielding the precipitation of a yellow solid, which was filtered off, washed with diethyl ether (2 × 50 mL), and vacuum-dried. Yield: 89% (0.696 g). Anal. Calcd for $FeRuC_{36}H_{28}Cl_2O_2P_2$: C, 55.27; H, 3.61. Found: C, 55.21; H, 3.54. IR (KBr, cm^{-1}): ν 2009 and 2070 (C≡O). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 15.34 and 38.78 (d, $^2J_{PP}$ = 25.3 Hz) ppm. ^1H NMR (CD_2Cl_2): δ 4.23, 4.30, 4.36, and 4.66 (br, 2H each, C_5H_4), 7.40−8.25 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 71.70, 72.27, 73.09, and 77.33 (d, $^2J_{CP}$ = 5.9 Hz, CH of C_5H_4), 74.48, 75.82, 77.47, and 78.05 (d, $^3J_{CP}$ = 8.9 Hz, CH of C_5H_4), 76.79 and 77.57 (d, $^1J_{CP}$ = 53.8 Hz, C of C_5H_4), 127.55−136.90 (m, Ph), 189.15 (dd, $^2J_{CP}$ = 123.4 and 9.7 Hz, CO), 195.21 (dd, $^2J_{CP}$ = 13.8 and 11.8 Hz, CO) ppm.

Synthesis of *cis,cis*-[RuCl$_2$(CO)(L)(dppf)] (L = BzNC (6b), Py (6c), PhNH$_2$ (6d)). General Procedure. A solution of complex [{RuCl(μ-Cl)(CO)(dppf)}$_2$] (**4a**) (0.755 g, 0.5 mmol) in 30 mL of dichloromethane was treated, at room temperature, with the appropriate ligand (5 mmol) for 2 h. After removing the solvent under reduced pressure, hexane (50 mL) was added to the residue, yielding the precipitation of a yellow solid, which was filtered off, washed with hexane (2 × 50 mL), and vacuum-dried. **6b**: yield 85% (0.741 g). Anal. Calcd for $FeRuC_{43}H_{35}Cl_2P_2NO$: C, 59.26; H, 4.05; N, 1.61. Found: C, 59.15; H, 3.98; N, 1.60. IR (KBr, cm^{-1}): ν 1977 (C≡O), 2221 (C≡N). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 17.35 and 42.83 (d, $^2J_{PP}$ = 25.7 Hz) ppm. ^1H NMR (CD_2Cl_2): δ 4.18, 4.25, 4.29, 4.41, and 4.55 (br, 2H each, C_5H_4 and NCH_2), 7.20−8.30 (m, 25H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 48.09 (s, NCH_2), 71.19, 71.72, 72.04, and 76.70 (d, $^2J_{CP}$ = 5.1 Hz, CH of C_5H_4), 74.44, 75.01, 77.17, and 78.16 (d, $^3J_{CP}$ = 8.7 Hz, CH of C_5H_4), 79.31 and 79.70 (d, $^1J_{CP}$ = 53.0 Hz, C of C_5H_4), 126.95−137.00 (m, Ph and C≡N), 198.23 (dd, $^2J_{CP}$ = 12.3 and 12.3 Hz, CO) ppm. **6c**: yield 95% (0.792 g). Anal. Calcd for $FeRuC_{40}H_{33}Cl_2P_2NO$: C, 57.64; H, 3.99; N, 1.68. Found: C, 57.47; H, 3.71; N, 1.65. IR (KBr, cm^{-1}): ν 1961 (C≡O). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 35.54 and 44.52 (d, $^2J_{PP}$ = 26.8 Hz) ppm. ^1H NMR (CD_2Cl_2): δ 4.22, 4.30, 4.61, and 4.69 (br, 2H each, C_5H_4), 6.90−8.80 (m, 25H, Ph and C_5H_5N) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 71.14, 71.22, 71.81, and 76.72 (d, $^2J_{CP}$ = 6.1 Hz, CH of C_5H_4), 74.37, 75.10, 78.19, and 79.25 (d, $^3J_{CP}$ = 8.6 Hz, CH of C_5H_4), 78.73 and 83.70 (d, $^1J_{CP}$ = 52.9 Hz, C of C_5H_4), 124.30−138.45 (m, Ph and C_5H_5N), 154.35 (s, C_5H_5N), 201.54 (dd, $^2J_{CP}$ = 15.3 and 15.3 Hz, CO) ppm. **6d**: yield 87% (0.737 g). Anal. Calcd for $FeRuC_{41}H_{35}Cl_2P_2NO$: C, 58.11; H, 4.16; N, 1.65. Found: C, 58.27; H, 4.28; N, 1.63. IR (KBr, cm^{-1}): ν 1944 (C≡O), 3343 (N−H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 41.32 and 47.11 (d, $^2J_{PP}$ = 28.9 Hz) ppm. ^1H NMR (CD_2Cl_2): δ 4.29 (br, 8H, C_5H_4), 6.71 (br, 2H, NH_2), 7.10−8.20 (m, 25H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 71.39, 72.11, 74.07, and 76.74 (d, $^2J_{CP}$ = 5.4 Hz, CH of C_5H_4), 74.11, 75.87, 77.68, and 78.12 (d, $^3J_{CP}$ = 8.6 Hz, CH of C_5H_4), 82.59 and 82.85 (d, $^1J_{CP}$ = 51.7 Hz, C of C_5H_4), 127.90−135.65 (m, Ph), 201.76 (dd, $^2J_{CP}$ = 15.1 and 15.1 Hz, CO) ppm.

General Procedure for Catalytic Transfer Hydrogenation of Ketones. Under inert atmosphere, the ketone (5 mmol), the ruthenium catalyst precursor (0.01 mmol, 0.4 mol % of Ru), and 45 mL of propan-2-ol were introduced into a Schlenk tube fitted with a condenser and heated at 82 °C for 15 min. Then NaOH was added (5 mL of a 0.096 M solution in propan-2-ol, 9.6 mol %), and the reaction monitored by gas chromatography. The corresponding alcohol and acetone were the only products detected in all cases. The identity of the alcohols was assessed by comparison with commercially available (Aldrich Chemical Co. or Acros Organics) pure samples.

X-ray Crystal Structure Determination of Complexes 2a, 4a′, and 6c. Crystals suitable for X-ray diffraction analysis were obtained, in all the cases, by slow diffusion of pentane in a saturated solution of the complex in dichloromethane. The most relevant crystal and refinement data are collected in Table 2. The crystal of complex **2a** possessed monoclinic symmetry with systematic absences corresponding to either space group *C*2/*c* or its noncentrosymmetric equivalent, *Cc*. Subsequent solution and refinement confirmed the centrosym-

(30) Anhydrous HCl (1.0 M solution in diethyl ether) is commercially available from Aldrich Chemical Co. The 1.0 M solution of HBr in diethyl ether was prepared as follows: $HBr_{(g)}$ (prepared in situ by slow addition of 54 mL of H_2SO_4 (95%, 17.83 M; 0.963 mol) to 16 g of KBr (0.134 mol)) was bubbled through 80 mL of diethyl ether at rt. The resulting solution (ca. 1.5 M) was diluted with 40 mL of diethyl ether.

Table 2. Crystallographic Data for Complexes 2a, 4a′, and 6c

	2a	4a′	6c
chemical formula	$C_{38}H_{33}P_2ClOFeRu$	$C_{70}H_{56}Cl_4P_4O_2Fe_2Ru_2 \cdot 4CH_2Cl_2$	$C_{40}H_{33}Cl_2P_2NOFeRu \cdot CH_2Cl_2$
fw	759.95	1848.37	918.36
T (°C)	−153(2)	−123(2)	−153(2)
wavelength (Å)	1.54180	1.54180	1.54180
space group	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	13.626(1)	12.3336(7)	11.1871(5)
b, Å	14.878(1)	12.7635(7)	11.2331(7)
c, Å	15.694(1)	13.2492(8)	16.938(1)
α, deg	90	90.154(4)	83.097(4)
β, deg	91.191(6)	103.397(3)	74.654(3)
γ, deg	90	113.446(3)	65.867(3)
Z	4	1	2
V, Å^3	3180.9(5)	1850.9(2)	1873.0(2)
ρ_{calcd}, g cm^{-3}	1.587	1.658	1.628
μ, cm^{-1}	9.462	11.492	10.081
weight function (a, b)	0.0600, 7.2573	0.0860, 1.1692	0.1034, 1.5616
R1[a] [$I > 2\sigma(I)$]	0.0554	0.0495	0.0517
wR2[a] [$I > 2\sigma(I)$]	0.1221	0.1317	0.1414
R1 (all data)	0.0744	0.0552	0.0653
wR2 (all data)	0.1319	0.1376	0.1527

[a] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

metric choice $C2/c$. The crystals of compounds **4a′** and **6c** possessed triclinic symmetry, space group $P\bar{1}$ (ascertained from structure determination). Data collections were performed on a Nonius Kappa CCD single-crystal diffractometer using Cu Kα radiation with a crystal−detector distance fixed at 29 mm, using the oscillation method, ϕ- and ω-scans with 2° oscillation, and 50 s (**2a** and **6c**) or 40 s (**4a′**) exposure time per frame. Data collection strategy was calculated with the program Collect.[31] Data reduction and cell refinement were performed with the programs HKL Denzo and Scalepack.[32] Absorption correction was applied by means of XABS2[33] (**2a** and **6c**) or SORTAV[34] (**4a′**).

All the structures were solved by Patterson interpretation and phase expansion using DIRDIF.[35] Isotropic least-squares refinement on F^2 using SHELXL97 was performed.[36] During the final stages of the refinements, all the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined (except the mutually *trans* Cl and CO ligands in **2a** and **6c**, and C1 and C1′ atoms of the allyl ligand in **2a**; these highly disordered groups were found and isotropically refined). The coordinates of H atoms in **2a** were found from difference Fourier maps and included in a refinement with isotropic parameters (with the exception of those connected to C1, C1′, and C2, which were geometrically located and their coordinates were refined riding on their parent atoms). For **4a′** and **6c**, the H atoms were geometrically located and their coordinates were refined riding on their parent atoms. The function minimized was $[\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ (a and b values are shown in Table 2) with $\sigma^2(F_o^2)$ from counting statistics and $P = (\max(F_o^2, 0) + 2F_c^2)/3$. Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[37] Geometrical calculations were made with PARST.[38] The crystallographic plots were made with PLATON.[39]

Acknowledgment. This work was supported by the Ministerio de Ciencia y Tecnología (MCyT) of Spain (Projects BQU2000-0227, BQU2000-0219, and CAJAL-01-03) and the Gobierno del Principado de Asturias (Project PR-01-GE-4). S.E.G.-G. thanks the MCyT for the award of a Ph.D. grant.

Supporting Information Available: X-ray crystallographic files, in CIF and PDF format, for the structure determinations of complexes **2a**, **4a′**, and **6c**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030530E

(31) *Collect*; Nonius BV: Delft, The Netherlands, 1997−2000.
(32) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307.
(33) Parkin, S.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53.
(34) Blessing, R. H. *Acta Crystallogr. Sect. A* **1995**, *51*, 33.
(35) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; García-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF Program System*; Technical Report of the Crystallographic Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1999.
(36) Sheldrick, G. M. *SHELXL97: Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.
(37) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV (Present distributor: Kluwer Academic Publishers: Dordrecht, The Netherlands).
(38) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95.
(39) Spek, A. L. *PLATON: A Multipurpose Crystallographic Tool*; University of Utrecht: The Netherlands, 2000.