Efficient Transfer Hydrogenation of Ketones Catalyzed by the Bis(isocyanide)−Ruthenium(II) Complexes *trans,cis,cis*-[$RuX_2(CNR)_2$(dppf)] (X = Cl, Br; dppf = 1,1′-Bis(diphenylphosphino)ferrocene): Isolation of Active Mono- and Dihydride Intermediates†

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

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The bis(isocyanide)−ruthenium(II) complexes *trans,cis,cis*-[$RuX_2(CNR)_2$(dppf)] (X = Cl, R = CH_2Ph (**2a**), Cy (**2b**), ^{t}Bu (**2c**), 2,6-$C_6H_3Me_2$ (**2d**), (*S*)-(−)-C(H)MePh (**2e**); X = Br, R = CH_2Ph (**3a**), Cy (**3b**), ^{t}Bu (**3c**), 2,6-$C_6H_3Me_2$ (**3d**), (*S*)-(−)-C(H)MePh (**3e**)) have been prepared by reaction of the bis(allyl)−ruthenium(II) derivative [Ru(η^3-2-$C_3H_4Me)_2$(dppf)] (**1**) with the appropriate isocyanide ligand, in CH_2Cl_2 at room temperature and in the presence of the corresponding hydrogen halide HX. The structure of the compound *trans,cis,cis*-[$RuCl_2$(CN-2,6-$C_6H_3Me_2)_2$(dppf)] (**2d**) has been confirmed by X-ray crystallography. The catalytic activity of complexes **2a**−**e** and **3a**−**e** in the transfer hydrogenation of acetophenone by propan-2-ol has been studied, and the most active complex, *trans,cis,cis*-[$RuCl_2(CNCH_2Ph)_2$(dppf)] (**2a**), has been also tested as a catalyst in the transfer hydrogenation of a large variety of ketones. The hydride derivatives *cis,cis*-[RuHCl(CN-2,6-$C_6H_3Me_2)_2$(dppf)] (**4**) and *cis,cis,cis*-[RuH_2(CN-2,6-$C_6H_3Me_2)_2$(dppf)] (**5**) have been isolated and characterized. Although both hydride complexes catalyze the transfer hydrogenation of acetophenone in the absence of base, the reactions proceed ca. 5 times faster with **5** than with **4**, pointing out that the real active species are dihydride−ruthenium complexes.

Introduction

Transfer hydrogenation (TH) of ketones by ruthenium(II) catalysts is currently one of the most appealing synthetic routes to alcohols and constitutes a good alternative to the widely used catalytic hydrogenation.[1] Despite the fact that the latter route has a much greater potential for industrial applications,[2] there has been a continuous interest in catalytic TH, since alcohols can be obtained in high yields, under relatively mild conditions, avoiding the use of H_2 gas.[1]

To date, a multitude of ruthenium complexes have proven to be efficient catalyst precursors in the TH of ketones, and there is both experimental and theoretical evidence regarding the role of ruthenium hydrides as the active catalytic species.[1] In general, they are rarely detected but can be easily generated in situ in the presence of a base as promoter, transferring the hydride group from the α-hydrogen of a secondary alcohol, i.e. ^{i}PrOH/NaOH.[1] In fact, only a few isolated ruthenium hydride complexes have been used as catalysts (the presence of a base is not required in this case). These include the following examples (see Chart 1): [$N(PPh_3)_2$][$Ru_4H_3(CO)_{12}$] (**A**; only one isomer is represented),[3] [RuH(H_2)($P(CH_2CH_2PPh_2)_3$)][BPh_4] (**B**),[4] [RuH(MeCONH)($PCy_3)_2$(CO)(^{i}PrOH)] (**C**),[5] [$RuH_2(PPh_3)_4$] (**D**),[6] [K][RuH_3(CO)($Cy_2P(CH_2)_4PCy_2$)]·KBH^sBu_3 (**E**),[7] [RuH-

* To whom correspondence should be addressed. E-mail: vcm@uniovi.es (V.C.), jgh@uniovi.es (J.G.).

† This work is respectfully dedicated to the memory of Dr. Juan Carlos Del Amo, who was a victim of the March 11th tragedy in Madrid.

(1) For general reviews and personal accounts 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) Ohkuma, T.; Noyori, R. In *Comprehensive Asymmetric Catalysis*; Jacobs, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: Berlin, 1999; Vol. 1, Chapter 6.1. (e) Noyori, R.; Yamakawa, M.; Hashiguchi, S. *J. Org. Chem.* **2001**, *66*, 7931. (f) Bäckvall, J. E. *J. Organomet. Chem.* **2002**, *652*, 105. (g) Carmona, D.; Lamata, M. P.; Oro, L. A. *Eur. J. Inorg. Chem.* **2002**, 2239. (h) Noyori, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2008. (i) Everaere, K.; Mortreux, A.; Carpentier, J. F. *Adv. Synth. Catal.* **2003**, *345*, 67. (j) Clapham, S. E.; Hadzovic, A.; Morris, R. H. *Coord. Chem. Rev.*, in press.

(2) In classical hydrogenations very large substrate to catalyst ratios can be reached, allowing their application to large-scale preparations (the highest ratio is about 2×10^6; more than 10^3−10^4 times higher than in TH). See for example: Doucet, H.; Ohkuma, T.; Murata, K.; Yokozawa, T.; Kozawa, M.; Katayama, E.; England, A. F.; Ikariya, T.; Noyori, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1703.

(3) Bhaduri, S.; Sharma, K.; Mukesh, D. *J. Chem. Soc., Dalton Trans.* **1993**, 1191.

(4) Bianchini, C.; Farnetti, E.; Graziani, M.; Peruzzini, M.; Polo, A. *Organometallics* **1993**, *12*, 3753.

(5) Yi, C. S.; He, Z.; Guzei, I. A. *Organometallics* **2001**, *20*, 3641.

(6) (a) Mizushima, E.; Yamaguchi, M.; Yamagishi, T. *Chem. Lett.* **1997**, 237. (b) Aranyos, A.; Csjernyik, G.; Szabó, K. J.; Bäckvall, J. E. *Chem. Commun.* **1999**, 351.

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

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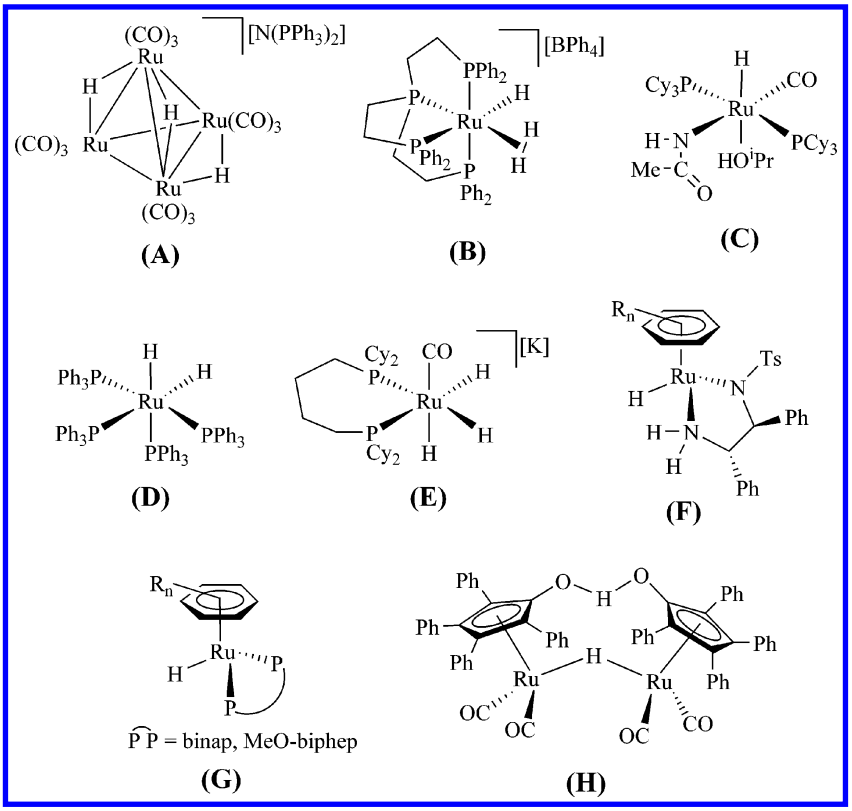
Chart 1



(aminoamido)(η^6-arene)] (**F**),[1e] [RuH(η^6-arene)(P⁀P)] (**G**; P⁀P = binap, MeO-biphep),[8] and the Shvo catalyst (**H**).[9]

In the context of our studies on ruthenium-catalyzed TH of ketones by propan-2-ol,[10] we have recently reported that the carbonyl−halide dimers [{RuX(μ-X)(CO)(P⁀P)}$_2$] (X = Cl, Br; P⁀P = 1,1′-bis(diphenylphosphino)ferrocene (dppf), 1,1′-bis(diisopropylphosphino)ferrocene (dippf)) (**I**; see Figure 1) are valuable precursors of extremely active catalytic species.[11,12] The effectiveness of these dimers is probably associated with their ability to generate the transient five-coordinate mononuclear species [RuX$_2$(CO)(P⁀P)] in solution, via halide-bridge cleavage, which readily provides the required vacant site for the ketone coordination.[13] Nevertheless, no detailed mechanism was proposed, since all attempts to isolate or detect any catalytic intermediate were unsuccessful.

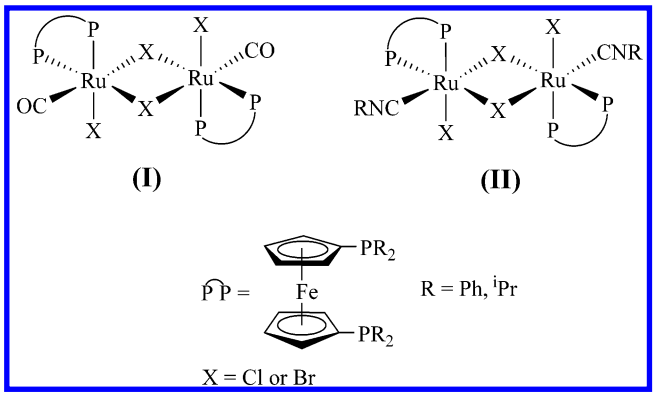


Figure 1. Structures of the dimers [{RuX(μ-X)(CO)(P⁀P)}$_2$] (**I**) and [{RuX(μ-X)(CNR)(P⁀P)}$_2$] (**II**).

To gain insight into the outcome of these catalytic processes, we believed it of interest to prepare the related isocyanide dimers [{RuX(μ-X)(CNR)(P⁀P)}$_2$] (**II**; see Figure 1), since an appropriate modulation of the electronic and/or steric properties of the isocyanide ligands could favor the isolation of intermediate species.[14] Since compounds **I** are readily obtained via HX-promoted releasing of η^3-allyl units in the complexes [RuX(η^3-2-C$_3$H$_4$R)(CO)(P⁀P)] (R = H, Me),[11,15] we devised the synthesis of the analogous isocyanide dimers **II** by the treatment of the known bis(allyl)−ruthenium(II) complex [Ru(η^3-2-C$_3$H$_4$Me)$_2$(dppf)] (**1**)[16] with HX in the presence of a stoichiometric amount of CNR ligands.

(8) Geldbach, T. J.; Pregosin, P. S. *Helv. Chim. Acta* **2002**, *85*, 3937.
(9) Pàmies, O.; Bäckvall, J. E. *Chem. Eur. J.* **2001**, *7*, 5052 and references therein.
(10) (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* **2003**, 3240. (f) Crochet, P.; Fernández-Zumel, M. A.; Beauquis, C.; Gimeno, J. *Inorg. Chim. Acta* **2003**, *356*, 114.
(11) Cadierno, V.; Crochet, P.; Díez, J.; García-Garrido, S. E.; Gimeno, J.; García-Granda, S. *Organometallics* **2003**, *22*, 5226.
(12) These examples belong to the limited series of catalysts bearing ligands with no N−H functionalities. It is well-known that the presence of an NH group in the catalyst is usually required to achieve efficient ketone transfer hydrogenations. See ref 1 and: (a) Noyori, R.; Ohkuma, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 40 and references therein. (b) Rautenstrauch, V.; Hoang-Cong, X.; Churlaud, R.; Abdur-Rashid, K.; Morris, R. H. *Chem. Eur. J.* **2003**, *9*, 4954 and references therein.
(13) Although several 16-electron species [RuX$_2$(CO)(PR$_3$)$_2$] (PR$_3$ = monodentate phosphine) are known,[11] only the involvement of [RuCl$_2$(CO)(P^{i}Pr$_3$)$_2$] in catalysis (hydrosilylation of alkynes) has been reported: (a) Katayama, H.; Tanaguchi, K.; Kobayashi, M.; Sagawa, T.; Minami, T.; Ozawa, F. *J. Organomet. Chem.* **2002**, *645*, 192. (b) Katayama, H.; Nagao, M.; Moriguchi, R.; Ozawa, F. *J. Organomet. Chem.* **2003**, *676*, 49.

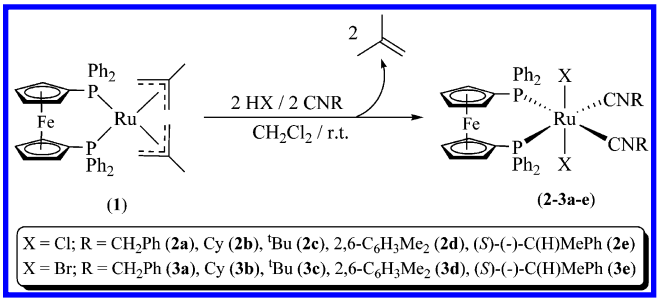
In this respect, it should be mentioned that Genêt and co-workers have reported that the treatment of the related bis(allyl) compounds [Ru(η^3-2-C_3H_4Me)$_2$(P⌒P)] (P⌒P = optically active diphosphine) with HX (X = Cl, Br) in acetone yields the halide-bridged dimeric species [{RuX(μ-X)(acetone)(P⌒P)}$_2$],[17] which are extremely efficient catalysts for the enantioselective hydrogenation of prochiral olefins and keto groups.[18]

In this paper we report that, in contrast to our expectations, the release of the η^3-allyl groups in [Ru(η^3-2-C_3H_4Me)$_2$(dppf)] (**1**) in the presence of isocyanides leads instead to the selective formation of the mononuclear bis(isocyanide)−ruthenium(II) complexes *trans*,*cis*,*cis*-[RuX$_2$(CNR)$_2$(dppf)] (X = Cl, Br; R = CH_2Ph, Cy, ^{t}Bu, 2,6-$C_6H_3Me_2$, (*S*)-(−)-C(H)MePh) (**2a**−**e** and **3a**−**e**). These complexes have also proven to be efficient catalysts in transfer hydrogenation of ketones by propan-2-ol. We also report the isolation and catalytic activity of the hydride complexes *cis*,*cis*-[RuHCl(CN-2,6-$C_6H_3Me_2$)$_2$(dppf)] (**4**) and *cis*,*cis*,*cis*-[RuH$_2$(CN-2,6-$C_6H_3Me_2$)$_2$(dppf)] (**5**).

Results and Discussion

Synthesis of the Bis(isocyanide)−Ruthenium(II) Complexes *trans*,*cis*,*cis*-[RuX$_2$(CNR)$_2$(dppf)] (X = Cl, R = CH_2Ph (2a), Cy (2b), ^{t}Bu (2c), 2,6-$C_6H_3Me_2$ (2d), (*S*)-(−)-C(H)MePh (2e); X = Br, R = CH_2Ph (3a), Cy (3b), ^{t}Bu (3c), 2,6-$C_6H_3Me_2$ (3d), (*S*)-(−)-C(H)MePh (3e)). Treatment of the bis(allyl)−ruthenium(II) complex [Ru(η^3-2-C_3H_4Me)$_2$(dppf)] (**1**) with 2 equiv of the appropriate HX acid, in dichloromethane at room temperature and in the presence of 1 equiv of benzyl isocyanide, generates the corresponding mononuclear bis(isocyanide) derivatives *trans*,*cis*,*cis*-[RuX$_2$-(CNCH$_2$Ph)$_2$(dppf)] (X = Cl (**2a**), Br (**3a**)) along with several unidentified species,[19] with release of 2-methylpropene. As expected, complexes **2a** and **3a** can be properly prepared using 2 equiv of benzyl isocyanide (95 and 93% yield, respectively) (Scheme 1). Other complexes, *trans*,*cis*,*cis*-[RuX$_2$(CNR)$_2$(dppf)] (X = Cl, R = Cy (**2b**), ^{t}Bu (**2c**), 2,6-$C_6H_3Me_2$ (**2d**), (*S*)-(−)-C(H)MePh (**2e**); X = Br, R = Cy (**3b**), ^{t}Bu (**3c**), 2,6-$C_6H_3Me_2$ (**3d**), (*S*)-(−)-C(H)MePh (**3e**)), containing alkyl- and aryl-substituted isocyanides, including the optically active (*S*)-(−)-α-methylbenzyl isocyanide, have been similarly obtained (91−97% yields; Scheme 1). We note that, despite the large number of six-coordinate compounds of general formula [RuX$_2$(CNR)$_2$(PR$_3$)$_2$] reported in the literature (PR$_3$ = monodentate phosphine; several stereoisomers have been described),[20] to the best of our knowledge complexes **2a**−**e** and **3a**−**e** represent the first examples of isocyanide complexes with the stoichiometry [RuX$_2$(CNR)$_2$(P⌒P)] containing a chelating diphosphine ligand.[21,22]

Scheme 1



Compounds **2a**−**e** and **3a**−**e** have been isolated as air-stable yellow solids. They 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 in agreement with the proposed trans,cis,-

(14) Despite the fact that the chemistry of isocyanide−halide−phosphine complexes of ruthenium(II) has been largely explored, the dimeric species [{RuX(μ-X)(CNR)L$_2$}$_2$] (L = monodentate phosphine; L$_2$ = chelate diphosphine) have been unknown until now: (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, U.K., 1987; Vol. 4, p 384. (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 327.

(15) It is well-known that η^3-allyl groups act as labile ligands, generating free coordination sites in acidic media: Braterman, P. S. In *Reactions of Coordinated Ligands*: Braterman, P. S., Ed.; Plenum Press: New York, 1986; Vol. 1, p 103.

(16) Smith Jr., D. C.; Cadoret, J.; Jafarpour, L.; Stevens, E. D.; Nolan, S. P. *Can. J. Chem.* **2001**, *79*, 626.

(17) These species are usually generated in situ and have not been characterized. See for example: (a) Genêt, J. P.; Pinel, C.; Mallart, S.; Jugé, S.; Thorimbert, S.; Laffitte, J. A. *Tetrahedron: Asymmetry* **1991**, *2*, 555. (b) Genêt, J. P.; Pinel, C.; Mallart, S.; Jugé, S.; Cailhol, N.; Laffitte, J. A. *Tetrahedron Lett.* **1992**, *33*, 5343. (c) Genêt, J. P.; Pinel, C.; Ratovelomanana-Vidal, V.; Mallart, S.; Pfister, X.; Caño de Andrade, M. C.; Laffite, J. A. *Tetrahedron: Asymmetry* **1994**, *5*, 665. (d) Genêt, J. P.; Pfister, X.; Ratovelomanana-Vidal, V.; Pinel, C.; Laffite, J. A. *Tetrahedron Lett.* **1994**, *35*, 4559. (e) Genêt, J. P.; Pinel, C.; Ratovelomanana-Vidal, V.; Mallart, S.; Pfister, X.; Bischoff, L.; Caño de Andrade, M. C.; Darses, S.; Galopin, C.; Laffite, J. A. *Tetrahedron: Asymmetry* **1994**, *5*, 675.

(18) For an overview see: Ratovelomanana-Vidal, V.; Genêt, J. P. *J. Organomet. Chem.* **1998**, *567*, 163.

(19) Analysis of the reaction mixtures by IR and NMR spectroscopy reveals that complexes **2a** and **3a** are the only isocyanide-containing species present in solution. This fact indicates clearly that the formation of mononuclear derivatives [RuX$_2$(CNR)$_2$(dppf)] is strongly favored vs the formation of the expected dimers [{RuX(μ-X)(CNR)-(dppf)}$_2$].

(20) For references dealing with the chemistry of the bis(isocyanide) complexes [RuX$_2$(CNR)$_2$(PR$_3$)$_2$] see: (a) Prater, B. E. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 1071. (b) Prater, B. E. *J. Organomet. Chem.* **1971**, *27*, C17. (c) Cenini, S.; Fusi, A.; Capparella, G. *J. Inorg. Nucl. Chem.* **1971**, *33*, 3576. (d) Prater, B. E. *J. Organomet. Chem.* **1972**, *34*, 379. (e) Chatt, J.; Richards, R. L.; Royston, G. H. D. *J. Chem. Soc., Dalton Trans.* **1973**, 1433. (f) Crociani, B.; Richards, R. L. *J. Organomet. Chem.* **1978**, *144*, 85. (g) Gussoni, D.; Mercati, G.; Morazzoni, F. *Gazz. Chim. Ital.* **1979**, *109*, 545. (h) Tsuihiji, T.; Akiyama, T.; Sugimori, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3451. (i) Jeffrey, J. C.; Rauchfuss, T. B. *Inorg. Chem.* **1979**, *18*, 2658. (j) Albers, M. O.; Coville, N. J.; Nicolaides, C. P.; Webber, R. A. *J. Organomet. Chem.* **1981**, *217*, 247. (k) Fehlhammer, W. P.; Bartel, K.; Weinberger, B.; Plaia, U. *Chem. Ber.* **1985**, *118*, 2220. (l) Yamamoto, Y.; Tanase, T.; Date, T.; Koide, Y.; Kobayashi, K. *J. Organomet. Chem.* **1990**, *386*, 365. (m) Katsuki, K.; Ooyama, Y.; Okamoto, M.; Yamamoto, Y. *Inorg. Chim. Acta* **1994**, *217*, 181. (n) Werner, H.; Stark, A.; Steinert, P.; Grünwald, C.; Wolf, J. *Chem. Ber.* **1995**, *128*, 49. (o) Lindner, E.; Geprägs, M.; Gierling, K.; Fawzi, R.; Steimann, M. *Inorg. Chem.* **1995**, *34*, 6106. (p) Werner, H.; Bank, J.; Wolfsberger, W. *Z. Anorg. Allg. Chem.* **1999**, *625*, 2178. (q) Al Dulaimi, J. P.; Clark, R. J. H.; Humphrey, D. G. *Dalton* **2000**, 933. (r) Clot, O.; Wolf, M. O.; Yap, G. P. A. *J. Organomet. Chem.* **2001**, *637*−*639*, 145.

(21) The closely related cationic bis(isocyanide)−carbonyl complex *cis*,*cis*-[RuCl(CO)(CN^{t}Bu)$_2$(dppf)][BF$_4$] has been recently reported: Kawano, H.; Nishimura, Y.; Onishi, M. *Dalton* **2003**, 1808.

(22) The preparation of the complexes [RuCl$_2$(CNR)$_2$(dppm)] has been unsuccessfully attempted. Thus, while the thermal reaction of *trans*-[RuCl$_2$(CNR)$_4$] (R = Ph, ^{t}Bu) with an excess of dppm generates the compounds *cis*,*cis*,*trans*-[RuCl$_2$(CNR)$_2$(κ^1*P*-dppm)$_2$] (R = Ph) and *mer*-[RuCl(CNR)$_3$(dppm)][Cl] (R = Ph, ^{t}Bu), treatment of *trans*-[RuCl$_2$-(dppm)$_2$] with 2 equiv of isocyanides in different reaction conditions affords *trans*,*trans*,*trans*-[RuCl$_2$(CNR)$_2$(κ^1*P*-dppm)$_2$] (R = Ph, ^{t}Bu), *trans*-[RuCl(CNR)$_2$(dppm)(κ^1*P*-dppm)][PF$_6$] (R = Ph, ^{t}Bu), and *trans*-[Ru(CNR)$_2$(dppm)$_2$][PF$_6$]$_2$ (R = Ph, ^{t}Bu): (a) Ruiz, J.; Riera, V.; Vivanco, M. *J. Chem. Soc., Dalton Trans.* **1995**, 1069. (b) Ruiz, J.; Mosquera, M. E. G.; Riera, V. *J. Organomet. Chem.* **1997**, *527*, 35. By using the unsymmetrical diphosphine Ph$_2$PCH$_2$P^{t}Bu$_2$, a mixture of *cis*,*trans*-[RuCl$_2$(CN^{t}Bu)$_2$(Ph$_2$PCH$_2$P^{t}Bu$_2$)] (characterized only by ^{31}P{^{1}H} NMR spectroscopy) and two isomers of *mer*-[RuCl(CN^{t}Bu)$_3$(Ph$_2$PCH$_2$P^{t}Bu$_2$)]$^+$ is obtained: (c) Mosquera, M. E. G.; Ruiz, J.; Riera, V.; García-Granda, S.; Salvadó, M. A. *Organometallics* **2000**, *19*, 5533.

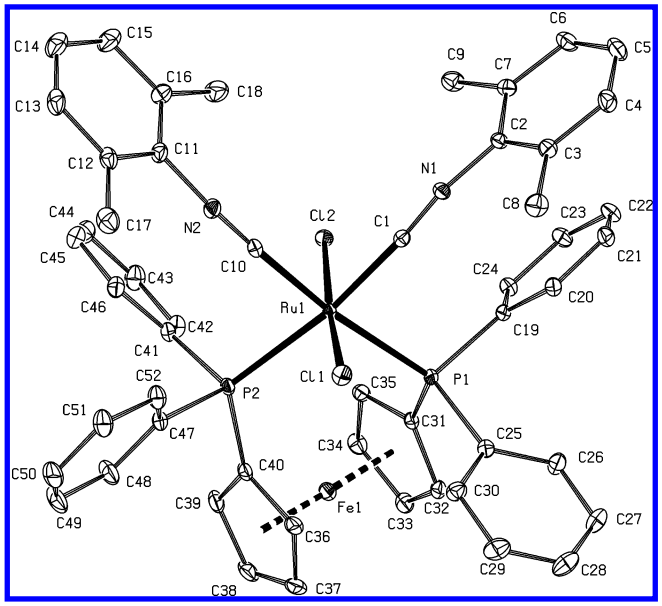
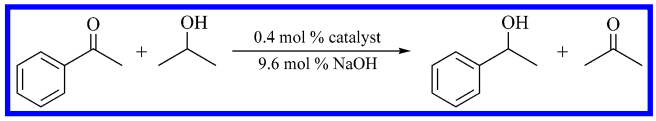


Figure 2. ORTEP-type view of the structure of *trans,cis,cis*-[$RuCl_2$(CN-2,6-$C_6H_3Me_2$)$_2$(dppf)] (**2d**) showing the crystallographic labeling scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 10% probability level. Selected bond distances (Å) and angles (deg): Ru−Cl(1) = 2.4268(7); Ru−Cl(2) = 2.4164(6); Ru−P(1) = 2.4784(6); Ru−P(2) = 2.4551(6); Ru−C(1) = 1.960(3); Ru−C(10) = 1.946(3); C(1)−N(1) = 1.159(3); C(10)−N(2) = 1.150(3); N(1)−C(2) = 1.404(3); N(2)−C(11) = 1.411(4); Fe−C* = 1.6428(4); Fe−C** = 1.6401(4); P(1)−Ru−P(2) = 98.17(2); P(1)−Ru−C(1) = 87.70(7); P(1)−Ru−C(10) = 172.85(8); P(1)−Ru−Cl(1) = 95.16(2); P(1)−Ru−Cl(2) = 85.42(2); P(2)−Ru−C(10) = 86.27(7); P(2)−Ru−C(1) = 171.65(7); P(2)−Ru−Cl(1) = 95.07(2); P(2)−Ru−Cl(2) = 90.03(2); Cl(1)−Ru−Cl(2) = 174.72(3); Cl(1)−Ru−C(1) = 90.28(7); Cl(1)−Ru−C(10) = 89.99(8); Cl(2)−Ru−C(1) = 84.50(7); Cl(2)−Ru−C(10) = 89.00(8); C(1)−Ru−C(10) = 87.32(10); Ru−C(1)−N(1) = 174.6(2); C(1)−N(1)−C(2) = 167.3(3); Ru−C(10)−N(2) = 177.5(2); C(10)−N(2)−C(11) = 163.9(3); C*−Fe−C** = 178.94(3). C* and C** denote the centroids of the cyclopentadienyl rings C(31), C(32), C(33), C(34), C(35) and C(36), C(37), C(38), C(39), C(40), respectively.

cis stereochemistry (see the Experimental Section for details). Key spectroscopic features are as follows: (i; IR) the presence of two strong ν(CN) absorption bands in the range 2081−2180 cm^{-1}, in accord with a mutually cis disposition of the isocyanide ligands, (ii; $^{31}P\{^1H\}$ NMR) the appearance of a singlet signal at 17.74−21.17 ppm, indicative of equivalent phosphorus nuclei of the dppf ligand; (iii; $^{13}C\{^1H\}$ NMR) only one signal for the isocyanide groups, at the expected downfield chemical shifts (δ 149.90−162.82 ppm), which appears as a doublet of doublets. The $^2J_{CP}$ values observed, in the ranges 111.1−129.9 and 21.5−25.3 Hz, clearly reveal that each isocyanide group is located in a trans and cis disposition with respect to the phosphorus nuclei of the diphosphine. Moreover, the structure of the complex *trans,cis,cis*-[$RuCl_2$(CN-2,6-$C_6H_3Me_2$)$_2$(dppf)] (**2d**) has been unequivocally confirmed by a single-crystal X-ray diffraction study. An ORTEP view of the molecular structure is depicted in Figure 2; selected bond distances and angles are listed in the caption. The ruthenium atom is in a slightly distorted octahedral environment with the two chloride ligands oriented mutually trans.

Scheme 2



The isocyanide groups are bound to ruthenium in a nearly linear fashion (Ru−C(1)−N(1) = 174.6(2)°; Ru−C(10)−N(2) = 177.5(2)°) with metal−carbon bond distances of 1.960(3) Å (Ru−C(1)) and 1.946(3) Å (Ru−C(10)). These bonding parameters fit well with those reported in the literature for other isocyanide-ruthenium(II) complexes.[14a,20l,o,r,22c]

Catalytic Transfer Hydrogenation of Ketones. The easy access to complexes *trans,cis,cis*-[$RuX_2(CNR)_2$(dppf)] (**2a**−**e** and **3a**−**e**) prompted us to check their catalytic activity in the transfer hydrogenation of ketones. We note that, despite the large number of ruthenium(II) catalysts reported for this particular transformation, no isocyanide−ruthenium species have been used to date.[1] The classical transfer hydrogenation of acetophenone by propan-2-ol was used as a model reaction (see Scheme 2). Thus, in a typical experiment, the ruthenium catalyst precursors **2a**−**e** and **3a**−**e** (0.4 mol %) 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. Selected results are summarized in Figure 3.

All of the complexes have proven to be active and efficient catalysts leading to nearly quantitative conversions (yield ≥96%) of acetophenone into 1-phenylethanol within 0.5−8 h (22 h in the case of **3d**; see Figure 3). The complex *trans,cis,cis*-[$RuCl_2(CNCH_2Ph)_2$(dppf)] (**2a**) shows the best performance, achieving 99% of conversion in 30 min (TOF = 500 h^{-1}). Remarkably, the catalytic activity of complex **2a** is retained at lower catalyst loadings; i.e. using 0.025 mol % of **2a**, acetophenone (0.1 M solution in ^{i}PrOH; ketone/Ru/NaOH ratio 4000/1/24) can be reduced in 98% yield within 5 h (TOF = 780 h^{-1}).[23] From the results depicted in Figure 3, the following features deserve comment. (i) There is a strong influence of the isocyanide substituents on the catalytic activity, increasing in the order CH_2Ph > C(H)MePh ≫ Cy > ^{t}Bu ≈ 2,6-$C_6H_3Me_2$. This indicates clearly that the steric requirements of the isocyanide ligands play a crucial role in the reaction. (ii) The catalytic performances shown by the chloride complexes **2a**−**e** are, in all cases, better than those of their bromide counterparts **3a**−**e**, due probably to the higher ability of the Ru−Cl bonds to favor the formation of the corresponding hydride-ruthenium(II) species. (iii) No chiral induction (0% ee) is observed when the optically active complexes *trans,cis,cis*-[RuX_2{CN-(*S*)-C(H)MePh}$_2$(dppf)] (**2e** and **3e**) are used as catalysts even at temperatures lower than 82 °C.

The most active complex, **2a**, has been tested in the hydride transfer hydrogenation of other ketones (results are shown in Tables 1 and 2). Thus, it has been shown to be particularly efficient in the reduction of dialkyl ketones (see Table 1), even when long-chain substituents are present: i.e., 2-octanone (98% of conversion

(23) Using 0.1 mol % of **2a**, acetophenone (0.1 M solution in ^{i}PrOH; ketone/Ru/NaOH ratio 1000/1/24) is reduced in 98% yield within 1 h (TOF = 980 h^{-1}).

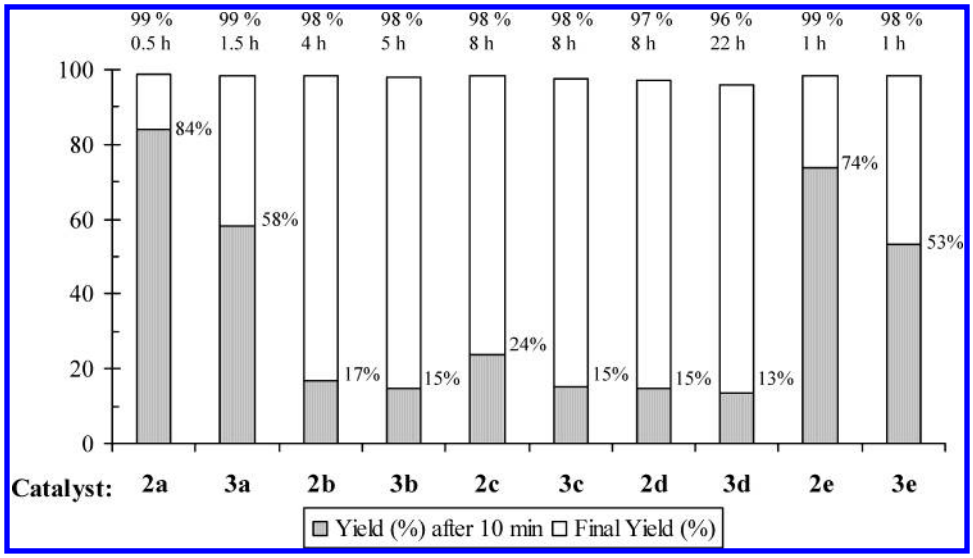


Figure 3. Catalytic transfer hydrogenation of acetophenone by the complexes *trans,cis,cis*-[$RuX_2(CNR)_2$(dppf)] (**2a**−**e** and **3a**−**e**). Conditions: reactions were carried out at 82 °C using 5 mmol of acetophenone (0.1 M in ^{i}PrOH). Ketone/Ru/NaOH ratio: 250/1/24. Yield of 1-phenylethanol determined by GC (the values are the average of two runs).

Table 1. Catalytic Transfer Hydrogenation of Dialkyl Ketones by Complex 2a[a]

Entry	Ketone	Product	Yield[b]	Final TOF
1			100%	1500 h^{-1}
2			95% (99%; 0.25 h)	990 h^{-1}
3			74% (99%; 0.5 h)	500 h^{-1}
4			55% (98%; 0.75 h)	330 h^{-1}
5			44% (98%; 1.5 h)	160 h^{-1}
6			9% (97%; 18 h)	10 h^{-1}

[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 10 min. Final yield and time are given in parentheses, determined by GC. The values given in the table are the average of two runs.

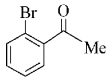
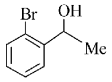
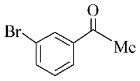
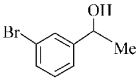
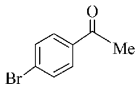
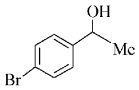
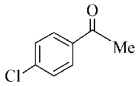
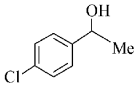
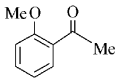
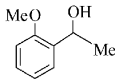
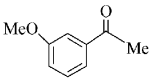
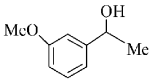
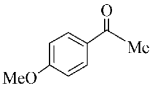
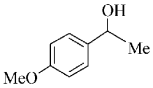
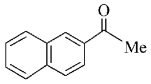
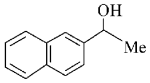
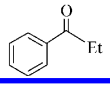
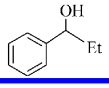
within 45 min; TOF = 330 h^{-1}; entry 4). Nevertheless, it should be noted that its catalytic activity is significantly reduced in the case of ketones containing bulky substituents: i.e., 3-methyl-2-butanone and pinacolone (TOF = 160 and 10 h^{-1}, respectively; entries 5 and 6). A large variety of aryl ketones have been also efficiently transformed into the corresponding alcohols using **2a** as catalyst (see Table 2). In comparison to acetophenone, slower reductions have been observed for its ortho-, meta-, and para-substituted derivatives (TOF = 60−330 h^{-1}) regardless of the presence of electron-withdrawing (Cl, Br; entries 1−4) or electron-donating (OMe; entries 5−7) groups.[24] These observations do not allow us to propose the turnover-limiting step in the catalytic cycle: i.e., ketone coordination vs hydride transfer from the metal to the coordinate ketone.[25] The effectiveness of **2a** is clearly demonstrated in the transfer hydrogenation of α-tetralone (entry 9), 1-indanone (entry 10), and propiophenone (entry 11), since the reduction of such substrates is usually difficult.[1]

Remarkably, the catalytic activity shown by complexes **2a**−**e** and **3a**−**e** is, under the same reaction conditions, comparable to that found for the dimeric species [{RuX(μ-X)(CO)(dppf)}$_2$] (X = Cl, Br) (**I**; see Figure 1), despite the ability of the latter to generate the unsaturated mononuclear species [RuX_2(CO)(dppf)] in solution (i.e. for the reduction of acetophenone 97% of conversion was attained within 3 (X = Cl) or 10 h (X = Br); to be compared with results in Figure 3).[11] We also note that the catalytic activity shown by the complex *trans,cis,cis*-[$RuCl_2(CNCH_2Ph)_2$(dppf)] (**2a**) is

(24) The catalytic activity is not attenuated when the methoxy group is introduced in an ortho position (TOF = 500 h^{-1}; see entry 5 in Table 2). This effect, attributed to chelate coordination of 2-methoxyacetophenone to ruthenium, has been previously described. See for example: Evans, D. A.; Nelson, S. G.; Gagné, M. R.; Muci, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 9800.

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

Table 2. Catalytic Transfer Hydrogenation of Aryl−Alkyl Ketones by Complex 2a[a]

Entry	Ketone	Product	Yield[b]	Final TOF
1			46% (99%; 0.75 h)	330 h^{-1}
2			22% (99%; 1 h)	250 h^{-1}
3			22% (99%; 2.5 h)	100 h^{-1}
4			22% (98%; 4 h)	60 h^{-1}
5			88% (100%; 0.5 h)	500 h^{-1}
6			54% (99%; 0.75 h)	330 h^{-1}
7			56% (93%; 4 h)	60 h^{-1}
8			32% (98%; 2 h)	120 h^{-1}
9			17% (89%; 24 h)	10 h^{-1}
10			30% (92%; 19 h)	10 h^{-1}
11			67% (99%; 0.75 h)	330 h^{-1}

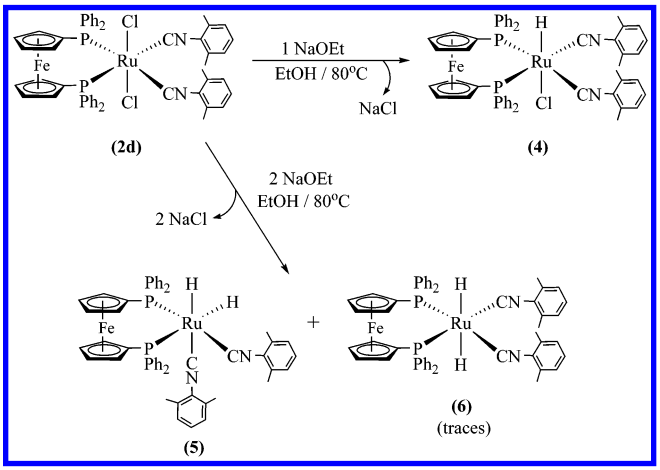
[a] Conditions: reactions were carried out at 82 °C using 5 mmol of ketone (0.1 M in ^{i}PrOH). Ketone/Ru/NaOH ratio: 250/1/24. [b] Yield of the corresponding alcohol after 10 min. Final yield and time are given in parentheses, determined by GC. The values given in the table are the average of two runs.

higher than that reported by Bäckvall and co-workers for the five-coordinate species $[RuCl_2(PPh_3)_3]$ (TOF = 1500 vs 890 h^{-1} for the reduction of cyclohexanone into cyclohexanol).[26]

Synthesis and Catalytic Activity of the Hydride Complexes *cis,cis*-[RuHCl(CN-2,6-$C_6H_3Me_2$)$_2$(dppf)] (4) and *cis,cis,cis*-[RuH_2(CN-2,6-$C_6H_3Me_2$)$_2$(dppf)] (5). Since metal−hydride derivatives are commonly proposed as active species in transfer hydrogenation reactions,[1] we sought the preparation of such compounds starting from the isocyanide−halide complexes **2a**−**e** and **3a**−**e**. The complex *trans,cis,cis*-[$RuCl_2$(CN-2,6-$C_6H_3Me_2$)$_2$(dppf)] (**2d**) was chosen as the model precursor due to its low catalytic activity. With this complex, we could anticipate a relatively favorable stabilization of the hydride intermediates.

In agreement with our expectations, we have found that the treatment of **2d** with 1 equiv of NaOEt, in EtOH at 80 °C, cleanly generates the monohydride complex *cis,cis*-[RuHCl(CN-2,6-$C_6H_3Me_2$)$_2$(dppf)] (**4**; 94% yield) (Scheme 3), via classical β-hydrogen elimination on the intermediate ethoxide complex.[27] In addition, when 2 equiv of NaOEt is used, the dihydride derivative *cis,cis,cis*-[RuH_2(CN-2,6-$C_6H_3Me_2$)$_2$(dppf)] (**5**) is formed along with minor amounts (~5%) of its isomer *trans,-*

Scheme 3



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

cis,cis-[RuH_2(CN-2,6-$C_6H_3Me_2$)$_2$(dppf)] (**6**) (Scheme 3).[28,29] Workup of this mixture allowed the selective isolation of complex **5** (83% yield).

Hydride complexes **4** and **5** have been obtained as yellow air-sensitive solids that can be stored under nitrogen at room temperature for short periods (2−3 days) without apparent decomposition. They have been characterized by IR and NMR (^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H}) spectroscopy as well as elemental analyses (details are given in the Experimental Section). The hydride ligand in **4** gives rise to a strong ν(Ru−H) IR absorption band at 1998 cm^{-1} and, in the ^{1}H NMR spectrum, to a triplet signal at δ −14.19 ppm that indicates equivalent coupling ($^2J_{HP}$ = 22.9 Hz) to two cis-disposed phosphorus nuclei. In accord with this, a singlet resonance is observed for the dppf ligand in the ^{31}P{^{1}H} NMR spectrum (δ 34.74 ppm). ^{13}C{^{1}H} NMR also supports the proposed stereochemistry for **4**, showing a single isocyanide resonance at 169.78 ppm (dd, $^2J_{CP}$ = 107.8 and 27.5 Hz). Two hydride (δ_H −7.08 (ddd, $^2J_{HP}$ = 78.9 and 33.4 Hz, $^2J_{HH}$ = 5.0 Hz) and −6.62 (ddd, $^2J_{HP}$ = 27.5 and 22.8 Hz, $^2J_{HH}$ = 5.0 Hz) ppm), isocyanide (δ_C 178.38 (dd, $^2J_{CP}$ = 89.1 and 9.1 Hz) and 181.07 (dd, $^2J_{CP}$ = 11.3 and 8.3 Hz) ppm) and Ph_2P (δ_P 42.97 and 51.22 (d, $^2J_{PP}$ = 25.7 Hz) ppm) resonances are observed in the NMR spectra of **5**, indicative of an all-cis stereochemistry for this complex. As expected, two ν(Ru−H) absorptions are also observed in the IR spectra of **5** at 1955 and 1999 cm^{-1}.

To assess whether mono- or dihydride complexes **4** and **5** are active species, the transfer hydrogenation of acetophenone with propan-2-ol was carried out in the absence of NaOH. We have found that both complexes are able to reduce acetophenone into 1-phenylethanol (96 and 95% yields, respectively (TOF = 50 and 10 h^{-1}); see Figure 4).[30] To the best of our knowledge, there is no precedent of mono- and dihydride species containing the same ruthenium(II) fragment which are active in TH of ketones in the absence of base.

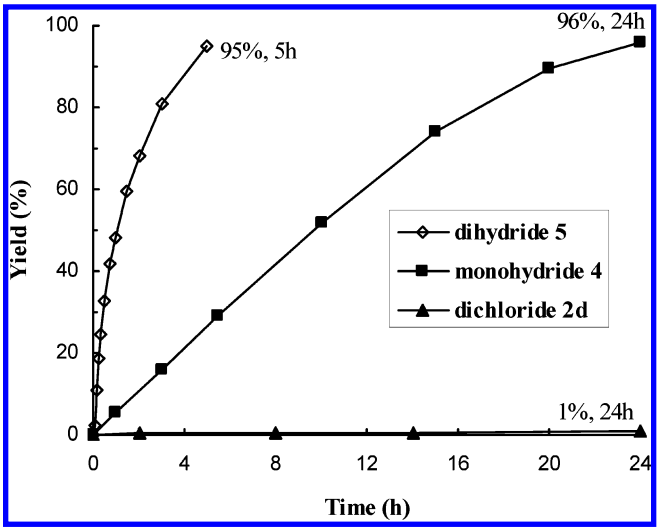


Figure 4. Catalytic transfer hydrogenation of acetophenone in the absence of base using *trans,cis,cis*-[$RuCl_2$(CN-2,6-$C_6H_3Me_2$)$_2$(dppf)] (**2d**), *cis,cis*-[RuHCl(CN-2,6-$C_6H_3Me_2$)$_2$(dppf)] (**4**), and *cis,cis,cis*-[RuH_2(CN-2,6-$C_6H_3Me_2$)$_2$-(dppf)] (**5**). Conditions: reactions were carried out at 82 °C using 5 mmol of acetophenone (0.1 M in ^{i}PrOH). Ketone/Ru ratio: 250/1. Yield of 1-phenylethanol determined by GC (the values are the average of two runs).

As far as the catalytic activity of both hydride complexes is concerned, the following features should be noted (see Figures 3 and 4): (i) the reactions in the absence of base proceed ca. 5 times faster with **5** than with **4**, (ii) using the same ruthenium loading (0.4 mol %), the catalytic activity of the dihydride complex **5** without NaOH is similar to that found for the dichloride complex **2d** in the presence of NaOH, and (iii) the activity of monohydride **4** in the absence of NaOH is, in contrast, remarkably lower than that of **2d** with NaOH. This indicates that the dihydride species **5** is remarkably more active than the monohydride **4**. All these observations support that the hydrogen transfer reactions catalyzed by the system *trans,cis,cis*-[RuX_2-(CNR)$_2$(dppf)] (**2a**−**e** and **3a**−**e**) and an excess of NaOH proceed essentially via the dihydride intermediates *cis,-cis,cis*-[RuH_2(CNR)$_2$(dppf)]. Although ruthenium(II) dihydride derivatives are commonly proposed as active species in TH processes catalyzed by octahedral Ru(II) dichloride complexes associated with a base, little experimental evidence has been published to date. Thus, in the study of catalytic TH reactions promoted by [$RuCl_2$(PPh_3){(2-(4′-phenyloxazolin-2′-yl)ferrocenyl)diphenylphosphine}], the detection by NMR spectroscopy of two ruthenium(II) dihydride species is mentioned, but no details are given.[31] Only the isolated and well-characterized complex [RuH_2(PPh_3)$_4$] has been experimentally proven to be an efficient catalyst, its activity being comparable to that of the system [$RuCl_2$(PPh_3)$_3$]/NaOH.[26]

With regard to the mechanism, we assume that the first step in the catalytic cycle involves the dissociation of one isocyanide ligand from [RuHY(CNR)$_2$(dppf)] to form the pentacoordinate species [RuHY(CNR)(dppf)], which readily provide the required vacant site for coordination of the ketone (see Scheme 4). Experimental

(27) Several monohydride−ruthenium(II) complexes containing isocyanide ligands are known: (a) Bancroft, G. M.; Mays, M. J.; Prater, B. E.; Stefanini, F. P. *J. Chem. Soc. A* **1970**, 2146. (b) Christian, D. F.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1971**, 1271. (c) Christian, D. F.; Clark, G. R.; Roper, W. R.; Waters, J. M.; Whittle, K. R. *J. Chem. Soc., Chem. Commun.* **1972**, 458. (d) Grundy, K. R. *Inorg. Chim. Acta* **1981**, *53*, L225. (e) Burns, I. D.; Hill, A. F.; Thompsett, A. R.; Alcock, N. W.; Claire, K. S. *J. Organomet. Chem.* **1992**, *425*, C8. (f) Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Inorg. Chem.* **1994**, *33*, 3515. (g) Lindner, E.; Pautz, S.; Fawzi, R.; Steimann, M. *Organometallics* **1998**, *17*, 3006. (h) Rocchini, E.; Rigo, P.; Mezzetti, A.; Stephan, T.; Morris, R. H.; Lough, A. J.; Forde, C. E.; Fong, T. P.; Drouin, S. D. *Dalton* **2000**, 3591. (i) Huang, D.; Koren, P. R.; Folting, K.; Davidson, E. R.; Caulton, K. G. *J. Am. Chem. Soc.* **2000**, *122*, 8916. (j) Coalter, J. N., III; Huffman, J. C.; Caulton, K. G. *Organometallics* **2000**, *19*, 3569. (k) Caballero, A.; Gómez-de la Torre, F.; Jalón, F. A.; Manzano, B. R.; Rodríguez, A. M.; Trofimenko, S.; Sigalas, M. P. *Dalton* **2001**, 427.

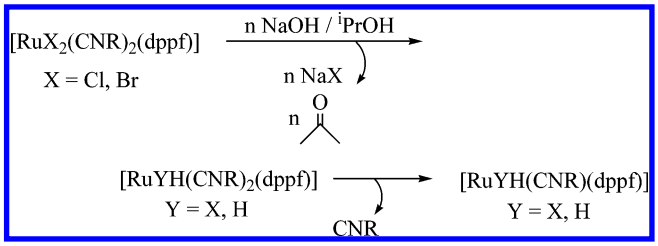
(28) The complexes *cis,cis,trans*-[RuH_2(CN^tBu)$_2$(PMe_3)$_2$] and *cis,mer*-[RuH_2($CNCH_2Ph$){κ^3*P,P,P*-PhP($CH_2CH_2CH_2PCy_2$)$_2$}] are, to the best of our knowledge, the only ruthenium(II) dihydride complexes containing isocyanide ligands reported to date: (a) Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1981**, 2088. (b) Jia, G.; Meek, D. W.; Gallucci, J. C. *Inorg. Chem.* **1991**, *30*, 403.

(29) Key spectroscopic data for **6** in C_6D_6 (obtained from the crude reaction mixture): δ_P 41.24 (s) ppm; δ_H −5.85 (t, 2H, $^2J_{HP}$ = 25.0 Hz, Ru−H) ppm.

(30) (a) As expected, *trans,cis,cis*-[$RuCl_2$(CN-2,6-$C_6H_3Me_2$)$_2$(dppf)] (**2d**) is almost inactive in the absence of NaOH (see Figure 4). (b) We also note that, in the absence of any ruthenium(II) source, NaOH catalyzes the reduction of acetophenone into 1-phenylethanol (acetophenone/base = 250/24) in only 5% yield after 4 h (13% yield after 24 h). This fact clearly indicates the crucial role of the metal in the catalytic system [RuX_2(CNR)$_2$(dppf)]/NaOH.

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

Scheme 4



support of this dissociation relies on the fact that the catalytic activity of dihydride **5** is completely inhibited in the presence of free 2,6-dimethylphenyl isocyanide ([isocyanide]/[Ru] = 50/1).[32] The rest of the steps could be analogous to those proposed by Bäckvall and coworkers for the transfer hydrogenation of ketones catalyzed by $[RuH_2(PPh_3)_3]$, and therefore, no further comment is warranted.[1f]

Conclusions

In this paper we have described an efficient and straightforward synthetic protocol for the stereoselective preparation of rare examples of bis(isocyanide)−ruthenium(II) complexes, namely *trans,cis,cis*-$[RuX_2(CNR)_2(dppf)]$ (**2a**−**e** and **3a**−**e**), starting from the readily available bis(allyl) derivative $[Ru(\eta^3\text{-}2\text{-}C_3H_4Me)_2(dppf)]$ (**1**). This route is based on the HX-promoted releasing of the η^3-allyl units of **1** in the presence of isocyanide ligands. Recently, we have also used this synthetic methodology for the preparation of the dimeric ruthenium(II) species $[\{RuX(\mu\text{-}X)(CO)(P\frown P)\}_2]$ (**I**; see Figure 1).[11] Halide complexes **2a**−**d** and **3a**−**d** have proven to be suitable catalysts for transfer hydrogenation of ketones by propan-2-ol in the presence of base, representing novel examples of efficient catalysts containing ligands with no N−H functionalities.[12] In addition, the hydride complexes *cis,cis*-$[RuHCl(CN\text{-}2,6\text{-}C_6H_3Me_2)_2(dppf)]$ (**4**) and *cis,cis,cis*-$[RuH_2(CN\text{-}2,6\text{-}C_6H_3Me_2)_2(dppf)]$ (**5**), belonging to the scarce series of ruthenium(II) hydride−isocyanide derivatives,[27,28] have also been isolated and characterized. These complexes catalyze the TH of acetophenone in the absence of base, showing that they are intermediates in the catalytic transformations using their halide precursors as catalysts. As far as we know, these are the first examples of related ruthenium hydride complexes of the types L_nRuHX and L_nRuH_2 which are both active catalysts in TH of ketones without base. The catalytic activity of the dihydride complex **5** can be compared to that shown by its dichloride precursor **2d** in the presence of an excess of base. This fact suggests that dihydride derivatives are the active species in the catalytic cycle. Moreover, the lability of these intermediates toward dissociation of one isocyanide ligand, leading to the putative formation of 16e species $[RuH_2(CNR)(dppf)]$, supports the observed catalytic activity.

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 the compound $[Ru(\eta^3\text{-}2\text{-}C_3H_4Me)_2(dppf)]$ (**1**), which was prepared by following the method reported in the literature.[16] 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. Gas chromatographic measurements were made on Hewlett-Packard HP6890 equipment using an HP-INNOWAX cross-linked poly(ethylene glycol) (30 m, 250 μm) or a Supelco Beta-Dex 120 (30 m, 250 μm) column. Optical rotations (α) were measured an a Perkin-Elmer 343 polarimeter. 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 standards. DEPT experiments have been carried out for all the compounds reported.

Synthesis of *trans,cis,cis*-$[RuX_2(CNR)_2(dppf)]$ (X = Cl, R = CH_2Ph (2a), Cy (2b), ^{t}Bu (2c), 2,6-$C_6H_3Me_2$ (2d), (*S*)-(−)-C(H)MePh (2e); X = Br, R = CH_2Ph (3a), Cy (3b), ^{t}Bu (3c), 2,6-$C_6H_3Me_2$ (3d), (*S*)-(−)-C(H)MePh (3e)). The corresponding isocyanide (2 mmol) was added, at room temperature, to a solution of the complex $[Ru(\eta^3\text{-}2\text{-}C_3H_4Me)_2(dppf)]$ (**1**; 0.765 g; 1 mmol) in 50 mL of dichloromethane. The appropriate HX acid (2.2 mL of a 1.0 M solution in diethyl ether; 2.2 mmol) was then added and the reaction mixture stirred at room temperature for 15 min. After the solvent was removed under reduced pressure, the resulting yellow solid residue was washed with hexanes (3 × 30 mL) and vacuum-dried. **2a**: yield 95% (0.913 g). Anal. Calcd for $FeRuC_{50}H_{42}Cl_2N_2P_2$: C, 62.51; H, 4.41; N, 2.92. Found: C, 62.74; H, 4.57; N, 2.85. IR (KBr, cm^{-1}): ν 2140 and 2178 (C≡N). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 19.40 (s) ppm. ^{1}H NMR (CD_2Cl_2): δ 4.27 and 4.73 (br, 4H each, C_5H_4), 4.64 (s, 4H, NCH_2), 7.20−7.90 (m, 30H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 48.35 (s, NCH_2), 71.85 and 76.38 (br, CH of C_5H_4), 80.32 (m, C of C_5H_4), 126.50−139.00 (m, Ph), 153.67 (dd, $^2J_{CP}$ = 129.9 and 22.5 Hz, C≡N) ppm. **2b**: yield 96% (0.907 g). Anal. Calcd for $FeRuC_{48}H_{50}Cl_2N_2P_2$: C, 61.03; H, 5.33; N, 2.97. Found: C, 61.15; H, 5.01; N, 2.98. IR (KBr, cm^{-1}): ν 2135 and 2164 (C≡N). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 20.55 (s) ppm. ^{1}H NMR (CD_2Cl_2): δ 1.25−1.75 (m, 20H, CH_2), 3.70 (m, 2H, NCH), 4.27 and 4.66 (br, 4H each, C_5H_4), 7.20−7.80 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 23.11, 25.48, and 33.14 (s, CH_2), 54.72 (s, NCH), 71.70 and 76.18 (br, CH of C_5H_4), 80.72 (m, C of C_5H_4), 127.20−137.50 (m, Ph), 151.13 (dd, $^2J_{CP}$ = 121.9 and 21.5 Hz, C≡N) ppm. **2c**: yield 96% (0.857 g). Anal. Calcd for $FeRuC_{44}H_{46}Cl_2N_2P_2$: C, 59.21; H, 5.19; N, 3.14. Found: C, 59.39; H, 5.07; N, 3.11. IR (KBr, cm^{-1}): ν 2139 and 2169 (C≡N). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 21.17 (s) ppm. ^{1}H NMR (CD_2Cl_2): δ 1.39 (s, 18H, CH_3), 4.35 and 4.73 (br, 4H each, C_5H_4), 7.30−7.85 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 30.72 (s, CH_3), 56.99 (s, $C(CH_3)_3$), 71.41 and 75.74 (br, CH of C_5H_4), 80.49 (m, C of C_5H_4), 126.50−137.50 (m, Ph), 150.31 (dd, $^2J_{CP}$ = 120.7 and 24.7 Hz, C≡N) ppm. **2d**: yield 95% (0.939 g). Anal. Calcd for $FeRuC_{52}H_{46}Cl_2N_2P_2$: C, 63.17; H, 4.69; N, 2.83. Found: C, 63.01; H, 4.76; N, 2.90. IR (KBr, cm^{-1}): ν 2100 and 2146 (C≡N). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 18.63 (s) ppm. ^{1}H NMR (CD_2Cl_2): δ 2.15 (s, 12H, CH_3), 4.34 and 4.76 (br, 4H each, C_5H_4), 7.00−8.30 (m, 26H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 18.54 (s, CH_3), 71.50 and 76.13 (br, CH of C_5H_4), 80.14 (m, C of C_5H_4), 125.60−136.40 (m, Ph), 162.82 (dd, $^2J_{CP}$ = 126.8 and 24.8 Hz, C≡N) ppm. **2e**: yield 94% (0.929 g). Anal. Calcd for $FeRuC_{52}H_{46}Cl_2N_2P_2$: C, 63.17; H, 4.69; N, 2.83. Found: C, 63.29; H, 4.51; N, 2.75. IR (KBr, cm^{-1}): ν 2131 and 2169 (C≡N). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 19.60 (s) ppm. ^{1}H NMR (CD_2Cl_2): δ 1.43 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH_3), 4.31 (br, 4H, C_5H_4), 4.60 and 4.84 (br, 2H each, C_5H_4), 4.87 (quartet, 2H, $^3J_{HH}$ = 6.8 Hz, NCH), 7.19−8.10 (m, 30H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 25.57 (s, CH_3), 56.55 (s, NCH), 71.68, 72.06, 76.14 and 76.37 (br, CH of C_5H_4), 80.31 (m, C of C_5H_4), 126.00−139.75 (m, Ph), 153.24 (dd, $^2J_{CP}$ = 121.1

(32) The lability of the isocyanide ligands can also explain the similar catalytic activity shown by complexes **2a**−**e** and **3a**−**e** and the dimeric species $[\{RuX(\mu\text{-}X)(CO)(dppf)\}_2]$ (X = Cl, Br) (**I**).

and 22.4 Hz, C≡N) ppm. $[\alpha]^{20}_D = -16.7°$ mL dm^{-1} g^{-1} (c = 0.001 M in $CHCl_3$). **3a**: yield 93% (0.976 g). Anal. Calcd for $FeRuC_{50}H_{42}Br_2N_2P_2$: C, 57.22; H, 4.03; N, 2.67. Found: C, 57.41; H, 4.16; N, 2.63. IR (KBr, cm^{-1}): ν 2141 and 2180 (C≡N). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 19.16 (s) ppm. ^1H NMR (CD_2Cl_2): δ 4.32 (br, 4H, C_5H_4), 4.72 (br, 8H, C_5H_4 and NCH_2), 7.20−7.80 (m, 30H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 48.34 (s, NCH_2), 71.62 and 76.68 (br, CH of C_5H_4), 81.77 (m, C of C_5H_4), 127.00−137.50 (m, Ph), 153.01 (dd, $^2J_{CP}$ = 119.8 and 21.5 Hz, C≡N) ppm. **3b**: yield 91% (0.940 g). Anal. Calcd for $FeRuC_{48}H_{50}Br_2N_2P_2$: C, 55.78; H, 4.88; N, 2.71. Found: C, 55.65; H, 4.92; N, 2.75. IR (KBr, cm^{-1}): ν 2137 and 2169 (C≡N). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 20.27 (s) ppm. ^1H NMR (CD_2Cl_2): δ 1.30−1.75 (m, 20H, CH_2), 3.76 (m, 2H, NCH), 4.33 and 4.77 (br, 4H each, C_5H_4), 7.20−7.85 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 23.13, 25.33, and 33.20 (s, CH_2), 54.71 (s, NCH), 71.63 and 76.41 (br, CH of C_5H_4), 81.63 (m, C of C_5H_4), 127.00−137.60 (m, Ph), 150.43 (dd, $^2J_{CP}$ = 121.1 and 23.4 Hz, C≡N) ppm. **3c**: yield 95% (0.932 g). Anal. Calcd for $FeRuC_{44}H_{46}Br_2N_2P_2$: C, 53.84; H, 4.72; N, 2.85. Found: C, 53.71; H, 4.89; N, 2.93. IR (KBr, cm^{-1}): ν 2133 and 2162 (C≡N). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 21.07 (s) ppm. ^1H NMR (CD_2Cl_2): δ 1.38 (s, 18H, CH_3), 4.39 and 4.78 (br, 4H each, C_5H_4), 7.15−7.75 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 31.10 (s, CH_3), 57.32 (s, $C(CH_3)_3$), 71.78 and 76.12 (br, CH of C_5H_4), 81.11 (m, C of C_5H_4), 125.35−137.80 (m, Ph), 149.90 (dd, $^2J_{CP}$ = 111.1 and 23.0 Hz, C≡N) ppm. **3d**: yield 97% (1.045 g). Anal. Calcd for $FeRuC_{52}H_{46}Br_2N_2P_2$: C, 57.96; H, 4.30; N, 2.60. Found: C, 57.81; H, 4.44; N, 2.70. IR (KBr, cm^{-1}): ν 2081 and 2125 (C≡N). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 17.74 (s) ppm. ^1H NMR (CD_2Cl_2): δ 2.21 (s, 12H, CH_3), 4.37 and 4.79 (br, 4H each, C_5H_4), 7.00−7.95 (m, 26H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 18.79 (s, CH_3), 71.33 and 76.49 (br, CH of C_5H_4), 81.37 (m, C of C_5H_4), 126.90−136.65 (m, Ph), 161.56 (dd, $^2J_{CP}$ = 124.3 and 25.3 Hz, C≡N) ppm. **3e**: yield 91% (0.980 g). Anal. Calcd for $FeRuC_{52}H_{46}Br_2N_2P_2$: C, 57.96; H, 4.30; N, 2.60. Found: C, 57.78; H, 4.21; N, 2.62. IR (KBr, cm^{-1}): ν 2130 and 2165 (C≡N). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 19.54 (s) ppm. ^1H NMR (CD_2Cl_2): δ 1.46 (d, 6H, $^3J_{HH}$ = 6.7 Hz, CH_3), 4.36 (br, 4H, C_5H_4), 4.68 and 4.89 (br, 2H each, C_5H_4), 4.92 (quartet, 2H, $^3J_{HH}$ = 6.7 Hz, NCH), 7.20−7.85 (m, 30H, Ph) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 25.72 (s, CH_3), 56.55 (s, NCH), 71.76, 71.93, 76.52, and 76.56 (br, CH of C_5H_4), 81.41 (m, C of C_5H_4), 126.00−139.85 (m, Ph), 152.52 (dd, $^2J_{CP}$ = 120.0 and 22.4 Hz, C≡N) ppm. $[\alpha]^{20}_D = -14.3°$ mL dm^{-1} g^{-1} (c = 0.001 M in $CHCl_3$).

Synthesis of *cis,cis*-[RuHCl(CN-2,6-$C_6H_3Me_2$)$_2$(dppf)] (4). NaOEt (2.02 mL of a 0.05 M solution in ethanol; 0.101 mmol) was added at room temperature to a solution of the complex *trans,cis,cis*-[$RuCl_2$(CN-2,6-$C_6H_3Me_2$)$_2$(dppf)] (**2d**; 0.100 g; 0.101 mmol) in 20 mL of ethanol. The reaction mixture was heated at 80 °C for 2 h and then evaporated to dryness. The solid residue was extracted with toluene (ca. 20 mL) and filtered over Kieselguhr. Evaporation of the solvent gave a yellow solid, which was washed with hexanes (3 × 10 mL) and vacuum-dried. Yield: 94% (0.091 g). Anal. Calcd for $FeRuC_{52}H_{47}N_2P_2Cl$: C, 65.45; H, 4.96; N, 2.94. Found: C, 65.31; H, 4.87; N, 2.95. IR (KBr, cm^{-1}): ν 1998 (Ru−H), 2063 and 2114 (C≡N). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 34.74 (s) ppm. ^1H NMR (C_6D_6): δ −14.19 (t, 1H, $^2J_{HP}$ = 22.9 Hz, Ru−H), 2.08 (s, 12H, CH_3), 3.93 (br, 4H, C_5H_4), 4.43 and 5.06 (br, 2H each, C_5H_4), 6.55−8.40 (m, 26H, Ph) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 17.64 (s, CH_3), 70.02, 70.57, 74.51, and 74.91 (br, CH of C_5H_4), 80.49 (m, C of C_5H_4), 125.30−139.15 (m, Ph), 169.78 (dd, $^2J_{CP}$ = 107.8 and 27.5 Hz, C≡N) ppm.

Synthesis of *cis,cis,cis*-[RuH_2(CN-2,6-$C_6H_3Me_2$)$_2$(dppf)] (5). NaOEt (4.04 mL of a 0.05 M solution in ethanol; 0.202 mmol) was added at room temperature to a solution of the complex *trans,cis,cis*-[$RuCl_2$(CN-2,6-$C_6H_3Me_2$)$_2$(dppf)] (**2d**; 0.100 g; 0.101 mmol) in 20 mL of ethanol. The reaction mixture was heated at 80 °C for 2 h and then evaporated to dryness. The solid residue was extracted with toluene (ca. 20 mL) and filtered over Kieselguhr. Evaporation of the solvent gave a yellow solid, which was washed with hexanes (5 × 10 mL) and vacuum-dried. Yield: 83% (0.077 g). Anal. Calcd for $FeRuC_{52}H_{48}N_2P_2$: C, 67.90; H, 5.26; N, 3.05. Found: C, 67.82; H, 5.24; N, 3.01. IR (KBr, cm^{-1}): ν 1955 and 1999 (Ru−H), 2014 and 2073 (C≡N). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 42.97 and 51.22 (d, $^2J_{PP}$ = 25.7 Hz) ppm. ^1H NMR (C_6D_6): δ −7.08 (ddd, 1H, $^2J_{HP}$ = 78.9 and 33.4 Hz, $^2J_{HH}$ = 5.0 Hz, Ru−H), −6.62 (ddd, 1H, $^2J_{HP}$ = 27.5 and 22.8 Hz, $^2J_{HH}$ = 5.0 Hz, Ru−H), 2.09 and 2.15 (s, 6H each, CH_3), 3.94 (br, 4H, C_5H_4), 4.29 (br, 2H, C_5H_4), 4.56 and 4.88 (br, 1H each, C_5H_4), 6.55−8.40 (m, 26H, Ph) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 19.12 and 19.17 (s, CH_3), 70.89, 71.51, 71.96, and 72.25 (d, $^2J_{CP}$ = 5.1 Hz, CH of C_5H_4), 74.71, 75.08, 75.58, and 77.39 (d, $^3J_{CP}$ = 9.4 Hz, CH of C_5H_4), 83.39 and 83.88 (d, $^1J_{CP}$ = 76.1 Hz, C of C_5H_4), 125.50−142.60 (m, Ph), 178.38 (dd, $^2J_{CP}$ = 89.1 and 9.1 Hz, C≡N), 181.07 (dd, $^2J_{CP}$ = 11.3 and 8.3 Hz, C≡N) ppm.

Table 3. Crystal Data and Structure Refinement Details for 2d

chem formula	$FeRuC_{52}H_{46}Cl_2N_2P_2$
fw	988.67
T (K)	296(2)
wavelength (Å)	1.541 84
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
cryst size, mm	0.28 × 0.12 × 0.10
a, Å	9.5193(2)
b, Å	15.2348(3)
c, Å	31.1384(5)
α, deg	90
β, deg	98.135(1)
γ, deg	90
Z	4
V, Å^3	4470.39(15)
ρ_{calcd}, g cm^{-3}	1.469
μ, mm^{-1}	7.408
F(000)	2024
θ range, deg	2.87−64.09
index ranges	$-10 \le h \le 11$ $-17 \le k \le 16$ $-35 \le l \le 32$
completeness to θ = 64.09	98.9
no. of data collected	26 943
no. of unique data	7350 (R_{int} = 0.0491)
no. params/restraints	725/0
refinement method	full-matrix least squares on F^2
goodness of fit on F^2	1.033
R1[a] ($I > 2\sigma(I)$)	0.0288
wR2[a] ($I > 2\sigma(I)$)	0.0726
R1 (all data)	0.0351
wR2 (all data)	0.0762
largest diff peak and hole, e Å^{-3}	0.311 and −0.358

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

General Procedure for Catalytic Transfer Hydrogenation of Ketones. Under an inert atmosphere, the ketone (5 mmol), the ruthenium catalyst precursor (0.02 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 Complex 2d. Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a saturated solution of the complex in dichloromethane. The most relevant crystal and refinement data are collected in Table 3. A yellow single crystal with prismatic shape was mounted on a glass fiber and transferred to a Bruker SMART 6K CCD area-detector three-circle diffractometer (Cu Kα radiation, λ = 1.541 84 Å).[33] X-ray data were collected at 296(2) K, with a combination of three

runs at different φ and 2θ angles. The data were collected using 0.3° wide ω scans (8 s/frame at $2\theta = 40°$ and 25 s/frame at $2\theta = 100°$) with a crystal-to-detector distance of 4.0 cm. The substantial redundancy in data allows empirical absorption corrections (SADABS)[34] to be applied using multiple measurements of symmetry-equivalent reflections (ratio of minimum to maximum apparent transmission 0.663 230). A total number of 26 943 reflections were collected, with 7350 independent reflections ($R_{int} = 0.0491$). The unit cell parameters were obtained by full-matrix least-squares refinements of 9668 reflections. The raw intensity data frames were integrated with the SAINT program,[35] which also applied corrections for Lorentz and polarization effects.

The software package WINGX was used for space group determination, structure solution, and refinement.[36] The space group determination was based on a check of the Laue symmetry and systematic absences and ascertained from the structure solution. The structure was solved by Patterson interpretation and phase expansion using DIRDIF,[37] completed with difference Fourier syntheses, and refined with full-matrix least squares using SHELXL-97.[38] Weighted R factors (R_w) and all goodness of fit values S are based on F^2; conventional R factors (R) are based on F. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located by difference maps and refined isotropically. The function minimized was $[\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0439P)^2 + 2.2802P]$ 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 ref 39. Geometrical calculations were made with PARST.[40] Plots were made with PLATON.[41]

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Supporting Information Available: Tables giving X-ray crystallographic data for the structure determination of complex **2d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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