Reactivity of the Bis(dihydrogen) Complex $[RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]$ toward N-Heteroaromatic Compounds. Regioselective Hydrogenation of Acridine to 1,2,3,4,5,6,7,8-Octahydroacridine

Andrzej F. Borowski,*[,†,‡] Sylviane Sabo-Etienne,*[,‡,§] Bruno Donnadieu,[‡] and Bruno Chaudret[‡]

Institute of Coal Chemistry, Polish Academy of Sciences, 5, Sowinskiego Street, 44-121 Gliwice, Poland, and Laboratoire de Chimie de Coordination du CNRS, Université Paul Sabatier, 205 Route de Narbonne, 31 077 Toulouse Cedex 04, France

Received December 10, 2002

The reaction of pyridine (Py), pyrrole (Pyr), or acridine with the bis(dihydrogen) complex $[RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]$ (**1**) produces compounds containing heteroaromatic ($[RuH_2(\eta^2\text{-}H_2)(\eta^1\text{-}(N)\text{-}C_5H_5N)(PCy_3)_2]$ (**2**), $[RuH(\eta^5\text{-}C_4H_4N)(PCy_3)_2]\cdot$Pyr (**3**)) or aromatic rings ($[RuH_2(\eta^4\text{-}C_{13}H_9N)(PCy_3)_2]$ (**5**)) coordinated in η^1(N) (**2**), η^5(N,C) (**3**), or η^4(C,C) (**5**) modes for Py, Pyr, and acridine, respectively. Complex **3** has been characterized by X-ray crystallography. Its protonation by HBF_4 affords the cationic dihydride complex $[RuH_2(\eta^5\text{-}C_4H_4N)(PCy_3)_2][BF_4]$ (**4**). The coordinated Py ligand in **2** and acridine in **5** can readily be displaced by dihydrogen, with regeneration of **1**. Regioselective hydrogenation of representative polynuclear heteroaromatic nitrogen compounds is achieved in the presence of **1** under mild reaction conditions (80 °C, 3 bar of H_2). Quinoline (Q) and isoquinoline (iQ) are hydrogenated to 5,6,7,8-tetrahydro derivatives, while acridine is quickly reduced to 1,2,3,4-tetrahydroacridine followed by much slower saturation to 1,2,3,4,5,6,7,8-octahydroacridine (8H-Acr), the nitrogen-containing aromatic ring remaining intact. 8H-Acr has been isolated in analytically pure form and characterized by ^{1}H and ^{13}C NMR as well as by X-ray crystallography. **5** is also active for catalytic acridine hydrogenation and can be regarded as an intermediate in the catalytic cycle. Saturation of a five-membered indole ring proceeds much slower than hydrogenation of six-membered aromatic rings in Q and iQ. Pyridine, pyrrole, and 7,8-benzoquinoline are not hydrogenated under the applied reaction conditions, as a result of the formation of new stable complexes.

Introduction

Catalytic hydrodenitrogenation (HDN) of petroleum- and coal-based feedstocks is one of the most important industrial processes. The ultimate purpose of HDN is the removal of nitrogen as NH_3 by the use of dihydrogen.[1] Non-heterocyclic nitrogen compounds such as aliphatic amines and anilines or nitriles undergo HDN quite rapidly under "normal" HDN catalysis. In contrast, heterocyclic compounds (six-membered pyridine and five-membered pyrrole rings) are much more difficult to process.[2] The nitrogen heterocyclic compounds can be classified in two families. The bases, as for example pyridine, quinoline, and acridine, contain a lone pair on the nitrogen atom, and hence, the compounds are easy to protonate or can interact with acidic sites. The second type refers to substrates such as pyrrole, indole, and carbazole, in which the unshared pair of electrons on the nitrogen atom is needed for aromaticity; thus, they are more likely to interact through their π-electron system.[3] Many HDN catalytic studies indicate that nitrogen removal from N-heteroaromatic compounds requires saturation of the N-aromatic ring, before rapid hydrogenolysis of the C−N bond occurs (at least with the typically used Ni−Mo/Al_2O_3 catalysts). In this respect, selective hydrogenation of the N-aromatic ring of a polynuclear compound is a critical step that needs to be controlled.[1,4,5] Reports on C−N bond scission in heteroaromatic rings with formation of heterometallacycles are quite numerous, and hydrogenolysis of C−N bonds has also been described.[2,6−8]

† Polish Academy of Sciences.
‡ Université Paul Sabatier.
§ E-mail: sabo@lcc-toulouse.fr.

(1) Girgis, M. J.; Gates, B. C. *Ind. Eng. Chem. Res.* **1991**, *30*, 2021.
(2) Weller, K. J.; Fox, P. A.; Gray, S. D.; Wigley, D. E. *Polyhedron* **1997**, *16*, 3139 and references therein.
(3) March, J. *Advanced Organic Chemistry: Mechanisms and Structure*, 4th ed.; Wiley: New York, 1992.
(4) Baralt, E.; Smith, S. J.; Hurwitz, J.; Horváth, I. T.; Fish, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 5187.
(5) (a) Topsøe, H.; Clausen, B. S.; Massoth, F. E. Hydrotreating Catalysis. In *Catalysis*: *Science and Technology*; Anderson, J. R., Boudart, M., Eds.; Springer-Verlag: Berlin, Heidelberg, 1996; Vol. 11. (b) Satterfield, C. N. *Heterogeneous Catalysis in Industrial Practice*; McGraw-Hill: New York, 1991; p 378.
(6) Angelici, R. J. *Polyhedron* **1997**, *16*, 3037 and references therein.
(7) Kvietok, F.; Allured, V.; Carperos, V.; Rakowski DuBois, M. *Organometallics* **1994**, *13*, 60.
(8) (a) Vicic, D. A.; Jones, W. D. *Organometallics* **1999**, *18*, 134. (b) Morikita, T.; Hirano, M.; Sasaki, A.; Komiya, S. *Inorg. Chim. Acta* **1999**, *291*, 341. (c) Werner, H.; Hoerlin, G.; Jones, W. D. *J. Organomet. Chem.* **1998**, *562*, 45.

10.1021/om020995p CCC: $25.00
Publication on Web 03/15/2003

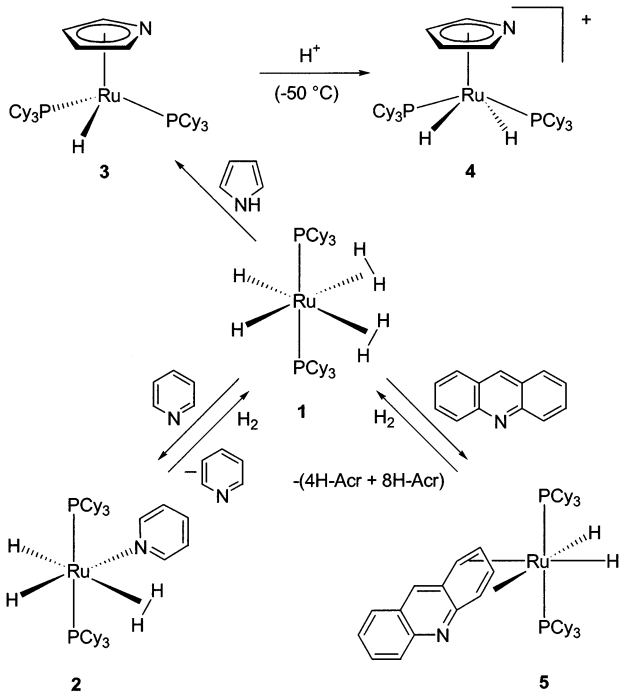
The complex chemical composition of petroleum has led to the examination of model compounds that resemble the nitrogen contaminants in petroleum distillates and other feedstocks.[2,6,9] There are thus numerous reports on the reactivity of N-heteroaromatic compounds with metal complexes, leading to the coordination of the heteroaromatic ligand to the metal center.[7,10] Several homogeneous systems based on transition-metal complexes are active in hydrogenation reactions of polynuclear heteroaromatics.[2,4,6] In the specific case of dihydrogen complexes, which are known to be active homogeneous reduction catalysts,[11] no relevant report involving polynuclear heteroaromatics has been found.

We have recently shown that the bis(dihydrogen) complex $[RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]$ (**1**)[12] can be an active catalyst precursor for arene hydrogenation under mild conditions.[13] We now describe the syntheses and properties of new ruthenium complexes resulting from the reactivity of **1** with some selected nitrogen heteroaromatics. We report an evaluation of the catalytic activity of **1** for hydrogenation of the selected substrates and show that the results are highly dependent on the capacity of the aromatic compounds to adopt different bonding modes.

Results and Discussion

Reaction of 1 with Pyridine. Treating a pentane suspension of **1** with excess pyridine results in a color change of the reaction mixture with concomitant gas evolution. After workup, we obtained a yellow solid that was characterized by NMR. The data indicate the presence of unreacted starting bis(dihydrogen) complex **1** (ca. 10%) and formation of a new compound formulated as the dihydrogen pyridine complex $[RuH_2(\eta^2\text{-}H_2)(\eta^1(N)\text{-}C_5H_5N)(PCy_3)_2]$ (**2**) (Scheme 1). Any efforts to isolate **2** in a pure form have failed. Complex **2** is characterized by three broad resonances in the ^1H NMR spectrum at δ 9.11, 6.77, and 6.35 and a triplet at δ −9.47 (J_{P-H} = 13.5 Hz), integrated in the ratio 2:1:2:4. The low-field resonances are assigned to the protons of one pyridine ligand coordinated to the metal through the lone pair of the nitrogen atom. Integration of the hydride signal is in favor of the presence of four hydrogen atoms around the coordination sphere of the metal. This is confirmed by the observation of a singlet at δ 71.9 in the $^{31}P\{^1H\}$ NMR spectrum, which is transformed into a quintet upon selective decoupling of PCy_3 protons, thus suggesting the presence of four hydrogens around the metal. The presence of a coordinated dihydrogen molecule is supported by the T_1^{min} value of 55 ms at 253 K (C_7D_8, 400 MHz). The observation of an H/D exchange between the solvent (C_6D_6, C_7D_8) and the hydrides is also in agreement with a dihydride dihydrogen formulation. Unfortunately, no decoalescence of the hydride/dihydrogen signal could be measured down to 183 K, as observed recently for the structurally similar complex $[RuH_2(\eta^2\text{-}H_2)(PCy_3)_2$(2-phenyl-3,4-dimethylphosphaferrocene)], but with the phosphaferrocene ligand being a better π-acceptor.[14] **2** is fairly stable in C_6D_6 or C_7D_8 solution, and no signs of decomposition have been observed after 24 h. H/D exchange was evidenced by ^1H NMR (the triplet at δ −9.47 changed into a broad signal disappearing after a few hours) with no change in the ^{31}P NMR spectrum.

Scheme 1. Reactivity of $[RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]$ toward Pyridine, Pyrrole, and Acridine

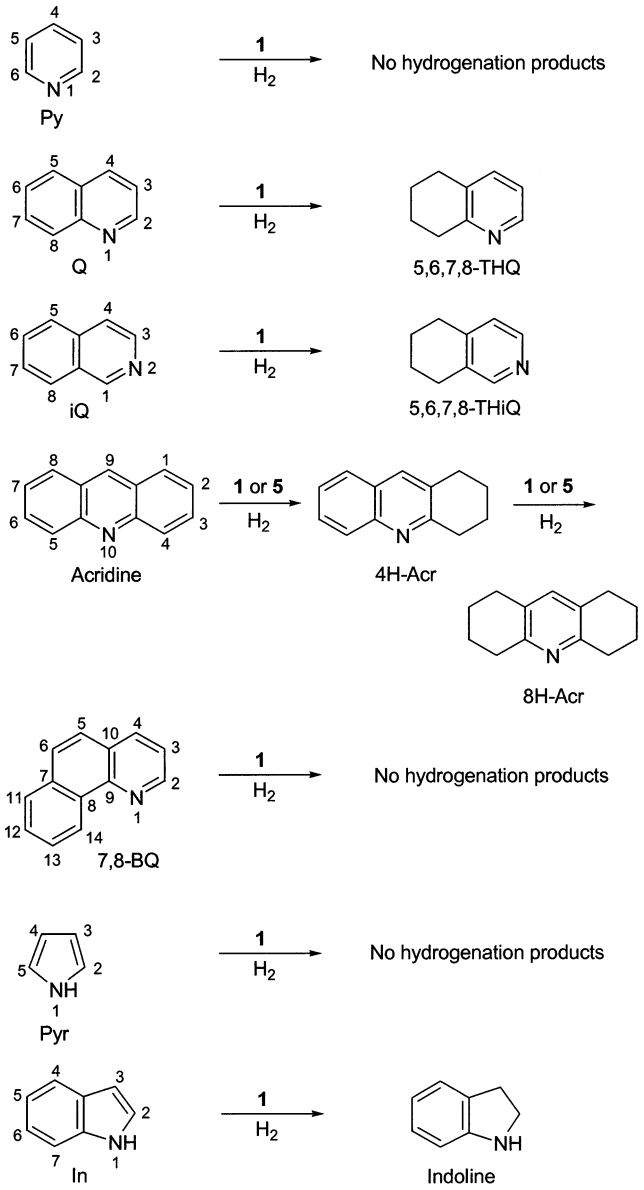


Decoordination of pyridine from **2** was readily achieved by bubbling dihydrogen (5 min, room temperature) through a C_6D_6 solution containing the yellow product. This resulted in total conversion into **1** and pyridine characterized by three new multiplets at δ 8.66, 7.08, and 6.77. Hydrogenation of pyridine was thus not observed, as evidenced by the absence of resonances corresponding to piperidine protons. The same result was obtained when testing pyridine hydrogenation in the presence of **1** under 3 bar of H_2 at 80 °C, with no conversion after 24 h. Indeed, examples of homogeneous catalytic hydrogenation of pyridine derivatives are rare.[15]

Hydrogenation of Quinoline (Q), Isoquinoline (iQ), and Indole (In). We were more successful when

(9) Chisholm, M. H. *Polyhedron* **1997**, *16*, 3071.
(10) (a) McComas, C. C.; Ziller, J. W.; Van Vranken, D. L. *Organometallics* **2000**, *19*, 2853. (b) Schulte, J. L.; Laschat, S.; Kotila, S.; Hecht, J.; Fröhlich, R.; Wibbeling, B. *Heterocycles* **1996**, *43*, 2713. (c) Joachim, J. E.; Apostolidis, C.; Kanellakopulos, B.; Meyer, D.; Raptis, K.; Rebizant, J.; Ziegler, M. L. *J. Organomet. Chem.* **1994**, *476*, 77. (d) Laschat, S.; Noe, R.; Riedel, M.; Krüger, C. *Organometallics* **1993**, *12*, 3738. (e) Myers, W. H.; Koontz, J. I.; Harman, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 5684. (f) Myers, W. H.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 6682. (g) Glueck, D. S.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 6682. (h) Cordone, R.; Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1991**, *113*, 5969. (i) Chaudret, B.; Jalon, F.; Perez-Manrique, M.; Lahoz, F. J.; Plou, F. J.; Sanchez-Delgado, R. *New J. Chem.* **1990**, *14*, 331. (j) Kershner, D. L.; Rheingold, A. L.; Basolo, F. *Organometallics* **1987**, *6*, 196. (k) Pyshnograeva, N. I.; Setkina, V. N.; Adrianow, V. G.; Struchov, Yu. T.; Kursanov, D. N. *J. Organomet. Chem.* **1980**, *186*, 331.
(11) Esteruelas, M. A.; Oro, L. A. *Chem. Rev.* **1998**, *98*, 577.
(12) (a) Sabo-Etienne, S.; Chaudret, B. *Coord. Chem. Rev.* **1998**, *170−180*, 381. (b) Borowski, A. F.; Donnadieu, B.; Daran. J.-C.; Sabo-Etienne, S.; Chaudret, B. *Chem. Commun.* **2000**, 543, 1697.
(13) Borowski, A. F.; Sabo-Etienne, S.; Chaudret, B. *J. Mol. Catal. A: Chem.* **2001**, *174*, 69.
(14) Toner, A. J.; Donnadieu, B.; Sabo-Etienne, S.; Chaudret, B.; Sava, X.; Mathey, F.; Le Floch, P. *Inorg. Chem.* **2001**, *40*, 3034.
(15) (a) Fish, R. H.; Baralt, E.; Smith, S. J. *Organometallics* **1991**, *10*, 54. (b) Borowski, A. F.; Cole-Hamilton, D. J. *Polyhedron* **1993**, *12*, 1757. (c) Studer, M.; Wedemayer-Exl, C.; Spindler, F.; Baser, H. U. *Monatsh. Chem.* **2000**, *131*, 1335.

Scheme 2. Hydrogenation of N-Aromatic Compounds Catalyzed by $[RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]$



testing hydrogenation of quinoline (Q) and isoquinoline (iQ). We have used **1** as a catalyst precursor under standard conditions (3 bar of H_2, 80 °C) (Scheme 2, Table 1). In both cases, reductions are efficient and regioselective, leading to 5,6,7,8-tetrahydro derivatives. Slightly higher conversion has been obtained for Q (99%) as compared to iQ (88.5%) after a 24 h process. It is remarkable that, in our system, saturation of the aromatic ring is observed, in contrast to the results reported using $[Cp^*RhL]^{2+}$ (L = $(NCMe)_3$, *p*-xylene),[15a,16] $[RuH(CO)(NCMe)_2(PPh_3)_2]^+$,[17] or $[Rh(COD)(PPh_3)_2]^+$ [18] as catalyst precursor, respectively. In the first two cases, considerable difference in activity (ca. 30 times) for Q and iQ reduction was observed. This was explained by

Table 1. Hydrogenation of N-Heteroaromatics Catalyzed by $[RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]$ (1) at 80 °C under 3 bar of H_2[a]

substrate	conversn (%)	products[b] (amt (%))	TON[c]
pyridine	0	none	0
quinoline	100.0	5,6,7,8-THQ (99)	49.5
		1,2,3,4-THQ (1)	0.5
isoquinoline	88.5	5,6,7,8-THiQ (100)	44.2
7,8-benzoquinoline	0	none	0
indole	24.6	indoline (100)	12.3
pyrrole	0	none	0
acridine	100.0	4H-Acr (4.5)	50.0[d]
		8H-Acr (95.5)	47.2[d]
acridine[e]	100.0	4H-Acr (12.5)	50.0[d]
		8H-Acr (87.5)	43.8[d]

[a] Unless stated otherwise, **1** is the catalyst precursor. Conditions: solvent, cyclohexane (10 mL); [Ru] = 3×10^{-3} M; [substrate] = 0.15 M; substrate/Ru = 50; 80 °C; 3 bar of H_2; 24 h. The products were analyzed by GC. [b] Products: THQ = tetrahydroquinoline; THiQ = tetrahydroisoquinoline; 4H-Acr = 1,2,3,4-tetrahydroacridine; 8H-Acr = 1,2,3,4,5,6,7,8-octahydroacridine. [c] TON is defined as mole of product formed per mole of Ru. [d] Calculations based on the assumption that 8H-Acr is formed in a two-stage reaction. It involves hydrogenation of acridine to 4H-Acr (stage 1) followed by its hydrogenation to 8H-Acr (stage 2). [e] $[RuH_2(\eta^4\text{-}C_{13}H_9N)(PCy_3)_2]$ (**5**) was used as a catalyst precursor. The reaction time was 18 h.

the higher basicity of the nitrogen atom in iQ compared to that in Q, which could have an influence on the stabilization of the postulated intermediate involving an η^1(N) coordination of the substrate. In our system, virtually the same catalytic activity is observed toward both isomers, and we have found that hydrogenation leads, almost exclusively, to saturated arene rings. A possible explanation for this difference could be the coordination of the substrate through the aromatic ring in a way similar to that reported for η^4-arene complexes.[19] It is noteworthy that we have previously demonstrated that the η^4-arene complex $[RuH_2(\eta^4\text{-}C_{14}H_{10})(PCy_3)_2]$ is involved in the catalytic hydrogenation of anthracene.[13] We cannot, however, exclude an η^1(N) coordination mode of the substrate and subsequent rearrangement to form a π-arene, as reported for some Cp ruthenium complexes.[20,10i]

To get some information on the binding mode of the substrate during the catalytic reaction, we have performed a stoichiometric study of the reaction of **1** with Q. We could not isolate any pure complex, but NMR data of a C_6D_6 mixture of **1** with Q support the formation of a new species tentatively formulated as $[RuH_2(\eta^4\text{-}C_9H_7N)(PCy_3)_2]$. The η^4(C,C)-coordinated quinoline ligand is characterized by four signals at δ 5.99 (br), 5.63 (br), 4.44 (d, 5.6 Hz), and 3.83 (d, 5.6 Hz), very similar in shape and very close to the positions of the four proton signals assigned to the arene protons of the acridine ligand, coordinated in an η^4(C,C) mode in $[RuH_2(\eta^4\text{-}C_{13}H_9N)(PCy_3)_2]$ (**5**) (see below and Experimental Section). Moreover, the hydride resonance of the new species at δ −11.58 (t, J_{P-H} = 28 Hz) and the phosphorus resonance at δ 70.1 are very close to the corresponding resonances in **5**. In addition, we have

(16) Fish, R. H.; Kim, H. S.; Babin, J. E.; Adams, R. D. *Organometallics* **1988**, *7*, 2250.

(17) (a) Rosales, M.; Navarro, J.; Sánchez, L.; González, A.; Alvorado, Y.; Rubio, R.; De La Cruz, C.; Ramajkina, T. *Transition Met. Chem.* **1996**, *21*, 11. (b) Rosales, M.; Alvorado, Y.; Boves, M.; Rubio, R.; Soscún, H. *Transition Met. Chem.* **1995**, *20*, 246.

(18) Sanchez-Delgado, R. A.; Rondon, D.; Andriollo, A.; Herrera, V.; Martin, G.; Chaudret, B. *Organometallics* **1993**, *12*, 4291.

(19) (a) Albright, J. O.; Datta, S.; Dezube, B.; Kouba, J. K.; Marynick, D. S.; Wreford, S. S.; Foxman, B. M. *J. Am. Chem. Soc.* **1979**, *101*, 611. (b) Leong, V. S.; Cooper, N. J. *Organometallics* **1988**, *7*, 2058. (c) Thompson, R. L.; Lee, S.; Rheingold, A. L.; Cooper, N. J. *Organometallics* **1991**, *10*, 1657. (d) Bennett, M. A.; Lu, Z.; Wang, X.; Brown, M.; Hockless, D. C. R. *J. Am. Chem. Soc.* **1998**, *120*, 10409.

(20) Fish, R. H.; Kim, H. S.; Fong, R. H. *Organometallics* **1991**, *10*, 770.

detected the concomitant formation of 5,6,7,8-tetrahydroquinoline (5,6,7,8-THQ), characterized by two triplets at δ 3.00 and 2.37 (J_{H-H} = 6.9 Hz). We have excluded the presence of 1,2,3,4-tetrahydroquinoline (1,2,3,4-THQ) on the basis of the lack of the expected broad resonance of the N−H proton at δ ca. 4−3.5 ppm. The GC/MS spectra of the Q hydrogenation products, of both the catalytic and stoichiometric mixtures, confirm that the 5,6,7,8-tetrahydro derivative is obtained as the main reaction product.

We have recently reported the hydrogenation of naphthalene to tetralin (and not to decalin) in the presence of **1** under the same conditions.[13] The reaction proceeds at a rate ca. one-third of that found for Q and iQ reduction studied in this work. In this respect, more facile hydrogenation of the aromatic rings in Q and iQ as compared with that of naphthalene seems to be connected to the presence of the nitrogen atom in the adjacent heteroaromatic ring and the tendency of these substrates to coordinate in an η^4(C,C) rather than an η^1(N) fashion. In contrast, easier hydrogenation of N-heteroaromatic rings in Q and iQ to form 1,2,3,4-tetrahydro derivatives has been explained by the lower stabilization energy of the heteroaromatic ring, as shown by ab initio SCF-MO calculations reported by Rosales et al.[17b]

In the case of 7,8-benzoquinoline (7,8-BQ), we did not get any evidence of hydrogenation under our standard conditions in the presence of **1** as catalyst precursor. It is noteworthy that phenanthrene, the hydrocarbon analogue of 7,8-BQ, was also found to be totally resistant to hydrogenation under analogous conditions (Scheme 2).[13] In contrast, the homogeneous hydrogenation of 7,8-BQ to the 1,2,3,4-tetrahydro derivative was reported by Fish et al. with the catalyst precursor they used for Q and iQ hydrogenation (see above).[15a] In our case, the lack of reduction of 7,8-BQ might be explained by the stability of a new organometallic complex resulting from the reaction of 7,8-BQ with **1**. Indeed, in the course of our studies on C−H activation, we have previously reported the synthesis of [RuH(η^2-H_2)L-(PR_3)$_2$] (R = ^{i}Pr, Cy), containing an ortho-metalated ligand L such as phenylpyridine or functionalized aromatic ketones.[21] In this latter case, we have demonstrated that these compounds are efficient catalysts for ethylene insertion into functional arenes at room temperature. More recently, we have isolated a similar complex, [RuH(η^2-H_2)($NC_{13}H_8$)(P^iPr_3)$_2$], by addition of 7,8-BQ to the analogous complex of **1**, but with triisopropylphosphine.[22] The benzoquinolyl ligand is coordinated to the ruthenium via the nitrogen atom and an ortho carbon bond of the external aromatic ring. This ortho-metalated complex proved to be very stable under dihydrogen pressure.

Using indole as a substrate, hydrogenation to indoline is selectively carried out (Scheme 2, Table 1). However, hydrogenation of the five-membered heteroaromatic ring occurs at a very slow rate of 0.5 TON/h, ca. 4 times slower than hydrogenation of the aromatic rings of Q and iQ. By comparison, Rosales et al. reported a similar activity for indole and iQ hydrogenation, but lower than that for Q (see above),[17] whereas virtually identical hydrogenation activities for these three substrates were reported for other Rh and Ir cationic complexes (50 °C, 5 bar of H_2).[23] In these latter systems, the authors proposed that the formation of metallic rhodium and iridium powders was responsible for the activity.

Reaction of 1 with Pyrrole. Synthesis of [RuH(η^5-C_4H_4N)(PCy_3)$_2$]·Pyr (3). Pyrrole has a much lower degree of aromaticity than benzene and thiophene (resonance energies for these three compounds are respectively 88, 152, and 121 kJ/mol).[3] Despite this property, we could not reduce pyrrole under our standard conditions, using **1** as a hydrogenation catalyst precursor. However, the change of color from beige to yellow upon addition of pyrrole to the solution containing **1** suggested that some reaction had occurred.

Indeed, stirring a suspension of **1** in pentane with an excess of pyrrole leads after workup to the isolation of yellow crystals. The new complex [RuH(η^5-C_4H_4N)-(PCy_3)$_2$]·Pyr (**3**) was characterized by NMR and X-ray data as a hydride complex with a pyrrolyl coordinated to the ruthenium via an η^5 mode (Scheme 1). The ^{31}P-{^{1}H} NMR spectrum (C_6D_6, 293 K) shows a single resonance at δ 66.5. The ^{1}H NMR spectrum of **3** displays two singlets of equal intensity for the pyrrolyl ligand at δ 6.05 ($H^{2,5}$) and 5.14 ($H^{3,4}$) and a high-field hydride triplet at δ −15.86 (J_{P-H} = 36.8 Hz) in a good integration ratio (2:2:1). Moreover, three other resonances observed at δ 6.52 ($H^{2,5}$), 6.38 ($H^{3,4}$), and 8.02 (N−H^1), also in a 2:2:1 ratio, are assigned to the protons of one solvate pyrrole molecule. This was confirmed by microanalysis and X-ray data. In **3**, the pyrrolyl protons are shifted to high field as a consequence of η^5 coordination to ruthenium. Further support is given by the ^{13}C NMR spectrum (C_6D_6), showing for **3** two signals at δ 105.7 and 78.0 for the $C^{2,5}$ and $C^{3,4}$ carbons of the η^5-coordinated pyrrolyl ligand, whereas the carbons for the free pyrrole resonate at δ 117.7 ($C^{2,5}$) and 108.5 ($C^{3,4}$).

The structure determined in solution for **3** was found to be the same in the solid state, as confirmed by an X-ray determination (Table 2). The molecular structure of **3**, depicted in Figure 1, exhibits a three-legged piano-stool geometry. The central ruthenium atom is bound to one hydride atom, a pyrrolyl ligand, and two tricyclohexylphosphines with a P−Ru−P angle of 106.87(3)°. The pyrrolyl ligand is essentially planar with almost identical C−C ring bonds of 1.398 Å (average) and slightly shorter C−N ring bonds of 1.378 Å (average). The distances between the ruthenium and each ring atom of the pyrrolyl ligand indicate a slight shift of the ring centroid, with shorter metal distances to C1 and C4 atoms (2.235(3) Å, average) than to C2 and C3 (2.243(3) Å, average) and the N atom (2.335(2) Å). Similar shifts have been noted in structural studies on other pyrrolyl complexes of Mn and Ru.[7,10a,j]

It is worth noting that bubbling dihydrogen (15 min, 20 °C) through a C_6D_6 solution of **3** did not cause any change in the ^{1}H and ^{31}P NMR spectra. Moreover, the stability of the pyrrolyl η^5-coordinated to the ruthenium is illustrated by the protonation reaction. Addition at

(21) (a) Guari, Y.; Sabo-Etienne, S.; Chaudret, B. *J. Am. Chem. Soc.* **1998**, *120*, 4228. (b) Toner, A. J.; Grundemann, S.; Clot, E.; Limbach, H.-H.; Donnadieu, B.; Sabo-Etienne, S.; Chaudret, B. *J. Am. Chem. Soc.* **2000**, *122*, 6777.

(22) Grundemann, S.; Toner, A.; Matthes, J.; Guari, Y.; Donnadieu, B.; Sabo-Etienne, S.; Clot, E.; Limbach, H.-H.; Chaudret, B. To be submitted for publication.

(23) Chin, C. S.; Park, Y.; Lee, B. *Catal. Lett.* **1995**, *31*, 239.

Table 2. Crystal Data for [RuH(η^5-C_4H_4N)(PCy_3)$_2$]·Pyr (3) and 1,2,3,4,5,6,7,8-Octahydroacridine (8H-Acr)

	3	8H-Acr
chem formula	$C_{44}H_{76}N_2P_2Ru$	$C_{13}H_{17}N$
fw	796.08	187.28
cryst syst, space group	triclinic, $P\bar{1}$	monoclinic, $P2_1/n$
Z; calcd density, Mg/m^3	2; 1.255	2; 1.193
abs coeff, mm^{-1}	0.480	0.069
F(000)	856	204
a, Å	10.7406(16)	9.252(2)
b, Å	14.063(2)	6.4870(10)
c, Å	15.132(3)	9.726(2)
α, deg	73.759(19)	
β, deg	85.968(19)	116.71(3)
γ, deg	73.722(18)	
V, Å^3	2106.3(6)	521.44(18)
temp, K	160(2)	180(2)
no. of data/restraints/ params	6089/0/450	978/0/69
goodness of fit on F^2	1.073	1.062
R1 ($I > 2\sigma(I)$)	0.0299	0.0462
wR2 ($I > 2\sigma(I)$)	0.0666	0.1202
R1 (all data)	0.0379	0.0562
wR2 (all data)	0.0697	0.1274
largest diff peak and hole, e Å^{-3}	0.674 and −0.454	0.157 and −0.217

−50 °C of 1 equiv of HBF_4 to an acetone solution of **3** yields after workup a new product analyzed as [RuH_2(η^5-C_4H_4N)(PCy_3)$_2$][BF_4] (**4**) (Scheme 1). The ^{1}H NMR spectrum of **4** in d_6-acetone (298 K) shows two singlets at δ 6.96 and 6.37 for the protons of the pyrrolyl ring and a hydride triplet at δ −10.30 (J_{P-H} = 24.4 Hz). The singlet at δ 79.5 in the ^{31}P{^{1}H} NMR spectrum transforms into a triplet upon selective decoupling of the protons of the phosphine ligands, confirming the presence of two hydrides. These data indicate that protonation does not take place on the pyrrolyl ring but on the metal. The initial kinetic product could be a dihydrogen complex, which would then isomerize to the dihydride tautomer, as previously reported for the protonation of several phosphine complexes of the type [Cp*$RuHL_2$].[24]

Reaction of 1 with Acridine. Reaction of **1** with a 2-fold molar excess of acridine in pentane yields a yellow microcrystalline product analyzed as [RuH_2(η^4-$C_{13}H_9N$)(PCy_3)$_2$] (**5**) (Scheme 1). The ^{1}H NMR spectrum of **5** shows four proton resonance signals of equal intensity for the coordinated arene ring of the acridine ligand at δ 5.72 (H^4), 5.43 (H^1), 4.58 (H^3), and 4.07 (H^2). They are shifted upfield by ca. 2−3 ppm as compared with the resonances of the corresponding aromatic protons of free acridine. The resonances of the remaining protons lie close to the positions observed for the uncomplexed aromatic and heteroaromatic rings of free acridine between δ 8.06 and 6.78 (see Experimental Section). The hydrides resonate as a triplet at δ −11.22 (J_{P-H} = 28.0 Hz), which is transformed into a singlet upon phosphorus decoupling. The ^{31}P{^{1}H} NMR spectrum (293 K, C_6D_6) shows a single peak at δ 70.5, which upon selective decoupling of protons of the cyclohexyl groups is transformed into a triplet with J_{P-H} = 28.0 Hz, indicative of the presence of two hydrides. We were unable to obtain a ^{13}C NMR spectrum due to the limited solubility and the instability of the complex in solution.

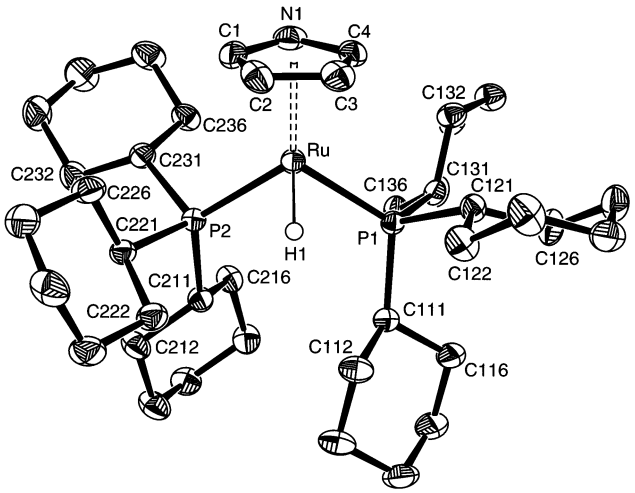


Figure 1. Molecular structure of [RuH(η^5-C_4H_4N)(PCy_3)$_2$]-(**3**). Selected bond lengths (Å) and angles (deg): Ru−H1, 1.56(3); Ru−C1, 2.233(3); Ru−C2, 2.242(3); Ru−C3, 2.244-(3); Ru−C4, 2.237(3); Ru−P1, 2.3096(8); Ru−P2, 2.3203-(7); C1−N1, 1.379(4); C2−C3, 1.404(4); C3−C4, 1.397(4); C4−N1, 1.376(4); P1−Ru−P2, 106.87(3); P1−Ru−H1, 77.3-(11); P2−Ru−H1, 81.5(11).

The pattern of the ^{1}H NMR spectrum of **5** resembles that of the complex [RuH_2(η^4-$C_{14}H_{10}$)(PCy_3)$_2$] ($C_{14}H_{10}$ = anthracene), coordinating anthracene in an η^4 mode.[13] Similar ^{31}P chemical shifts are obtained for these two complexes (δ 70.5 for **5** vs 67.9 ppm for the anthracene complex) as well as similar hydride resonances (a triplet at δ −11.2 with J_{P-H} = 28 Hz) and IR spectra (ν(Ru−H) 2015 and 1987 cm^{-1} for **5** vs 2013 and 1975 cm^{-1} for the anthracene complex). All these data are in agreement with an η^4 coordination mode of one arene ring of acridine, thus allowing the complex to reach an 18-valence-electron configuration. It is worth mentioning that the number of transition-metal complexes coordinating acridine is scarce, and most of them contain N-bound heterocycles or η^6-arene coordination.[25,10i]

Hydrogenation of Acridine. Total conversion of acridine was accomplished using **1** as catalyst precursor under our standard conditions (80 °C, 3 bar of H_2), producing within less than 2 h a mixture of 1,2,3,4-tetrahydroacridine (4H-Acr) and 1,2,3,4,5,6,7,8-octahydroacridine (8H-Acr) (Scheme 2, Table 1). The hydrogenation rate of the first arene ring of acridine to produce 4H-Acr is fairly high: at least 25 TON/h. Keeping the reaction mixture under a dihydrogen atmosphere causes a gradual increase of 8H-Acr concentration at the expense of 4H-Acr (Figure 2). We can assume that total conversion of acridine into 4H-Acr is first achieved. After hydrogenation of the first aromatic ring, the reaction proceeds, leading to hydrogenation of the second external ring, but with a considerably slower rate. The final hydrogenation product 8H-Acr has been isolated as a white solid after a 30 h process and characterized by GC/MS, ^{1}H and ^{13}C NMR, and X-ray crystallography.

Crystals of 8H-Acr suitable for X-ray analysis have been obtained from acetone solutions (Table 2). The molecular structure along with selected bond lengths

(24) (a) Jia, G.; Lough, A. J.; Morris, R. H. *Organometallics* **1992**, *11*, 161. (b) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166.

(25) (a) Sloufova, I.; Slouf, M. *Acta Crystallogr., Sect. C: Cryst. Commun.* **2000**, *56*, 1312. (b) Sloufova. I.; Slouf. M. *Acta Crystallogr., Sect. C: Cryst. Commun.* **2001**, *57*, 248.

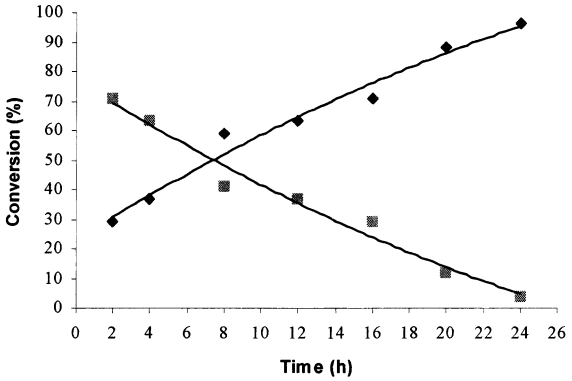


Figure 2. Product distribution profile for acridine hydrogenation: (■) 1,2,3,4-tetrahydroacridine (4H-Acr); (◆) 1,2,3,4,5,6,7,8-octahydroacridine (8H-Acr). Catalyst precursor: **1**. Reaction conditions: $T = 80$ °C, $P = 3$ bar of H_2.

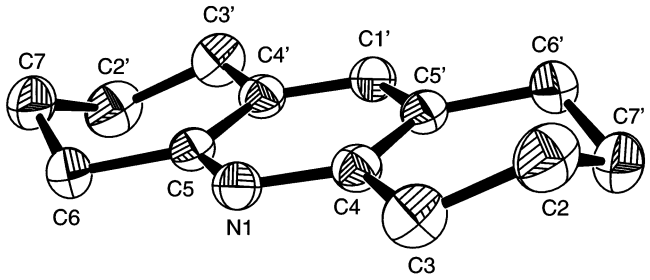
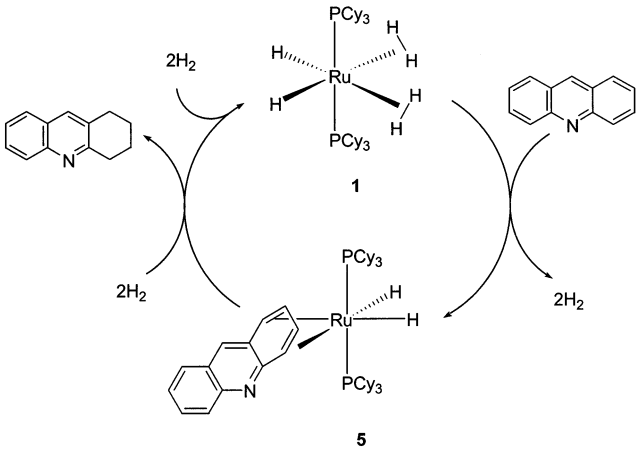


Figure 3. Molecular structure of 1,2,3,4,5,6,7,8-octahydroacridine (8H-Acr). Selected bond lengths (Å) and angles (deg): C2−C3, 1.514(2); C2−C7′, 1.515(2); C4−C5′, 1.3996(19); C6−C7, 1.518(2); C5−N1, 1.3575(18); C5−C6, 1.5062(17); C4−N1, 1.3632 (18); C5−N1−C4, 120.59(11); N1−C5−C4′, 119.65(12); C5′−C4−C3, 121.49(12); C3−C2−C7′, 110.33(12); C4−C3−C2, 113.14(12); C2′−C7−C6, 110.01(12).

are depicted in Figure 3. The central ring containing the nitrogen atom is virtually planar and retains its aromatic character, as evidenced by a comparison with the data reported for the heteroaromatic ring of acridine previously characterized by X-ray crystallography.[26] Hydrogenation of the two external aromatic rings of acridine is confirmed with C−C bond distances and angles close to 1.52 Å and 112°, respectively, as is commonly found for cyclohexyl rings.

There are very few reports in the literature concerning the process of homogeneous hydrogenation of acridine. In all cases but one, selective hydrogenation of the central ring was obtained, leading to the formation of 9,10-dihydroacridine (9,10-2H-Acr).[15a,17,23,27,28] The only exception, to our knowledge, concerns the formation of 4H-Acr (36%) along with 9,10-2H-Acr (64%) in the course of acridine hydrogenation (85 °C, 21.4 bar of H_2) in the presence of $[RhCl(PPh_3)_3]$.[27b] Rosales et al. proposed a mechanism involving substrate coordination to the ruthenium through the nitrogen atom and heterolytic activation of dihydrogen.[17] In the work of Fish et al., the importance of initial η^1(N) bonding to the metal center for catalytic activity is highlighted for a

Scheme 3. Catalytic Cycle for Partial Hydrogenation of Acridine



number of mono- and polynuclear heteroaromatics, including acridine.[15a,27] Unlike those processes, for anthracene hydrogenation, the structural hydrocarbon analogue of acridine, a radical mechanism for the reduction of C^9 and C^{10} carbons has been postulated.[29] Interestingly, during our studies no 9,10-2H-Acr has been detected. Apparently, in the reduction of acridine catalyzed by **1**, neither of the two mechanisms (η^1(N) coordination or radical pathway) is operating.

Formation of 8H-Acr has also been observed in the course of heterogeneous hydrogenation of acridine catalyzed by Pd/Al_2O_3. In the mechanism postulated by Mochida et al., the primary hydrogenation product, 9,-10-2H-Acr, undergoes hydrogenative isomerization to form the more stable 4H-Acr. Further hydrogenation leads to 8H-Acr, the process being thermodynamically favorable at a temperature of 250 °C.[30] Our process occurs at much lower temperature (80 °C), and the presence of 9,10-2H-Acr has not been observed.

Hydrogenation of Acridine with 5 Used as a Catalyst Precursor. 5 acts also as a hydrogenation catalyst precursor, leading to a total conversion of acridine into a mixture of 4H-Acr (12.5%) and 8H-Acr (87.5%) after an 18 h process (Table 1). Since **5** readily forms from **1** by substitution of the two dihydrogen molecules, it is very likely that **5** may be involved, as a transient form, in a catalytic cycle for acridine hydrogenation. This hypothesis is supported by the observation that bubbling dihydrogen (10 min, 296 K) through a C_6D_6 solution of **5** in an NMR tube restores **1**. 4H-Acr and 8H-Acr are also detected, with no traces of free acridine.

The above findings allow us to propose a very simple catalytic cycle for the hydrogenation of acridine to 4H-Acr (Scheme 3), which begins with the dissociation of two dihydrogen molecules, creating two vacant sites for the coordination of acridine through an arene ring to form an η^4-bound substrate. The rest of the catalytic cycle, although not investigated, is presumably straightforward. At the end of the catalytic reaction cycle, either a new acridine molecule coordinates to Ru, forming **5** and restarting a new catalytic cycle, or the bis(dihydrogen) complex **1** regenerates upon coordination of two

(26) Phillips, D. C.; Ahmed, F. R.; Barnes, W. H. *Acta Crystallogr.* **1960**, *13*, 365.
(27) (a) Fish, R. H.; Thormodsen, A. D.; Cremer, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 5234. (b) Fish, R. H.; Tan, J. L.; Thormodsen, A. D. *J. Org. Chem.* **1984**, *49*, 4500.
(28) Lee, C.; Steele, B. R.; Sutherland, R. G. *J. Organomet. Chem.* **1980**, *186*, 265.
(29) Feder, H. M.; Halpern, J. *J. Am. Chem. Soc.* **1975**, *97*, 7186.
(30) Sakanishi, K.; Ohira, M.; Mochida, I. *J. Chem. Soc., Perkin Trans.* **1988**, 1769.

dihydrogen molecules. Reduction of the second arene ring of 4H-Acr begins presumably when most (or all) of the acridine is consumed. Further experiments, particularly the influence of dihydrogen pressure, will be necessary to get more information.

Conclusion

Our group has extensively studied the properties of the bis(dihydrogen) complex **1** and shown its versatile reactivity toward, in particular, substitution reactions, hydrogen transfer, and catalytic C−H, Si−H, and (very recently) B−H activation.[12,13,21,22,31] The present results show that **1** can also activate N-heteroaromatic compounds to produce new pyridine, pyrrole, or acridine complexes. Similar studies on the reactivity of [Mo(PMe$_3$)$_6$] toward heterocyclic nitrogen compounds have just been reported by Parkin et al.[32] All these new N-heteroaromatic complexes serve as models for HDN catalysis. In our system, **1** catalyzes the hydrogenation of quinoline and isoquinoline. Reduction into 5,6,7,8-tetrahydro derivatives differs from what is generally observed with other catalysts. Moreover, we have successfully achieved acridine reduction into 1,2,3,4,5,6,7,8-octahydroacridine and identified at least one intermediate in the catalytic cycle. Selective hydrogenation of polynuclear N-heteroaromatic compounds, such as acridine, is important for the production of useful functionalized organic intermediates. In this respect, a synthesis aimed at a large-scale production of 8H-Acr has been recently described.[33] It is a multistep process that requires the not readily available starting material 2,2′-methylenebis(cyclohexanone) or 2-hydroxytricyclo-[7.3.1.0^{2,7}]tridecan-13-one. In contrast, our synthesis is a one-pot catalytic reaction, using commercially available acridine. This result emphasizes the interest in simple mechanistic studies of hydrogenation reactions.

Similar studies, but with S-heteroaromatic substrates, will be reported in due course.

Experimental Section

General Procedures. Microanalyses were performed by the Laboratoire de Chimie de Coordination Microanalytical Service. Proton and phosphorus spectra were recorded on a Bruker AC 200 (at 200.132 and 81.015 MHz, respectively) and on an AMX 400 (at 400.130 and 161.985 MHz) apparatus. ^{1}H and ^{13}C NMR spectra of acridine and 8H-Acr were recorded on a Varian Inova-300 instrument (300.078 and 75.455 MHz, respectively). Other ^{13}C NMR spectra were obtained by using Bruker AM 250 (50.323 MHz) and AMX 400 (100.624 MHz) spectrometers, all operating in the Fourier transform mode. IR spectra (KBr) were recorded on an Bio-Rad FTS 165 spectrometer at the Institute of Coal Chemistry, Polish Academy of Sciences, Gliwice, Poland. All manipulations were carried out under argon using standard Schlenk-line techniques. All solvents were freshly distilled from standard drying agents and thoroughly degassed under argon prior to use. Acridine (Aldrich) was purified by sublimation. $RuCl_3 \cdot 3H_2O$ was purchased from Johnson Mattey Ltd., and all other reagents were purchased from Aldrich or Fluka and were used as obtained but degassed before use. Reaction products were analyzed by GC on a Hewlett-Packard 5890 apparatus fitted with a FID detector using a capillary column (30 mm × 0.32 mm) packed with cross-linked methyl silicone. GC/MS (EI, 70 eV) determinations were performed on an HP 5970 MSD apparatus. Special care must be taken in considering GC/MS analysis data of the hydrogenation products of Q and iQ. Results based on the mass spectra libraries may be ambiguous. Homogeneity of the reaction mixtures has been confirmed by tests with liquid mercury, which is known to inhibit colloidal catalysis.[34] **1** was prepared by the published method, and hydrogenations were performed as previously described.[13]

[RuH$_2$(η^2-H$_2$)(η^1(*N*)-C$_5$H$_5$N)(PCy$_3$)$_2$] (2). On addition of pyridine (0.036 mL, 0.45 mmol) to a suspension of **1** (0.100 g, 0.15 mmol) in pentane (3 mL), an immediate change of color of the mixture from beige to yellow-orange was observed, with gas evolution and formation of a yellow solid. The suspension was stirred overnight, after which the yellow precipitate was filtered off, washed with pentane (3 × 1.5 mL), and dried under a stream of argon followed by vacuum drying. The solid was characterized by ^{1}H and ^{31}P NMR as [RuH$_2$(η^2-H$_2$)(η^1(*N*)-C$_5$H$_5$N)(PCy$_3$)$_2$] (**2**) contaminated with **1** (ca. 10%). ^{1}H NMR (400 MHz, C$_7$D$_8$, 293 K): δ 9.11 (br, 2H, H^{2,6}), 6.77 (br, 1H, H^4), 6.35 (br, 2H, H^{3,5}), 2.3−1.2 (m, 66H, PCy$_3$), −9.47 (t, 4H, J_{P-H} = 13.5 Hz, Ru−H). ^{31}P{^{1}H} NMR (121 MHz): δ 71.9 (s). ^{13}C{^{1}H} NMR (100 MHz): δ 158.4 (br, C^{2,6}), 122.9 (s, C^{3,5}); the other Py signals were obscured by solvent resonances.

[RuH(η^5-C$_4$H$_4$N)(PCy$_3$)$_2$]·Pyr (3). Pyrrole (0.11 mL, 1.59 mmol) was added to a suspension of **1** (0.06 g, 0.09 mmol) in pentane (3 mL). A gradual dissolution of **1** was observed with formation of a yellow solution. After 2 h, the solvent was evaporated under vacuum and 5 mL of diethyl ether was added. After filtration, the solution was concentrated to ca. 2 mL, yielding a yellow crystalline product. It was filtered off and washed with methyl alcohol (2 × 2 mL) before drying in vacuo. Yield: 0.06 g (84%). Anal. Calcd for C$_{44}$H$_{76}$N$_2$P$_2$Ru (the complex crystallizes with one pyrrole molecule): C, 66.38; H, 9.62; N, 3.52. Found: C, 66.25; H, 9.57; N, 3.64. ^{1}H NMR (300 MHz, C$_6$D$_6$, 293 K): δ 6.05 (s, 2H, η^5-C$_4$H$_4^{2,5}$N), 5.14 (s, 2H, η^5-C$_4$H$_4^{3,4}$N), 2.3−1.2 (m, 66H, PCy$_3$), −15.86 (t, 1H, J_{P-H} = 36.8 Hz, Ru−H). ^{31}P{^{1}H} NMR (81 MHz): δ 66.5 (s). ^{13}C NMR (75 MHz): δ 105.7 (d, J_{C-H} = 185 Hz, C^2), 78.0 (d, J_{C-H} = 179 Hz, C^3).

[RuH$_2$(η^5-C$_4$H$_4$N)(PCy$_3$)$_2$][BF$_4$] (4). A diethyl ether solution of HBF$_4$·O(CH$_2$CH$_3$)$_2$ (85%; 0.037 mL, 0.21 mmol) was added to a cooled (−50 °C) suspension of **2** (0.17 g, 0.21 mmol) in dry acetone (5 mL). The mixture was warmed to room temperature with stirring. The resulting colorless solution was stirred for 0.5 h followed by evaporation to dryness. The colorless crystalline product that formed was washed with cold (−10 °C) acetone (2 × 1 mL) and dried under vacuum. Yield: 0.124 g (71%). Anal. Calcd for C$_{40}$H$_{72}$BF$_4$NP$_2$Ru: C, 58.80; H, 9.24; N, 1.71. Found: C, 58.70; H, 9.24; N, 1.62. ^{1}H NMR (300 MHz, (CD$_3$)$_2$CO, 298 K): δ 6.96 (s, 2H, η^5-C$_4$H$_4^{2,5}$N), 6.37 (s, 2H, η^5-C$_4$H$_4^{3,4}$N), 2.3−1.2 (m, 66H, PCy$_3$), −10.30 (t, 2H, J_{P-H} = 24.4 Hz, Ru−H$_2$). ^{31}P{^{1}H} NMR (81 MHz): δ 79.5 (s). ^{13}C-{^{1}H} NMR (50 MHz): δ 109.5 (s, C^2), 95.1 (s, C^3).

[RuH$_2$(η^4-C$_{13}$H$_9$N)(PCy$_3$)$_2$] (5). A suspension of **1** (0.108 g, 0.162 mmol) with acridine purified by sublimation (0.058 g, 0.324 mmol) in 4 mL of pentane was stirred for 2 h, yielding a yellow microcrystalline product that was separated, washed with pentane (3 × 2 mL), and dried in vacuo. Yield: ca. 0.12 g (88.1%). Anal. Calcd for C$_{49}$H$_{77}$NP$_2$Ru: C, 69.78; H, 9.21; N,

(31) See for example: (a) Delpech, F.; Sabo-Etienne, S.; Daran, J.-C.; Chaudret, B.; Hussein, K.; Marsden, C. J.; Barthelat, J.-C. *J. Am. Chem. Soc.* **1999**, *121*, 6668. (b) Atheaux, I.; Donnadieu, B.; Rodriguez, V.; Sabo-Etienne, S.; Chaudret, B.; Hussein, K.; Barthelat, J.-C. *J. Am. Chem. Soc.* **2000**, *122*, 5664. (c) Delpech, F.; Mansas, J.; Leuser, H.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **2000**, *19*, 5750. (d) Montiel-Palma, V.; Lumbierres, M.; Donnadieu, B.; Sabo-Etienne, S.; Chaudret, B. *J. Am. Chem. Soc.* **2002**, *124*, 5624.

(32) Zhu, G.; Tanski, J. M.; Churchill, D. G.; Janak, K. E.; Parkin, G. *J. Am. Chem. Soc.* **2002**, *124*, 13658.

(33) Pilato, M. L.; Catalano, V. J.; Bell, T. W. *J. Org. Chem.* **2001**, *66*, 1525.

(34) (a) Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855. (b) Morton, D.; Cole-Hamilton, D. J.; Utuk, I. D.; Paneque-Sosa, M.; López-Poveda, M. *J. Chem. Soc., Dalton Trans.* **1989**, 489.

1.66. Found: C, 69.87; H, 9.93; N, 1.63. IR: ν(Ru−H) 2015 (vs) and 1987 (vs) cm^{-1}. ^1H NMR (200 MHz, C_6D_6, 293 K): δ 8.06 (d, 1H, H^5, $J_{H-H} = 7.9$ Hz), 7.4−7.1 (m, 3H, $H^{6,7,8}$), 6.78 (s, 1H, H^9), 5.72 (br, 1H, H^4), 5.43 (br, 1H, H^1), 4.58 (d, 1H, H^3, $J_{H-H} = 5.9$ Hz), 4.07 (d, 1H, H^2, $J_{H-H} = 5.9$ Hz), 2.3−1.2 (m, 66H, PCy_3), −11.22 (t, 2H, $J_{P-H} = 28.0$ Hz, Ru−H). $^{31}P\{^1H\}$ NMR (81 MHz): δ 70.5 (s).

Acridine (NMR data given for comparison, C_6D_6, 293 K.) ^1H NMR (300 MHz): δ 8.56 (d, 2H, $H^{4,5}$, $J_{3-4,5-6} = 8.8$ Hz), 8.20 (s, 1H, H^9), 7.66 (d, 2H, $H^{1,8}$, $J_{1-2,7-8} = 8.0$ Hz), 7.49 (dd, 2H, $H^{3,6}$, $J_{2-3,6-7} = 8.0$ Hz, $J_{3-4,5-6} = 8.8$ Hz), 7.25 (dd, 2H, $H^{2,7}$, $J_{1-2,7-8} = 8.0$ Hz, $J_{2-3,6-7} = 8.0$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz): δ 152.2 (s, $C^{4a,10a}$), 137.9 (s, C^9), 132.8 (s, $C^{1,8}$), 132.3 (s, $C^{4,5}$), 130.7 (s, $C^{3,6}$), 129.2 (s, $C^{8a,9a}$), 128.0 (s, $C^{2,7}$).

1,2,3,4,5,6,7,8-Octahydroacridine (8H-Acr). 1 (0.02 g, 0.03 mmol) and acridine (purified by sublimation) (0.2688 g, 1.5 mmol) were placed in a Fisher−Porter flask under argon. Degassed cyclohexane (10 mL) was then added, and after pressurization with dihydrogen to 3 bar, the reactor was placed in an oil bath. During the course of warming the initially yellow suspension dissolved, giving a yellow solution. The reaction mixture was heated at 80 °C for 30 h, after which the reactor was cooled to room temperature and depressurized. The solvent was removed in vacuo, and the remaining solid was extracted with several portions of pentane. The pentane extracts were passed through "Celite" to remove solid impurities, after which pentane was removed under vacuum to give a colorless crystalline solid. Yield: 0.21 g (ca. 75%). Anal. Calcd for $C_{13}H_{17}N$: C, 83.37; H, 9.15; N, 7.48. Found: C, 83.38; H, 9.07; N, 7.43. ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ 7.02 (s, 1H, H^9), 2.85 (t, 4H, $H^{4,5}$, $J_{H-H} = 6.2$ Hz), 2.68 (t, 4H, $H^{1,8}$, $J_{H-H} = 6.2$ Hz), 1.86 (quint, 4H, $H^{3,6}$, $J_{H-H} = 6.1$ Hz), 1.77 (quint, 4H, $H^{2,7}$, $J_{H-H} = 6.1$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz): δ 154.0 (s, $C^{4a,10a}$), 137.4 (s, C^9), 129.2 (s, $C^{8a,9a}$), 32.3 (s, $C^{1,8}$), 28.4 (s, $C^{4,5}$), 23.4 (s, $C^{3,6}$), 22.9 (s, $C^{2,7}$).

X-ray Data. Data were collected at low temperature, $T = 160$ K for **3** and $T = 180$ K for 8H-Acr, on a Stoe imaging plate diffraction system (IPDS) equipped with an Oxford Cryosystems cooler device.The crystal-to-detector distance was 70 mm, and 192 exposures were obtained for **3** and 133 for 8H-Acr, with the crystals oscillating 1.3 and 1.5° in φ, respectively. The final unit cell parameters were obtained by least-squares refinement of 5000 reflections. No significant fluctuation of the intensity was observed. Structures were solved by direct methods using the program SIR92[35] and refined by least-squares procedures on F^2 using SHELXL-97.[36] All hydrogen atoms were located on a difference Fourier map, but they were introduced in calculations in idealized positions with an isotropic thermal parameter fixed at 20% higher than those of the carbon atoms to which they were connected. The hydride H(1) and the hydrogen H(2) connected to the pyrrole molecule in **3** and the hydrogen atom H(1) connected to C(1) in 8H-Acr were isotropically refined. All non-hydrogen atoms were anisotropically refined. Concerning the molecule of 1,2,3,4,5,6,7,8-octahydroacridine (8H-Acr), although the model does not show any centrosymmetry settle on an inversion center, the atoms C(1) and N(1) sit on two different sites. Therefore, these two atoms were refined by using a mixing of 50% of C(1) and 50% of N(1) on two distinct positions. Least-squares refinements were carried out by minimizing the function $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. A weighting scheme was used in the last refinement cycles, where weights are calculated from the following expression: $w = [\text{weight}] \times [1 - (\Delta(F)/6\sigma(F)]^2$.[36] Models reached convergence with $R_w = [\sum w(||F_o| - ||F_c|)^2/\sum(|F_o|)^2]^{1/2}$. The criteria for a satisfactory complete analysis were the ratios of rms shift to standard deviation being less than 0.1 and no significant features in the final difference maps. All calculations were performed by using the program WinGX, version 1.64-04.[37] The molecules were drawn with the aid of ORTEP32,[38] and the atomic scattering factors were taken from ref 39.

Further details on the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ, U.K., on quoting the full journal citation.

Acknowledgment. This work was supported by the Polish Academy of Sciences and the CNRS under Contract No. 9774 and the Committee for Scientific Research (KBN) (A.F.B.) under Contract No. PBZ-KBN 15/T09/99/01d.

Supporting Information Available: Tables giving X-ray crystallographic data for **3** and 8H-Acr. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020995P

(35) Altomare, A.; Cascarano, G.; Giacovazzo G.; Guagliardi A.; Burla M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(36) Sheldrick, G. M. SHELX-97, Program for Crystal Structure Analysis; Universität Göttingen, Göttingen, Germany, 1998.

(37) WINGX Program: Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

(38) ORTEP3 for Windows: Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

(39) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.