Ruthenium Phosphine/Diimine Complexes: Syntheses, Characterization, Reactivity with Carbon Monoxide, and Catalytic Hydrogenation of Ketones†

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The cis-[$RuCl_2(PPh_3)_2(N-N)$] (N−N = bipy (**1**), Me-bipy (**2**), phen (**3**), and bathophen (**4**)) complexes were used to synthesize five new electron-rich phosphine-containing complexes *cis*-[$RuCl_2$(dcype)(N−N)] (N−N = bipy (**1a**), Me-bipy (**2a**), phen (**3a**), and bathophen (**4a**)) and *cis*-[$RuCl_2(PEt_3)_2$(bipy)] (**1c**) by phosphine exchange. These complexes were obtained and characterized by NMR ($^{31}P\{^1H\}$, ^1H), cyclic voltammetry, and elemental analysis. Electrochemical studies of these complexes reveal a single reduction process (Ru^{III}/Ru^{II}). These complexes are more easily oxidized than their analogues *cis*-[$RuCl_2$(dppb)(N−N)]. The reactivity of complexes *cis*-[$RuCl_2$(dcype)(N−N)] with carbon monoxide was tested, and dissociation of one chloride was observed, leading to the formation of four new cationic species with general formula [RuCl(CO)(dcype)(N−N)](PF_6) (bipy (**1b**), Me-bipy (**2b**), phen (**3b**), and bathophen (**4b**)). The complexes described here and elsewhere with general formulas *cis*-[$RuCl_2$(P−P)(N−N)], [RuCl(CO)(dcype)(N−N)](PF_6), and *cis*-[$RuCl_2(P)_2$(N−N)] were used as precatalysts in the transfer hydrogenation of functionalized aryl-ketones, and most of them were active. X-ray structures of *cis*-[$RuCl_2(PEt_3)_2$(bipy)] (**1c**) and [RuCl(CO)(dcype)(bipy)]-(PF_6) (**1b**) will be presented.

Introduction

It has been shown that complexes containing the "Ru(P−P)" (P−P = diphosphine) core per ruthenium atom are efficient catalysts in homogeneous catalyzed hydrogenation reactions. As a result, several ruthenium complexes containing this motif were synthesized and their properties were studied by spectroscopical and electrochemical techniques.[1−13] Recently Morris and coworkers[10] proposed a classification of several mechanisms for reduction of polar double bonds, mechanisms that involve hydrogenation of substrate by use of molecular hydrogen and those that hydrogen transfer from the solvent or other hydrogen source.

One of the most important mechanisms for H_2-hydrogenation of imines and ketones was proposed by Noyori,[9,11] and some insights were given by Morris[12,13] using mixed ruthenium phosphine and diamine complexes. These reactions lead themselves to selecting C=O or C=N bonds over C=C bonds by a ligand-assisted mechanism, where a ancillary ligand *cis* to the hydride must have an NH or OH group.[10] Noyori [14] has coined the term "metal−ligand bifunctional catalysis" to refer

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to the catalytic systems utilizing the outer sphere hydrogenation ligand-assisted mechanism.

Independent of the hydrogen source, which determines if the mechanism is hydrogen transfer or hydrogenation, the classification proposed by Morris[10] involves an outer sphere mechanism for reduction of C=O and C=N double bonds, and the substrate is reduced without coordination to the metal center. The other possibility involves the classical mechanism of coordination of the substrate to the metal center (inner sphere), and a vacant site at the metal coordination sphere is a requisite.[15a] As in the outer sphere, this also can follow either a hydrogen-transfer or hydrogenation pathway.

This topic has been attracting much attention, and as a result, recent published works developed by other research groups have presented different types of complexes that are very active in the hydrogenation of ketones including N-heterocyclic carbene (NHC) containing complexes.[14−18] N-heterocyclic carbenes can be applied with high activity in H_2-hydrogenation of inactivated internal olefins as described by Fogg and co-workers.[19a] The complex [RuHCl(CO)(NHC)(PPh_3)] is able to quantitatively hydrogenate cyclooctene within 10 min at 50 psi and 80 °C at low catalyst loading (0.05 mol % Ru).

Recently, Williams and co-workers showed the complex [$Ru(H)_2(CO)(Imes)(PPh_3)_2$] to be very active for direct and transfer hydrogenation of ketones in the absence of base based on an interesting C−H activation.[19b]

James and co-workers[20] have studied the hydrogenation of imines catalyzed by ruthenium complexes containing bidentate ligands. The complex [RuHCl(dppb)]$_3$ catalyzes the hydrogenation of $PhCH_2N$=CMePh at 20 °C, 1000 psi H_2 in MeOH.[7] Chloride-bridged dimers of the type [$RuCl_2$(P−P)]$_2$ and [Ru_2Cl_5(P−P)$_2$] were found to be more effective precatalysts under these conditions. Konno et al.[21] demonstrate that a hydride on ruthenium can be made hydridic by use of chelating terpyridine and bipyridine ligands in [RuH(terpy)(bipy)]$^+$, even though the complex carries a positive charge. Ketones and imines react with the dihydrogen complex [$Ru(H)_2(H_2)(PPh_3)_3$] at 20 °C and with *cis*-[$RuH_2(PPh_3)_4$] at about 60 °C.[22−25] By contrast, the complexes [Ru(H)(Cl)(CO)(PPh_3)$_3$] and [Ru(H)(Cl)(CO)(PPh_3)(diphosphine)] with electron-withdrawing CO and Cl groups and aryl-substituted phosphines do not readily react with ketones and become active as catalysts only at relatively elevated temperatures, >100 °C.[26−28] Parenthetically the anionic hydride complex [$Ru(H)_3(CO)$(dcypb)]$^-$, dcypb = $PCy_2(CH_2)_4PCy_2$, is an active catalyst for the hydrogenation and transfer hydrogenation of benzophenone.[29] The active species in ^{i}PrOH is postulated to be [$Ru(H)_2(H_2)(CO)$(dcypb)] by analogy with [$Ru(H)_2(H_2)(PPh_3)_3$].[27] This catalyst system is an exception to the rule that carbonyl ligands are deactivating; this may be specific for aromatic phosphine-containing complexes. Here the bulky, electron-donating diphosphine ligand dcypb counterbalances the presence of the electron-withdrawing CO ligand, and both hydrogenation and the hydrogen-transfer mechanism appear to apply.

Jun and co-workers studied the effect of polydentate versus monodentate ligands on the activity of catalysts for the hydrogenation of cyclohexanone and propanal.[28] For cyclohexanone, the activity of monohydrides of the type [RuHCl(CO)(PR_3)$_3$] increased as (PR_3)$_3$ = monodentate (PPh_3)$_3$ < bidentate ($PPh_2CH_2CH_2PPh_2$) < tridentate (PPh_2CH_2)$_3$CMe. Cationic complexes containing phosphorus and nitrogen donors with the general formula [$RuCl(PPh_3)_2$(*P*,*N*,*N*′-$PPh_{3-x}(py)_x$)](PF_6) (x = 2, 3, py = 2-pyridyl) catalyze the hydrogenation of an aldimine at 20 °C, 36 atm H_2 in MeOH.[30] The complex [RuH(Tp*)(cod)], Tp* = hydrido-tris(3,5-dimethylpyrayoyl)borate, cod = 1,5-cyclooctadiene, affords the bis-dihydrogen complex [RuH(Tp*)(H_2)$_2$], and the last one is an H_2-hydrogenation catalyst and ^{i}PrOH transfer hydrogenation catalyst for ketones.[31] These are rare examples of a Ru hydrogenation catalyst without phosphine ligands.

More enhancements are the result of the achievement of Morris and co-workers[32] for H_2-hydrogenation of acetophenone with respect to the changes in the properties of the dihydride complexes by successively replacing the amine donor groups. For the complexes [RuHCl(N−N)(PPh_3)$_2$] (where N−N = 2,2′-bipyridine, bipy, or 1,10-phenanthroline, phen) that have *cis*-phosphine but no amino group coordinated, the hydrogenation of acetophenone in benzene (or without additional solvent) was not observed, despite the presence of an excess of KO^{t}Bu. However when 2-(aminomethyl)pyridine or 1,2-(*R*,*R*)-diaminocyclohexane was used as the N-donor group, the reduction of acetophenone was quantitatively achieved. Here we present the syntheses, characterization, electrochemistry, and NMR behavior of complexes with the general formula *cis*-[$RuCl_2$(dcype)(N−N)] and *cis*-[$RuCl_2(PEt_3)_2$(bipy)] (see Scheme 1) and the carbonyls [RuCl(CO)(dcype)(N−N)](PF_6). The new *cis*-[$RuCl_2$-

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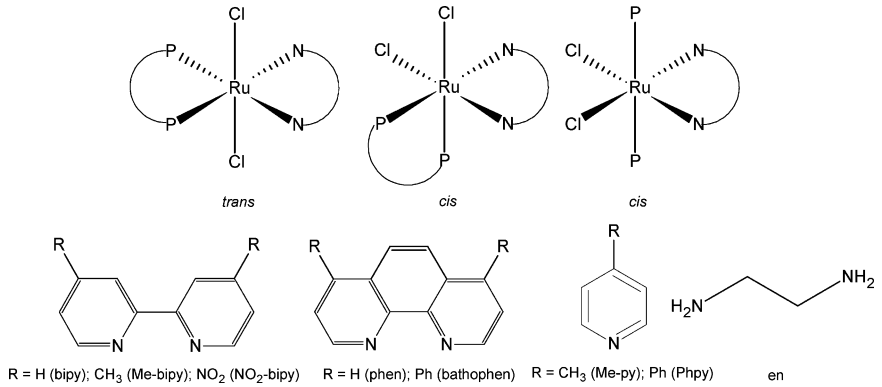
Scheme 1. Geometries for the Complexes Studied in This Work[a]



[a] P−P = dppb for *trans*, dcype for *cis*; P = PPh_3 and PEt_3; N−N = ethylenediamine, diimines, or monopyridines.

(dcype)(N−N)] complexes, *cis*-[$RuCl_2(PEt_3)_2$(bipy)], [RuCl(CO)(dcype)(N−N)](PF_6), and other compounds previously synthesized in our research group were used as precatalysts in reduction reactions of acetophenone and substituted ones in ^{i}PrOH and in the presence or absence of KOH as base and in the presence or absence of dihydrogen in order to verify the activity of such complexes containing no protic N−H group and to evaluate the mechanism of hydrogen transfer or hydrogenation. X-ray diffraction structures of *cis*-[$RuCl_2$-(PEt_3)$_2$(bipy)] (**1c**) and [RuCl(CO)(dcype)(bipy)](PF_6) (**1b**) were determined and will be discussed.

Experimental Section

Materials and Instrumentation. All manipulations were carried out under purified argon using standard Schlenk techniques. Reagent grade solvents were appropriately distilled and dried before use. The $RuCl_3 \cdot 3H_2O$ was supplied by Johnson Matthey Ltd. or purchased from Aldrich. Triphenylphosphine (PPh_3) (Aldrich), 1,4-bis(diphenylphosphino)-butane (dppb) (Aldrich), 1,2-bis(dicyclohexylphosphino)ethane (dcype) (Strem), triethylphosphine (PEt_3) (Strem), 2,2′-bipyridine (bipy) (Aldrich), 1,10 phenanthroline (phen) (Aldrich), and 4,7-diphenyl-1,10-phenanthroline (bathophen) (Aldrich) were used as received. 4,4′-Dimethyl-2,2′-bipyridine (Me-bipy) and 4,4′-dinitro-2,2′-bipyridine (NO_2-bipy) were synthesized following published procedures.[33]

The *cis* and *trans* used in the text refer to the position of chlorides with respect to each other.

The complexes *cis*-[$RuCl_2(PPh_3)_2$(bipy)] (**1**), *cis*-[$RuCl_2(PPh_3)_2$-(Me-bipy)] (**2**), *cis*-[$RuCl_2(PPh_3)_2$(phen)] (**3**), *cis*-[$RuCl_2(PPh_3)_2$-(bathophen)] (**4**), *cis*-[$RuCl_2$(dppb)(bipy)] (**5**), *trans*-[$RuCl_2$-(dppb)(bipy)] (**6**), *cis*-[$RuCl_2$(dppb)(phen)] (**7**), *trans*-[$RuCl_2$-(dppb)(phen)] (**8**), *trans*-[$RuCl_2$(dppb)(NO_2-bipy)] (**9**), *trans*-[$RuCl_2$(dppb)(4-Phpy)$_2$] (4-Phpy = 4-phenylpyridine) (**10**), *trans*-[$RuCl_2$(dppb)(Me-bipy)] (**11**), and *mer*-[$RuCl_3$(dppb)H_2O] (**12**) were prepared according to published procedures.[1,2,34]

Carbon monoxide used for synthesis of carbonyl compounds was generated from the dehydration reaction of formic acid by sulfuric acid.

Ultraviolet−visible (UV−vis) spectra were recorded in solution on a Hewlett-Packard 8452A diode array and are presented as λ_{max} (nm)/ϵ_{max} (M^{-1} cm^{-1}) or sh (shoulder). IR spectra were recorded as CsI pellets on a Bomem-Michelson 102 spectrophotometer. Cyclic voltammetry (CV) experiments were carried out at room temperature in CH_2Cl_2 using a BAS-100B/W, Bioanalytical Systems Instruments; the working and auxiliary electrodes were stationary Pt foils, and the reference electrode was Ag/AgCl, 0.10 M $Bu_4N^+ClO_4^-$ (TBAP) (Fluka Purum), a medium in which ferrocene is oxidized at 0.43 V (Fc^+/Fc). Elemental analyses were performed in the Chemistry Department of Universidade Federal de São Carlos.

The NMR data of the compounds were acquired using a Bruker DRX-400 or 200 spectrometer using $CDCl_3$ as deuterated solvent. Chemical shifts are reported with respect to the phosphorus signal of 85% phosphoric acid (H_3PO_4) for ^{31}P and the residual solvent proton for ^{1}H.

Syntheses of Complexes. Synthesis of *cis*-[$RuCl_2$-(dcype)(N−N)]. A representative synthesis is as follow for *cis*-[$RuCl_2$(dcype)(bipy)] (**1a**).

N−N = bipy (1a). dcype (50.0 mg, 0.118 mmol) was added to a CH_2Cl_2 (15 mL) suspension of [$RuCl_2(PPh_3)_2$(bipy)] (101.0 mg, 0.118 mmol). The resulting suspension was stirred at room temperature (RT) for 24 h. The resulting dark red solution was filtered in Celite to separate unreacted starting complex, the solution volume was reduced to ∼5 mL, and addition of *n*-hexane (10 mL) precipitated a red solid, which was collected, washed well with *n*-hexane, and dried under vacuum. Yield: 84.0 mg, 94%. Anal. Calcd for $C_{36}H_{56}Cl_2N_2P_2Ru$: exptl (calc) C, 57.61 (57.59); H, 7.50 (7.52); N, 3.69 (3.73). ^{31}P{^{1}H} NMR: δ(ppm) 64.8 (d, ^2J 20.5 Hz), 57.2 (d, ^2J 20.5 Hz). ^{1}H NMR (400 MHz, $CDCl_3$): aromatic hydrogens for bipy δ(ppm) 10.11 (d, 1H, ^3J = 5.49 Hz); 8.62 (d, 1H, ^3J = 5.86 Hz); 8.13 (d, 1H, ^3J = 8.10 Hz); 8.03 (d, 1H, ^3J = 7.84 Hz); 7.73 (ps t, 1H, ^3J = 7.72 Hz); 7.67 (ps t, 1H, ^3J = 7.94 Hz); 7.48 (ps t, 1H, ^3J = 6.42 Hz); 7.05 (ps t, 1H, ^3J = 6.42 Hz) 2.90−0.00 (overlaped signals, 44H cyclohexyl and 4H CH_2). UV−vis (CH_2Cl_2, 10^{-3} M): λ/nm (ϵ/M^{-1} cm^{-1}) 298 (2.2 × 10^4), 354 (4.1 × 10^3), 492 (3.6 × 10^3), 592sh (1.6 × 10^3).

N−N = Me-bipy (2a). dcype (49.9 mg, 0.118 mmol), [$RuCl_2$-(PPh_3)$_2$(Me-bipy)] (104.0 mg, 0.1181 mmol). Yield: 91.0 mg, 99%. Anal. Calcd for $C_{38}H_{60}Cl_2N_2P_2Ru$: exptl (calc) C, 58.61 (58.60); H, 7.75 (7.76); N, 3.56 (3.60). ^{31}P{^{1}H} NMR: δ(ppm) 64.6 (d, ^2J 20.0 Hz), 57.2 (d, ^2J 20.0 Hz). ^{1}H NMR (400 MHz, $CDCl_3$): aromatic hydrogens for Me-bipy δ(ppm) 10.00 (d, 1H, ^3J = 5.69 Hz); 8.42 (d, 1H, ^3J = 5.69 Hz); 7.60 (s, 1H); 7.80 (s, 1H); 7.29 (d, 1H, ^3J = 5.69 Hz); 6.82 (d, 1H, ^3J = 5.69 Hz); 3.48 (s, 3H, CH_3); 2.47 (s, 3H, CH_3'); 2.80−0.00 (overlaped signals, 44H cyclohexyl and 4H CH_2). UV−vis (CH_2Cl_2): λ/nm (ϵ/M^{-1} cm^{-1}) 295 (2.0 × 10^4), 349 (3.6 × 10^3), 433 (2.9 × 10^3), 478 (3.3 × 10^3), 572sh (1.6 × 10^3).

N−N = phen (3a). dcype (36.1 mg, 0.0885 mmol), $RuCl_2$-(PPh_3)$_2$(phen) (75.0 mg, 0.0885 mmol). Yield: 65.0 mg, 98%. Anal. Calcd for $C_{38}H_{56}Cl_2N_2P_2Ru$: exptl (calc) C, 58.99 (58.91); H, 7.27 (7.29); N, 3.60 (3.62). ^{31}P{^{1}H} NMR: δ(ppm) 64.5 (d, ^2J 22.0 Hz), 57.9 (d, ^2J 22.0 Hz). ^{1}H NMR (400 MHz, $CDCl_3$): aromatic hydrogens for phen δ(ppm) 10.44 (d, 1H, ^3J = 5.18 Hz); 9.03 (d, 1H, ^3J = 5.66 Hz); 8.40 (d, 1H, ^3J = 8.00 Hz);

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8.22 (d, 1H, ^3J = 8.00 Hz); 7.97 (d, 1H, ^3J = 8.82 Hz); 7.88 (d, 1H, ^3J = 8.52 Hz); 7.44 (dd, 1H, $^3J_1$ = 5.65 Hz, $^3J_2$ = 8.00 Hz); 7.02 (dd, 1H, $^3J_1$ = 5.33 Hz, $^3J_2$ = 8.13 Hz); 3.00−0.00 ppm (m, overlaped signals, 44H cyclohexyl and 4H CH_2). UV−vis (CH_2Cl_2): λ/nm (ϵ/M^{-1} cm^{-1}) 271 (3.4 × 10^4), 293sh (1.2 × 10^4), 473 (5.5 × 10^3), 586sh (1.8 × 10^3).

N−N = bathophen (4a). dcype (41.1 mg, 0.0972 mmol), [$RuCl_2(PPh_3)_2$(bathophen)] (100.0 mg, 0.0972 mmol). Yield: 88.0 mg, 98%. Anal. Calcd for $C_{50}H_{64}Cl_2N_2P_2Ru$: exptl (calc) C, 64.82 (64.78); H, 7.01 (6.96); N, 3.05 (3.02). $^{31}P\{^1H\}$ NMR: δ(ppm) 63.7 (d, ^2J 20.2 Hz), 56.5 (d, ^2J 20.2 Hz). ^1H NMR (400 MHz, $CDCl_3$): aromatic hydrogens for bathophen δ(ppm) 9.12 (d, 1H, ^3J = 4.73 Hz); 7.99 (d, 1H, ^3J = 8.68 Hz); 7.87 (d, 1H, ^3J = 8.68 Hz); 7.85 (d, 1H, ^3J = 4.73 Hz); 7.54 (s, br, 5H); 7.50 (s, br, 5H); 3.50−0.15 ppm (m, overlaped signals, 44H cyclohexyl and 4H CH_2). UV−vis (CH_2Cl_2): λ/nm (ϵ/M^{-1} cm^{-1}) 283 (4.3 × 10^4), 317sh (1.3 × 10^4), 484 (7.3 × 10^3), 600sh (2.5 × 10^3).

***cis*-[$RuCl_2(PEt_3)_2$(bipy)] (1c).** PEt_3 (44 μL, 0.297 mmol), [$RuCl_2(PPh_3)_2$(bipy)] (100.0 mg, 0.117 mmol). Yield: 60.1 mg, 91%. Anal. Calcd for $C_{22}H_{38}Cl_2N_2P_2Ru$: exptl (calc) C, 46.78 (46.81); H, 6.82 (6.79); N, 5.00 (4.96). $^{31}P\{^1H\}$ NMR: δ(ppm) 7.0 (br s). ^1H NMR (400 MHz, $CDCl_3$, −10 °C): δ(ppm) 9.94 (br, 2H); 7.98 (br, 2H); 7.71 (br, 2H); 7.34 (br, 2H); 1.51 (br, 12H, CH_2-PEt_3); 0.68 (br, 18H, CH_3-PEt_3). UV−vis (CH_2Cl_2, 10^{-3}M): λ/nm (ϵ/M^{-1} cm^{-1}) 234 (5.5 × 10^3), 298 (6.1 × 10^3), 378 (1.6 × 10^3), 536sh (8.7 × 10^2). IR: ν_{Ru-Cl} (cm^{-1}) 252 and 232.

Syntheses of [RuCl(CO)(dcype)(N−N)](PF_6). A representative synthesis is as follows for [RuCl(CO)(dcype)(bipy)](PF_6) (**1b**).

N−N = bipy (1b). In a Schlenk tube complex **1** (50.0 mg, 0.0666 mmol) was dissolved in CH_2Cl_2 (10 mL). The tube was evacuated and refilled with CO(g). The red solution was stirred until a yellow solution was obtained. The solution was evaporated to dryness, the yellow residue was dissolved in CH_3OH (10 mL), and NH_4PF_6 (32.6 mg, 0.200 mmol) was added. The resulting yellow solution was stirred under argon atmosphere for 60 min. A yellow solid was obtained, which was filtered, washed with CH_3OH (2 × 5 mL) and *n*-hexane (2 × 5 mL), and dried under vacuum. Yield: 58.0 mg, 98%. Anal. Calcd for $C_{37}H_{56}ClN_2P_2ORuPF_6$: exptl (calc) C, 49.99 (50.03); H, 6.29 (6.35); N, 3.10 (3.15). $^{31}P\{^1H\}$ NMR: δ(ppm) 64.9 (d, ^2J 16.3 Hz), 32.5 (d, ^2J 16.3 Hz). ^1H NMR (400 MHz, $CDCl_3$): aromatic hydrogens for bipy δ(ppm) 9.95 (d, 1H, ^3J = 5.48 Hz); 8.49 (d, 1H, ^3J = 5.48 Hz); 8.41 (d, 1H, ^3J = 7.98 Hz); 8.37 (d, 1H, ^3J = 8.10 Hz); 8.18 (ps t, 1H, ^3J = 7.87 Hz); 8.12 (ps t, 1H, ^3J = 7.75 Hz); 7.80 (ps t, 1H, ^3J = 6.67 Hz); 7.68 (ps t, 1H, ^3J = 6.67 Hz); 3.02−(−0.11) ppm (overlaped signals, 44H cyclohexyl and 4H CH_2). UV−vis (CH_2Cl_2, 10^{-3} M): λ/nm (ϵ/M^{-1} cm^{-1}) 247 (2.2 × 10^4), 290 (2.2 × 10^4), 314sh (1.1 × 10^4), 355 (4.5 × 10^3). IR: ν_{CO} (cm^{-1}) 1984.

N−N = Me-bipy (2b). Complex **2** (60.0 mg, 0.0770 mmol), NH_4PF_6 (37.6 mg, 0.231 mmol). Yield: 69.8 mg, 99%. Anal. Calcd for $C_{39}H_{60}ClN_2P_2ORuPF_6$: exptl (calc) C, 51.17 (51.12); H, 6.65 (6.60); N, 3.10 (3.06). $^{31}P\{^1H\}$ NMR: δ(ppm) 65.1 (d, ^2J 17.3 Hz), 31.8 (d, ^2J 17.3 Hz). ^1H NMR (400 MHz, $CDCl_3$): aromatic hydrogens for Me-bipy δ(ppm) 9.71 (d, 1H, ^3J = 5.70 Hz); 8.25 (d, 1H, ^3J = 5.70 Hz); 8.22 (s, 1H); 8.17 (s, 1H); 7.55 (d, 1H, ^3J = 5.70 Hz); 7.44 (d, 1H, ^3J = 5.70 Hz); 2.66 (s, 3H, CH_3); 2.59 (s, 3H, CH_3); 2.40−0.00 ppm (overlaped signals, 44H cyclohexyl and 4H CH_2). UV−vis (CH_2Cl_2, 10^{-3} M), λ/nm (ϵ/M^{-1} cm^{-1}) 252 (7.9 × 10^3), 287 (8.4 × 10^3), 311sh (4.1 × 10^3), 350 (1.7 × 10^3). IR: ν_{CO} (cm^{-1}) 1979.

N−N = phen (3b). Complex **3** (55.0 mg, 0.0710 mmol), NH_4PF_6 (34.7 mg, 0.213 mmol). Yield: 62.2 mg, 96%. Anal. Calcd for $C_{39}H_{56}ClN_2P_2ORuPF_6$: exptl (calc) C, 51.41 (51.34); H, 6.23 (6.19); N, 3.10 (3.07). $^{31}P\{^1H\}$ NMR: δ(ppm) 66.1 (d, ^2J 16.9 Hz), 32.2 (d, ^2J 16.9 Hz). ^1H NMR (400 MHz, $CDCl_3$): aromatic hydrogens for phen δ(ppm) 10.22 (d, 1H, ^3J = 5.36 Hz); 8.92 (d, 1H, ^3J = 5.33 Hz); 8.62 (d, 1H, ^3J = 8.23 Hz); 8.56 (d, 1H, ^3J = 8.13 Hz); 8.23 (dd, 1H, $^3J_1$ = 5.36 Hz, $^3J_2$ = 8.23 Hz); 8.12 (d, 1H, ^3J = 8.83 Hz); 8.08 (d, 1H, ^3J = 8.83 Hz); 7.68 (dd, 1H, $^3J_1$ = 5.33 Hz, $^3J_2$ = 8.13 Hz); 3.12−(−1.01) ppm (m, overlaped signals, 44H cyclohexyl and 4H CH_2). UV−vis (CH_2Cl_2, 10^{-3} M): λ/nm (ϵ/M^{-1} cm^{-1}) 264 (1.2 × 10^4), 274 (1.1 × 10^4), 335sh (2.2 × 10^3), 371sh (1.6 × 10^3). IR: ν_{CO}(cm^{-1}) 1984.

N−N = bathophen (4b). Complex **4** (45.5 mg, 0.0491 mmol), NH_4PF_6 (24.0 mg, 0.147 mmol). Yield: 44.6 mg, 98%. Anal. Calcd for $C_{51}H_{64}ClN_2P_2ORuPF_6$: exptl (calc) C, 57.50 (57.54); H, 5.99 (6.06); N, 2.59 (2.63). $^{31}P\{^1H\}$ NMR: δ(ppm) 65.6 (d, ^2J 16.8 Hz), 32.2 (d, ^2J 16.8 Hz). ^1H NMR (400 MHz, $CDCl_3$): aromatic hydrogens for bathophen δ(ppm) 10.29 (d, 1H, ^3J = 5.25 Hz); 8.96 (d, 1H, ^3J = 5.01 Hz); 8.20 (d, 1H, ^3J = 5.25 Hz); 8.11 (s, 2H); 7.91 (d, 1H, ^3J = 5.01 Hz); 7.40−7.80 (s, 10H, phenyl-bathophen); 3.1−(−1.00) (overlaped m, 48H, cyclohexyl and CH_2-dcype). UV−vis (CH_2Cl_2, 10^{-3} M): λ/nm (ϵ/M^{-1} cm^{-1}) 272sh (2.7 × 10^4), 292 (3.4 × 10^4), 340 (1.3 × 10^4), 383sh (6.5 × 10^3). IR: ν_{CO} (cm^{-1}) 1977.

X-ray Crystallographic Analysis of *cis*-[$RuCl_2(PEt_3)_2$(bipy)][1c] and [RuCl(CO)(dcype)(bipy)](PF_6).[1b] X-ray data of crystals for compounds **1c** and **1b** were measured on an Enraf-Nonius Kappa-CCD diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. Data were collected up to 50° in 2θ, with a redundancy of 4, and the final unit cell parameters were based on all reflections. Data collections were carried out using the COLLECT program,[35] integration and scaling of the reflections were performed with the HKL Denzo-Scalepack system of programs,[36] and absorption corrections were carried out using the multiscan method.[37] The structures were solved by direct methods with SHELXS-97,[38] and models were refined by full-matrix least-squares on F^2 using SHELXL-97.[39] All hydrogen atoms were stereochemically positioned and refined with the riding model.[39]

Table 1 summarizes data collection and experimental details for complexes **1c** and **1b**, whereas relevant interatomic bond lengths, bond angles, and ORTEP[40] projections of the structures are shown in Figure 1 and Figure 2.

Coordinates and other crystallographic data have been deposited with the CCDC, deposition code 261843 for complex **1c** and 261842 for complex **1b**.

Results and Discussion

Synthesis and Characterization of Ruthenium Diimine Complexes. The chemical reactivity of the dcype ligand with complexes such as *cis*-[$RuCl_2(PPh_3)_2$(N−N)] allowed us to synthesize complexes with general formula *cis*-[$RuCl_2$(dcype)(N−N)] containing the "Ru(P−P)(N−N)" core in mild conditions by simple phosphine exchange (see Scheme 2).

Using this methodology it was possible to obtain only the *cis*-isomer, even when reactions were carried out "in situ" in the absence of light. Using $^{31}P\{^1H\}$ NMR the *trans*-isomers were not observed and the formation of *cis*-isomers was easily attributed since two well-defined doublets were observed.

It is interesting to point out that using the [$RuCl_2$(dppb)]$_2$(μ-dppb) or [$RuCl_2$(dppb)(PPh_3)] complexes as a precursor the *trans*-[$RuCl_2$(dppb)(N−N)][1] isomers are

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(39) Sheldrick, G. M. *SHELXL-97*, Program for Crystal Structures Analysis; University of Göttingen: Göttingen, Germany, 1997.
(40) Farrugia, L. J. ORTEP3 for Windows. *J. Appl. Crystallogr.* **1997**, *30*, 565.

Table 1. Crystal Data, Data Collection, Solution, and Refinement for 1c and 1b

	cis-[$RuCl_2(PEt_3)_2$(bipy)] (**1c**)	[RuCl(CO)(dcype)(bipy)]PF_6 (**1b**)
empirical formula	$C_{22}H_{38}N_2P_2Cl_2Ru$	$C_{37}H_{54}ClN_2OP_2Ru(PF_6)$
fw	564.45	886.25
temperature	120(2) K	120(2) K
wavelength	0.71073 Å	0.71073 Å
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
unit cell dimens	a = 9.2517(3) Å, α = 73.489(2)°	a = 10.6084(3) Å, α = 93.125(2)°
	b = 10.7705(3) Å, β = 73.682(2)°	b = 13.1357(4) Å, β = 105.887(2)°
	c = 15.3802(4) Å, γ = 64.955(1)°	c = 15.0116(5) Å, γ = 100.942(2)°
volume	1308.25(7) $Å^3$	1962.8(1) $Å^3$
Z	2	2
density(calcd)	1.433 Mg/m^3	1.500 Mg/m^3
absorp coeff	0.937 mm^{-1}	0.651 mm^{-1}
F(000)	584	916
cryst size	0.24 × 0.17 × 0.02 mm^3	0.16 × 0.08 × 0.02 mm^3
θ range for data collection	3.82 to 27.56°	2.81 to 25.00°
index ranges	$-12 \le h \le 12$, $-14 \le k \le 13$, $-19 \le l \le 19$	$-12 \le h \le 12$, $-15 \le k \le 15$, $-17 \le l \le 17$
no. of reflns collected	11356	24287
no. of indep reflns	5972 [R(int) = 0.0202	6904 [R(int) = 0.0592
completeness to θ	99.4% (θ = 27.56°)	99.9% (θ = 25.00°)
absorp corr	semiempirical from equivalents	multiscan
max. and min. transmn	0.9815 and 0.8063	0.9871 and 0.9030
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
computing[a]	COLLECT, HKL Denzo and Scalepack, SHELXS-97, SHELXL-97	COLLECT, HKL Denzo and Scalepack, SHELXS-97, SHELXL-97
no. of data/restraints/params	5972/0/268	6904/0/463
goodness-of-fit on F^2	1.048	1.040
final R indices [$I > 2\sigma(I)$]	R1 = 0.0340, wR2 = 0.0826	R1 = 0.0346, wR2 = 0.0785
R indices (all data)	R1 = 0.0455, wR2 = 0.0891	R1 = 0.0501, wR2 = 0.0851
largest diff peak and hole	0.476 and −0.630 e·$Å^{-3}$	0.628 and −0.911 e·$Å^{-3}$

[a] Data collection, data processing, structure solution, and structure refinement, respectively.

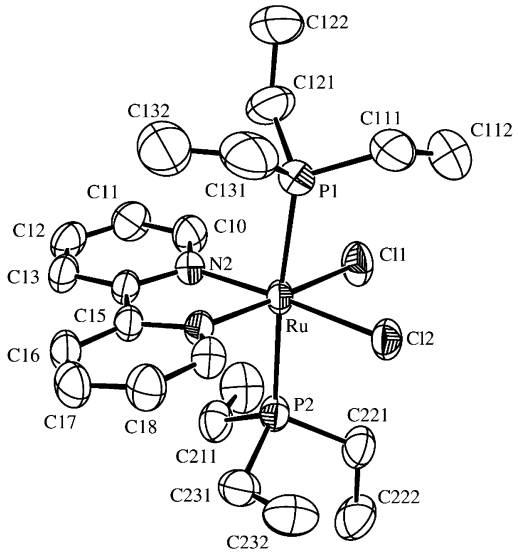

Figure 1. ORTEP view of the complex *cis*-[$RuCl_2(PEt_3)_2$(bipy)] showing the atom labeling and 50% probability ellipsoids. Bond lengths (Å): Ru−N(1) 2.040(2); Ru−N(2) 2.042(2); Ru−P(2) 2.3699(7); Ru−P(1) 2.3699(7); Ru−Cl(2) 2.4419(6); Ru−Cl(1) 2.4630(7). Bond angles (deg): N(1)−Ru−N(2) 79.07(8); N(1)−Ru−P(2) 88.40(6); N(2)−Ru−P(2) 91.80(6); N(1)−Ru−P(1) 93.66(6); N(2)−Ru−P(1) 93.45(6); P(2)−Ru−P(1) 174.64(2); N(1)−Ru−Cl(2) 95.85(6); N(2)−Ru−Cl(2) 174.88(6); P(2)−Ru−Cl(2) 87.39(2); P(1)−Ru−Cl(2) 87.47(2); N(1)−Ru−Cl(1) 172.31(6); N(2)−Ru−Cl(1) 93.82(6); P(2)−Ru−Cl(1) 88.92(3); P(1)−Ru−Cl(1) 89.65(3); Cl(2)−Ru−Cl(1) 91.23(2).

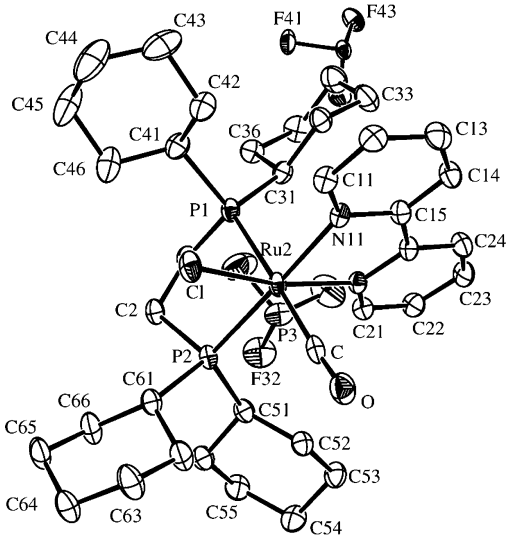

Figure 2. ORTEP view of the complex [RuCl(CO)(dcype)(bipy)](PF_6), showing the atom labeling and 50% probability ellipsoids. Bond lengths (Å): Ru−C 1.884(3); Ru−N(21) 2.107(2); Ru−N(11) 2.139(2); Ru−P(2) 2.3628(7); Ru−P(1) 2.4443(8); Ru−Cl 2.4057(7); C−O 1.139(4). Bond angles (deg): C−Ru−N(21) 91.07(11); C−Ru−N(11) 87.15(11); N(21)−Ru−N(11) 77.23(9); C−Ru−P(2) 92.05(9); C−Ru−P(1) 175.97(9); Ru−C−O 176.3(3); P(2)−Ru−P(1) 84.71(3).

obtained and the corresponding *cis*-isomers can be easily isolated by photochemical isomerization of the *trans*-isomer. The process can be followed by UV−vis,[1] $^{31}P\{^1H\}$ NMR,[41] or cyclic voltammetry.[42] The differences observed in the reactivity of the precursors consist in the fact that in the former case (Scheme 2) the precursor is a hexacoordinated species with the two chlorides in *cis*-position, and this configuration remains during the reaction leading to the formation of the thermodynami-

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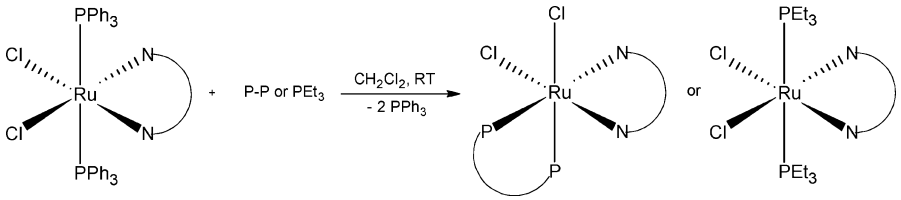
(42) Queiroz, S. L.; de Araujo, M. P.; Batista, A. A.; MacFarlane, K. S.; James, B. R. *J. Chem. Educ.* **2001**, *78*, 89.

Scheme 2. Synthesis of *cis*-[RuCl$_2$(P−P)(N−N)] and *cis*-[RuCl$_2$(PEt$_3$)$_2$(bipy)]



cally more stable product (*cis*-isomer, in this case is also the kinetic product). This is observed even when the reaction is carried out in the dark. For the latter, the precursors are pentacoordinated with the two chlorides in *trans*-position, and substitution of the bridging dppb or PPh_3 leads to the formation of a kinetic product (*trans*-isomer), which in the presence of light isomerizes to the *cis*-isomer (thermodynamic product).

To confirm that the absence of the *trans*-isomers is a function of the starting compound and not due to the diphosphine type, the same reaction using complex **1** was carried out using the dppb diphosphine, and the same result was achieved; in another words, the *trans*-isomer was again not observed.

The $^{31}P\{^1H\}$ NMR spectrum of *cis*-[RuCl$_2$(dcype)(bipy)] (**1a**) in dry CH_2Cl_2 presents a well-defined AX system with chemical shifts at 64.8 ppm (d) and at 57.2 ppm (d) (^2J = 20.5 Hz), which is consistent with a structure in which the chlorides are mutually in *cis*-position; another confirmation can be found from observation of resonances for two nonequivalent ortho-hydrogens of diimine ligands, in agreement with the unsymmetrical form (*cis*-isomer). The presence of two resonances for the methyl groups of 4,4′-dimethyl-2,2′-bipyridine (Me-bipy) (3.48 and 2.47 ppm, singlets) also supports the *cis*-isomer formation.

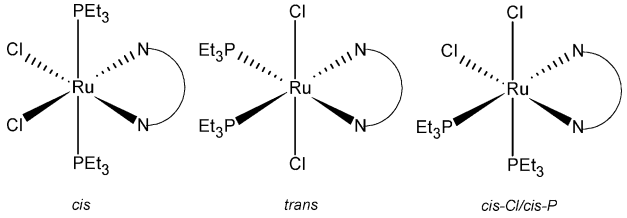
Complex **1a** easily dissociates one chloride in the presence of a donor species, such as H_2O and CH_3CN. A CH_2Cl_2 solution with traces of water causes the broadening of the two doublets, indicating that a dynamic process is occurring. When CH_3CN is added to a CH_2Cl_2 solution of *cis*-[RuCl$_2$(dcype)(bipy)], four new doublets are observed and are attributed to the formation of two isomers of the solvento complex [RuCl(CH_3-CN)(dcype)(bipy)]Cl, δ 67.08 and 60.86 ppm (^2J = 17.01 Hz) (CH_3CN *trans* to nitrogen) and δ 62.04 and 60.63 ppm (^2J = 19.86 Hz) (CH_3CN *trans* to phosphorus). This attribution is based on similarities of donor atoms *trans* to phosphorus. When CH_3CN is *trans* to a phosphorus atom, both phosphorus atoms are *trans* to nitrogen donors, one nitrogen from 2,2′-bipyridine and another from CH_3CN.

This characteristic is also observed for the complex *cis*-[RuCl$_2$(dppb)(bipy)] (**5**),[1a] but the chloride dissociation is faster for the dcype analogues. This difference observed in the dissociation rates can be explained by the presence of the more basic diphosphine (dcype) increasing the electron density on ruthenium and making easier the chloride dissociation.

The [RuCl$_2$(dcype)(bipy)] (**1a**) and [RuCl$_2$(dcype)(Me-bipy)] (**2a**) complexes were also structurally characterized by X-ray crystallography, but unfortunately the selected crystals did not allow complete refinement of the structure (the structures were refined to R_w 0.2403 and 0.2974, respectively). The determined bond lengths and angles are not sufficiently accurate for meaningful discussion; however, useful information may still be gleaned from the diffraction study, especially the connectivity; thus the X-ray structures are concordant with the isomer detected in solution by $^{31}P\{^1H\}$ and ^1H NMR.

Complex **1a** is chiral at Ru, crystallizing as a racemate, and the asymmetric unit shows two independents molecules, the two enantiomers (Λ and Δ). The unit cell was found to contain four molecules of the complex, as two enantiomeric pairs. The same behavior was observed for the structure of complex **2a**, but in this case the unit cell was found to contain two molecules as an enantiomeric pair.

Scheme 3. Isomeric Forms of *cis*-[RuCl$_2$(PEt$_3$)$_2$(bipy)] (1c)



The [RuCl$_2$(PEt$_3$)$_2$(bipy)] (**1c**) complex was synthesized by the same pathway used for synthesis of the *cis*-[RuCl$_2$(dcype)(N−N)] complexes. Its $^{31}P\{^1H\}$ NMR spectrum shows a singlet (δ 7.00 ppm), and ^1H NMR also reveals a symmetric structure since only one singlet at δ 9.94 ppm was observed for the ortho-hydrogens of the 2,2′-bipyridine derivative. Both $^{31}P\{^1H\}$ and ^1H NMR data suggest a symmetrical form for complex **1c**; thus the *cis-Cl/cis-P* isomer can be disregarded (see Scheme 3). The IR spectrum of the complex revealed the presence of two ν_{Ru-Cl} stretching vibrations (252 and 232 cm^{-1}), indicating chlorides in *cis*-position to each other and allowing the attribution of the structure as *cis* (Scheme 3).

The confirmation of the suggested structure for the *cis*-[RuCl$_2$(PEt$_3$)$_2$(bipy)] complex was obtained from the X-ray experiment (Figure 1), in which the chlorides are in *cis*-position and the phosphorus are mutually in *trans*-position. The geometry around ruthenium is slightly distorted octahedral, as shown by P(1)−Ru−P(2) and N(1)−Ru−Cl(2) angles (174.64(2)° and 95.85(6)°, respectively). The Ru−P distances for **1c** (2.3699(2) Å for both Ru−P) are longer than its analogous complex *cis*-[RuCl$_2$(PPh$_3$)$_2$(bipy)][43] (**1**) (av 2.3317 Å). The Ru−Cl bond lengths are quite longer for **1c** (av 2.4525 Å) than for **1** (av 2.4082 Å) due to higher electron density on Ru of the PEt_3 derivative, and consequently the Ru−N bond lengths of *cis*-[RuCl$_2$(PEt$_3$)$_2$(bipy)] (2.040(2) and 2.042(2) Å) are shorter than those observed for complex **1** (2.089(4) and 2.090(4) Å).

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Table 2. NMR and Electrochemical Data for the New Complexes Synthesized in This Work

complex	$^{31}P\{^{1}H\}$, δ(ppm)	^{2}J(Hz)	$E_{1/2}$ (V)
cis-[$RuCl_2$(dcype)(bipy)]	64.8(d), 57.2(d)	20.5	0.41
cis-[$RuCl_2$(dcype)(Me-bipy)]	64.6(d), 57.2(d)	20.0	0.35
cis-[$RuCl_2$(dcype)(phen)]	64.5(d), 57.9(d)	22.0	0.41
cis-[$RuCl_2$(dcype)(bathophen)]	63.7(d), 56.5(d)	20.2	0.42
cis-[$RuCl_2$(dppb)(bipy)]			0.60[a]
trans-[$RuCl_2$(dppb)(bipy)]			0.45[a]
cis-[$RuCl_2(PEt_3)_2$(bipy)]	2.0(s)		0.25
cis-[$RuCl_2(PPh_3)_2$(bipy)]			0.42[a]
[RuCl(CO)(dcype)(bipy)]PF_6	64.9(d), 32.5(d)	16.29	1.52[b]
[RuCl(CO)(dcype)(Me-bipy)]PF_6	65.1(d), 31.8(d)	17.29	1.50[b]
[RuCl(CO)(dcype)(phen)]PF_6	66.1(d), 32.2(d)	16.92	1.53[b]
[RuCl(CO)(dcype)(bathophen)]PF_6	65.6(d), 32.2(d)	16.82	1.52[b]

[a] Literature data (refs 1 and 18). [b] For these complexes the values are for E_p since the processes are irreversible.

Cyclic Voltammetric Studies of *cis*-[$RuCl_2$(dcype)(N−N)] and *cis*-[$RuCl_2(PEt_3)_2$(bipy)]. The half-wave potentials ($E_{1/2}$) for the $Ru^{III/II}$ couple for complexes with dcype (**1a**−**4a**) are less anodic than for the similar complexes containing the dppb ligand (see Table 2), showing clearly the effect of the electron-rich diphosphine (dcype) on the metal center.

The $E_{1/2}$ potentials for the *cis*-[$RuCl_2$(dcype)(N−N)] complexes are comparable with those potentials of the *trans*-isomers for the [$RuCl_2$(dppb)(N−N)] series, in which the competition between dppb and the bipy derivative ligands for the π-electrons of the ruthenium atom results in a more electron-rich metal center and the reduction potential decreases[1a] when compared to the *cis*-isomer. For example *cis*-[$RuCl_2$(dcype)(bipy)] presents $E_{1/2} = 0.41$ V, which is 0.19 and 0.04 V lower than *cis*- (0.60 V) and *trans*-[$RuCl_2$(dppb)(bipy)][1a] (0.45 V), respectively.

For the series *cis*-[$RuCl_2$(dcype)(N−N)] (**1a**−**4a**) the reduction potential follows the basicity of the diimine ligand; consequently the complex *cis*-[$RuCl_2$(dcype)(Me-bipy)] is more easily oxidized than the other three complexes due to the higher basicity of the Me-bipy compared with the other N-heterocyclic derivatives. As discussed above, the half-wave potential ($E_{1/2} = 0.25$ V) for the *cis*-[$RuCl_2(PEt_3)_2$(bipy)] complex is much lower than the potential for its analogue with triphenylphosphine, *cis*-[$RuCl_2(PPh_3)_2$(bipy)] ($E_{1/2} = 0.42$ V).[34]

Reactivity of *cis*-[$RuCl_2$(dcype)(N−N)] with Carbon Monoxide. When a dichloromethane solution of *cis*-[$RuCl_2$(dcype)(N−N)] (**1a**−**4a**) complexes is placed under an atmosphere of carbon monoxide, the color changes almost instantaneously from dark red to yellow. The yellow solids obtained from these solutions as a PF_6^- salt were characterized as cationic carbonyl complexes with general formula [RuCl(CO)(dcype)(N−N)](PF_6). The ν_{CO} is in the range 1984−1977 cm^{-1}, which is in agreement with a relatively strong π-interaction (back-bonding Ru→CO).

The $^{31}P\{^{1}H\}$ NMR spectra of **1b** and **2b** displayed two doublets, showing the magnetic nonequivalence of the two phosphorus atoms, indicating the formation of an unsymmetrical structure in which N−N ligands are not in the same plane of the dcype ligand. This was confirmed by ^{1}H NMR analysis by the observation of nonequivalent hydrogens of the N−N ligands. Especially, attention should be given to methyl resonances of 4,4′-dimethyl-2,2′-bipyridine in the complex [RuCl(CO)(dcype)(Me-bipy)](PF_6) (**2a**), which appear as two singlets at 2.66 and 2.59 ppm.

The large difference in chemical shift of one phosphorus atom (in ***bold***) compared with that observed in the precursor (for example for *cis*-[$RuCl_2$(dcype)(bipy)], δ (ppm) 64.8 and ***57.2*** and for [RuCl(CO)(dcype)(bipy)]$^+$ δ (ppm) 64.9 and ***32.5***) clearly shows that this phosphorus atom is in *trans*-position with the carbonyl group. The shielding observed for one phosphorus atom *trans* to the carbonyl group in the $^{31}P\{^{1}H\}$ NMR spectra is due to the *trans*-weakening caused by the carbonyl to Ru−P bonds, and this is in agreement with the observed shielding of phosphorus when *trans* to strong π-accepting groups, previously published by us and others.[1a,44a]

These behaviors, besides the fact that dcype is an electron-rich phosphine, suggest that the π-interaction between Ru and P atoms (of dcype) plays a role in the Ru−P bonding since it was noticed that for some NO^+ complexes (NO^+ is a stronger π-acceptor ligand than CO) it exerts little or no structural effects on *trans* π-innocent ligands (*trans*-influence), such as NH_3 or amino,[44b] and due to the observed existence of π-accepting properties for PMe_3.[45] In the absence of π-accepting ability for dcype, no great change in chemical shift ($^{31}P\{^{1}H\}$ NMR) or bond lengthening for Ru−P should be observed, but shielding of one phosphorus atom is observed, as discussed before for $^{31}P\{^{1}H\}$ NMR. The Ru−P bond lengthening *trans* to CO for complex [RuCl(CO)(dcype)(bipy)](PF_6) will be presented next.

The structure for **1b** has been unambiguously established by X-ray crystallography, and its ORTEP drawing is shown in Figure 2. The geometry around the ruthenium is slightly distorted octahedral, as evidenced by P(2)−Ru−P(1) = 84.71(3)° and C−Ru−P(2) = 92.05(9)°. As can be seen, the position of the CO in Figure 2 is *trans* to a phosphorus atom (C−Ru−P(1) 175.97(9)°), in agreement with $^{31}P\{^{1}H\}$ and ^{1}H NMR data.

The Ru−P bond lengths for [RuCl(CO)(dcype)(bipy)]$^+$ (Ru−P(2) 2.3628(7) Å and Ru−P(1) 2.4443(8) Å) are in the range observed for other complexes.[1,46,47] The Ru−P bond length for the phosphorus *trans* to the carbonyl group is longer than the Ru−P for phosphorus *trans* to nitrogen of bipyridine, in agreement with the inversely related chemical shift δ versus the Ru−P bond length

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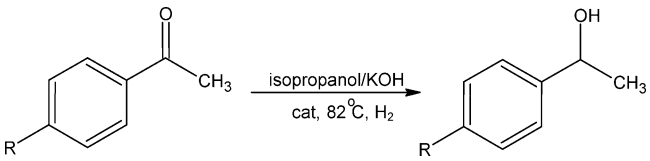
observed previously.[1a] The Ru−C distance (1.884(3) Å) for **1b** is slightly longer than for [Ru(dppe)(CO)(OTf)(Me-bipy)]$^+$ [46a] (Ru−C bond length 1.869(2) Å), but the C−O bond distance (1.139(4) Å) for **1b** is essentially the same as that found for [Ru(dppe)(CO)(OTf)(Me-bipy)]$^+$ (1.140(3) Å)[46b] and is within the usual range.[48−50]

Cyclic Voltammetric Studies of *cis*-[RuCl(CO)(dcype)(N−N)](PF$_6$). In the cyclic voltammogram of the series [RuCl(CO)(dcype)(N−N)](PF$_6$) only one irreversible, and monoelectronic reduction potential attributed to the couple Ru(III)/Ru(II) was observed. The E_p values found for these cationic carbonyl complexes [RuCl(CO)(dcype)(N−N)](PF$_6$) (see Table 2) are in agreement with the expected values since an increase of 0.60 V due to chloride substitution by the neutral ligand is expected.[51] The additional increasing is due to the presence of carbon monoxide shifting electron density from ruthenium and stabilizing the Ru(II) form.

Catalytic Hydrogenation of Ketones. Several complexes have been used and show high activity in the hydrogenation of ketones,[9−16] including work dealing with ruthenium and electron-rich pincer ligands.[52a]



Our experience on "Ru(P−P)" systems and in special N−N-containing "Ru(P−P)" complexes has led us to apply such complexes (with no "N−H" group) in the homogeneous reduction of imines and ketones.[1a−c,2,41,42] To extend the studies in the area of ketone reduction and searching for simple and active systems, we have started to study the catalytic activity of complexes with the "RuP$_2$N$_2$" core.

Several complexes were tested, prior to the use of [RuCl$_2$(P−P)(N−N)], as precatalyst for reduction of acetophenone in order to evaluate the activity, and most of them presented only diphosphine, such as [RuCl$_2$(dppb)]$_2$[4] (less than 20% of conversion, conditions were the same as used in Table 3).

The first complex to present good activity in such reactions was *cis*-[RuCl$_2$(dppb)(bipy)], and then after, applying other complexes (Table 3), we have decided to use electron-rich phosphines because electron-rich phosphine-containing complexes have the best activity compared with less electron-donating ones.[17d,52b] Due to availability, we have started to use triethylphosphine (PEt$_3$) and 1,2-bis(dicyclohexylphosphino)ethane (dcype) for the syntheses of analogous complexes.

Table 3. Results for Hydrogenation of Acetophenone Using Several Metal Complexes

entry	precatalyst	time (h)	conversion (%)[a]
1	*cis*-[RuCl$_2$(dppb)(bipy)]	3.0	78
2	*cis*-[RuCl$_2$(dppb)(phen)]	3.0	78
3	*mer*-[RuCl$_3$(dppb)H$_2$O]	3.0	28
4	*mer*-[RuCl$_3$(dppb)H$_2$O]/ethylenodiamine	3.0	80[c]
5	*mer*-[RuCl$_3$(dppb)H$_2$O]/phen	3.0	77[c]
6	*cis*-[RuCl$_2$(dppb)(bipy)]	24	50[d]
7	*trans*-[RuCl$_2$(dppb)(4-Mepy)$_2$]	3.0	33
8	*trans*-[RuCl$_2$(dppb)(4-Phpy)$_2$]	3.0	41
9	*cis*-[RuCl$_2$(PPh$_3$)$_2$(bipy)]	2.5	90
10	*cis*- [RuCl$_2$(PPh$_3$)$_2$(Me-bipy)]	3.0	81
11	*cis*- [RuCl$_2$(PEt$_3$)$_2$(bipy)]	12	50
12	*cis*-[RuCl$_2$(dcype)(bipy)]	2.5	>99
13	*cis*-[RuCl$_2$(dcype)(Me-bipy)]	2.5	86
14	*trans*-[RuCl$_2$(dppb)(NO$_2$-bipy)]	3.0	50
15	*trans*-[RuCl$_2$(dppb)(bipy)]	3.0	77
16	*trans*-[RuCl$_2$(dppb)(phen)]	3.0	82
17	[RuCl(CO)(dcype)(bipy)]PF$_6$	3.0	31
18	[RuCl(CO)(dcype)(Me-bipy)]PF$_6$	3.0	36
19	[RuCl(CO)(dcype)(phen)]PF$_6$	3.0	21

[a] Acetophenone (10 mmol, 0.2 M) in 2-propanol, 1 mL of KOH (0.2 M) in 2-propanol; precatalyst (10 μmol); H$_2$(g) (1 atm) temp = 82 °C, time = 3 h; acetophenone/precatalyst/KOH = 1000:1:20. [b] Turnover number (TON), moles of acetophenone converted to 1-phenylethanol per mole of precatalyst. [c] Precatalyst generated "in situ" *mer*-[RuCl$_3$(dppb)H$_2$O]/ethylenodiamine or 1,10-phenanthroline = 1. [d] Reaction carried out as in (a) but under argon and in the absence of molecular hydrogen. In each experiment at least two runs were conducted to check the reproducibility.

As shown by Noyori,[9,11] complexes of the same type as those used in this work, but containing diamines, are very active in these types of reactions, in which high activity and asymmetric induction were achieved. The high activity and asymmetric induction are attributed to the bifunctional mechanism in which the "RuH−NH" unit plays an important role. Obviously the bifunctional mechanism (outer sphere) proposed by Noyori[9,11] cannot take place for the complexes studied in this work (except for entry 4, Table 3), and the mechanism should involve the coordination of ketones to the metal center. In another words, the hydrogenation involves an inner sphere mechanism and the hydride is transferred from the metal center to the coordinated ketones.[10,15a] The results obtained for acetophenone hydrogenation are summarized in Table 3.

This study shows that the presence of H$_2$(g) is essential to improve the catalytic activity of complexes such as *cis*-[RuCl$_2$(dppb)(bipy)] (with aromatic diphosphine), shown in Table 3. For example, when the reaction was carried out in the absence of dihydrogen, the activity drops drastically, resulting in conversion of only 50% after 24 h of reaction (entry 6). But when the reaction was conducted under 1 atm of dihydrogen, the conversion was 78% after 3 h, showing that the mechanism involved is dominated by a hydrogenation pathway. On the other hand, for complexes containing the electron-rich dcype diphosphine dihydrogen played a different role in their activity. A reaction using *cis*-[RuCl$_2$(dcype)(bipy)] (same conditions as applied in Tables 3 and 4) but with no dihydrogen showed only slight decreases in rate (TOF$_{30min}$ 800 h^{-1}), leading to a conversion of 83% in 2 h. Another reaction was carried out in benzene in the presence KO^{t}Bu and under 15 atm of dihydrogen, and conversion was only 1.8% in 3 h. This change in the rate in the absence of dihydrogen is

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Table 4. Catalytic Perfomance for Some Complexes

entry	precatalyst	conversion (%)[a] 0.5 h	1.0 h	2.0 h	TOF (h^{-1})[f]
20	*cis*-[$RuCl_2$(dcype)(bipy)]	54	77	97	1080
21	*cis*-[$RuCl_2$(dcype)(Me-bipy)]	33	56	77	660
22	*cis*-[$RuCl_2$(dcype)(bipy)][b]	68	85	89	1360
23	*cis*-[$RuCl_2$(dcype)(bipy)][c]	40	55	83	800
24	*cis*-[$RuCl_2$(dcype)(bipy)][d]	3.0	13	42	60
25	*cis*-[$RuCl_2(PPh_3)_2$(bipy)]	14	50	87	280
26	*cis*-[$RuCl_2(PPh_3)_2$(Me-bipy)]	20	45	71	400
27	*cis*-[$RuCl_2$(dppb)(bipy)]	38	53	76	760
28	*cis*-[$RuCl_2$(dppb)(bipy)][e]	47	65	83	940

[a] Same conditions as in Table 3 except as otherwise stated. [b] 13.6 atm H_2. [c] No H_2. [d] No base. [e] 3 atm H_2. [f] TOF, mol of 1-phenylethanol/mol of precatalyst·h at 0.5 h.

indicative that both mechanisms (hydrogen transfer and hydrogenation) should be involved in the reduction of ketones,[53] but it is clearly shown that the hydrogen-transfer pathway is dominant over the hydrogenation one. Probably the presence of dihydrogen has the effect of increasing the rate of the formation of the active species, since a longer induction period was observed in its absence. The increase in rate is also evidenced using a higher pressure of dihydrogen.

These results show the *cis*-[$RuCl_2$(dcype)(bipy)] complex to be the most active precatalyst, achieving quantitative conversion of acetophenone in 1-phenylethanol in 2.5 h, and reduction of acetophenone was monitored for the most active complexes studied in this work. These results are presented in Table 4.

As observed, complex **1a** achieves a TOF_{30min} of 1080 h^{-1} at 30 min of reaction, and this is the highest value found for our complexes (entry 20, Table 4). The hydrogen pressure also affects the rates; the same complex **1a** under 13.6 atm has an increasing rate, as observed for its TOF_{30min} of 1360 h^{-1}, although the final conversion is reduced from 97% to 89% (entry 22, Table 4). More drastic was the reaction in the absence of base (with H_2) (TOF_{30min} 60 h^{-1}) and conversion of 42% in 2 h, showing the need of an added base for formation of the active catalyst.

The same effect on rate was observed for complex **5**: under 1 atm of H_2 the TOF_{30min} was 760 h^{-1} and under H_2 pressure of 3 atm the TOF_{30min} is increased to 940 h^{-1}, with the final conversion being essentially the same (see entries 27 and 28, Table 4).

In the conditions applied in this work for the reduction of ketones the presence of a N-donor ligand such as ethylenediamine or phen (see Table 3, entries 3, 4, and 5) is of great importance, and the observed activity for bipyridines or phenanthroline derivatives is comparable to ethylenediamine, as evidenced in Table 3 (entries 1, 2, 4, and 5). For example, when the *mer*-[$RuCl_3$(dppb)H_2O] complex was used in the catalytic process, a conversion of only 28% was achieved in 3 h (see entry 3, Table 3), which is a very poor activity when compared with the results when ethylenediamine or phen is added to the solution prior to the addition of acetophenone. These data are comparable with the results found for *cis*-[$RuCl_2$(dppb)(phen)] and *cis*-[$RuCl_2$(dppb)(bipy)] complexes and are explained because the *mer*-[$RuCl_3$(dppb)H_2O] complex in the presence of a bidentate N-donor forms complexes such as [$RuCl_2$(dppb)(N−N)]$^+$,[54] which can be reversibly reduced to its neutral Ru(II) forms. The reactivity of *mer*-[$RuCl_3$(dppb)H_2O] allows its use as an "in situ" precatalyst, which has an advantage due to its air-stability and can also be applied in asymmetric hydrogenation since the analogue containing a chiral diphosphine (*mer*-[$RuCl_3$(diop)H_2O]) can be synthesized.[2]

The type of N-heterocyclic ligand also plays a role in the catalytic activity of such complexes. *trans*-[$RuCl_2$(dppb)$(N)_2$] complexes have lower activity for N_2 = 4-Me-py or 4-Ph-py (entries 7 and 8, Table 3) when compared with their analogues *cis*/*trans*-[$RuCl_2$(dppb)(N−N)] (entries 1, 2, 15, and 16, Table 3), and a decrease in activity is also observed when electron-withdrawing groups are introduced in the ring of bipyridine (entry 14, Table 3).

The activity is also dependent on the electron-donor ability of the phosphine. The behavior of the *cis*-[$RuCl_2(PPh_3)_2$(bipy)] (entry 10, Table 3) complex was more active, with a conversion of 90% in 2.5 h of reaction, compared with the result found for *cis*-[$RuCl_2(PEt_3)_2$(bipy)] (entry 11, Table 3), with conversion of 50% in 12 h of reaction.

Besides the fact that LePage and James[55] report up to 60% conversion of acetophenone to 1-phenylethanol within 4 h at 34 mol % NaOH in refluxing 2-propanol without adding catalyst, in our standard conditions (2 mol % KOH relative to acetophenone) in the absence of ruthenium only 2% and 24% conversion of acetophenone occurs after 3 and 24 h, respectively.

In view of the fact that complexes such as *cis*-[$RuCl_2$(dppb)(bipy)][1a] and *cis*-[$RuCl_2$(dcype)(bipy)] easily dissociate one chloride in the presence of coordinating solvents such as methanol or acetonitrile, as discussed previously, it is reasonable to believe that this is the first step for formation of the active species in catalytic systems such as mono- or dihydride[10,13] complexes or for coordination of the ketones. The dissociation step is fast, and no change in hydrogenation rate and in the final conversion was observed when the isolated solvento complex [RuCl(dppb)(bipy)(MeOH)]$^+$[56] was applied as precatalyst.

The carbonyl complexes [RuCl(CO)(dcype)(N−N)](PF_6) (N−N = bipy, Me-bipy, and phen) were also used as precatalyst in the reduction of acetophenone. These complexes presented a very poor activity, achieving conversions up to 36% with an acetophenone concentration of 0.2 M (same conditions applied for complexes in Table 3). But in this case the derivative with Me-bipy (36%) was slightly better than that with bipy (31%).

The results for reduction of substituted ketones by the *cis*-[$RuCl_2$(dcype)(bipy)] complex are summarized in Table 5. As can be seen from these results, the electron-donor-substituted ketones (which increases their abilities for coordination with the metal center) lower the electrophilic character of the carbonyl group and a decrease in conversion was observed (entries 30 and 31, Table 5) when compared with acetophenone (entry 29,

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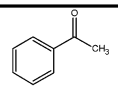
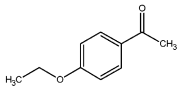
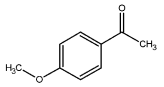
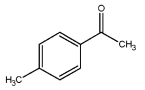
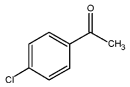
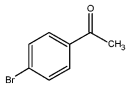
(56) Several solvento complexes will be published elsewhere.

Table 5. Results for Hydrogenation of *p*-Substituted Ketones Catalyzed by *cis*-[$RuCl_2$(dcype)(bipy)] (1a)

Entry	Ketones	Conversion(%)[a]
29		>99
30		83
31		90
32		100
33		100
34		65

[a] Acetophenone (10 mmol) in 2-propanol (3 mL), 1 mL of KOH (0.2 M) in 2-propanol; precatalyst (10 μmol); H_2(g) (1 atm) temp = 82 °C, time = 3 h; acetophenone/precatalyst/KOH = 1000:1:20.

Table 5) and *p*-methylacetophenone (entry 32, Table 5). For CH_3- and C-*p*-substituted acetophenones (entries 32 and 33, Table 5, respectively) the activities are the same, but for *p*-bromoacetophenone the activity was lower than for *p*-chloroacetophenone, which is in agreement with the higher mesomeric effect caused by −Br, which is in agreement with that found in the literature for ruthenium complexes.[15a]

Conclusions

In this work a series of ruthenium phosphine/diimine complexes have been made accessible and characterized. Ruthenium complexes containing the "RuP_2N_2" core (P_2 = diphosphines or bis-monophosphines and N_2 = diimines or ethylenediamine) were synthesized, and their catalytic activities in the hydrogenation of ketones were studied. This unit appears to be essential in the activity in hydrogenation reactions, and an inner sphere mechanism is suggested to be present, except as stated before for the ethylenediamine derivative. Most of the complexes presented here are active, especially those presenting the electron-rich diphosphine (dcype). The conditions applied for the catalytic experiments were [sub]:[KOH]:[cat] = 1000:20:1, and the presence of molecular hydrogen was determined to be essential for the process when dppb-containing complexes were applied as precatalyst, implying the dominant mechanism involved hydrogenation over hydrogen transfer. For dcype analogues the presence of dihydrogen increases the rate, but the mechanism is dominated by a hydrogen-transfer pathway. It is worth noting that most work presented in the literature uses a [sub]:[cat] ratio generally around 200:1 or 50:1.[17b,52,57−59]

The electronic properties of the ruthenium play an important role in the catalytic process and can be easily modified to improve the activity of the catalyst, by simply changing the type of phosphine and the N-heterocyclic ligands, as demonstrated in this work.

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Supporting Information Available: CIF files for complexes **1b** and **1c** are available free of charge at http://pubs.acs.org.

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