

Room Temperature Activation of Aromatic C–H Bonds by Non-Classical Ruthenium Hydride Complexes Containing Carbene Ligands

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Dedicated to Prof. Manfred T. Reetz on the occasion of his 60th birthday.

Abstract: Non-classical ruthenium hydride complexes are promising lead structures for the C–H bond activation and functionalization of aromatic compounds. In the present paper, the preparation and crystallographic characterisation of the first organometallic complexes bearing dihydrogen ligands and *N*-heterocyclic carbene ligands in the same coordination sphere are described. The mixed phosphine/carbene complex [(IMes)Ru(H)₂(H₂)₂(PCy₃)] (IMes = 1,3-dimesityl-1,3-dihydro-2*H*-imidazol-2-ylidene;

3a) shows a unique reactivity pattern in the inter- and intramolecular activation of C–H bonds. In particular, complex **3a** effects a rapid and remarkably selective intermolecular activation of *sp*² C–H bonds in simple aromatic compounds at room temperature.

Keywords: C–H bond activation; deuterium exchange; homogeneous catalysis; *N*-heterocyclic carbenes; hydrido complexes; ruthenium complexes

Introduction

The functionalization of aromatic compounds by direct conversion of C–H to C–C or C–X (X = N, O) bonds can open new sustainable pathways for the synthesis of substituted aromatics.^[1] In 1993, Murai first reported on the ruthenium-catalyzed coupling of aromatic compounds with unsaturated substrates such as olefins or carbon monoxide.^[2] The Murai reaction shows a broad scope for both coupling partners and provides a promising synthetic approach to the waste-free construction of structurally diverse C–C skeletons.^[3] Cleavage of an aromatic *sp*² C–H bond in *ortho*-position to a suitable anchoring group (e.g., C=O or C=NR) constitutes a key step in the catalytic cycle.^[3b,4]

The first and still widely used generation of catalysts consists of ruthenium carbonyl hydride complexes such as [(PPh₃)₃Ru(CO)(H)₂] (**1**).^[3] Generally, these complexes require high reaction temperatures (≥ 110 °C) and high catalyst loadings (≥ 10 mol %). More recently, Chaudret reported that his non-classical ruthenium hydride complex [(PCy₃)₂Ru(H)₂(H₂)₂] (PCy₃ = tricyclohexylphosphine, **2**)^[5] is able to initiate the Murai-type

coupling of acetophenone and ethylene even at room temperature.^[6] We found that the scope of the two types of catalysts is complementary in certain cases, for example, with electron-poor acetophenones being more reactive with **2** as compared to **1**.^[7] Unfortunately, catalyst **2** has a very limited lifetime under catalytic conditions resulting from a rapid deactivation process and loss of PCy₃ from the catalytically active ruthenium centre.^[8]

The substitution of PCy₃ for strongly bulky and basic *N*-heterocyclic carbene ligands^[9] has been proven a successful approach to generate active and stable ruthenium catalysts, e.g., for olefin metathesis.^[10] However, there are currently no examples for organometallic compounds containing a basic carbene ligand in the vicinity of the strongly acidic M–H₂ moiety.^[11,12] This prompted us to target the synthesis of the carbene analogues of Chaudret's complex, [(IMes)_xRu(H)₂(H₂)₂(PCy₃)_{2-x}] (IMes = 1,3-dimesityl-1,3-dihydro-2*H*-imidazol-2-ylidene; **3a**: x = 1; **3b**: x = 2).

In the present paper, we report on the preparation and X-ray crystallographic characterization of **3a** and **3b**. Furthermore, we describe that **3a** is able to activate C–H

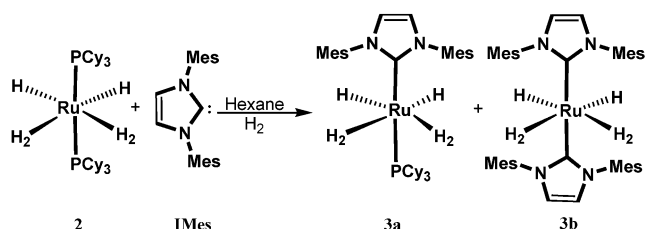
bonds in simple aromatic compounds very efficiently. In particular, this is evidenced by a rapid and selective H/D exchange process at room temperature. The intermolecular exchange process is accompanied by two different modes of sp^3 C–H bond activation in the coordination sphere of the ligand.

Results and Discussion

Initial attempts to prepare complexes **3** via the direct hydrogenation route^[7] starting from [(cod)Ru(η^3 -C₄H₇)₂] and free IMes were unsuccessful, most likely due to a surprising lack of reactivity of the carbene ligand with the ruthenium precursor. Fortunately, we found that the mixed carbene/phosphine complex **3a** is obtained readily by treatment of Chaudret's complex **2** with IMes under H₂ atmosphere in hydrocarbon solvents (Scheme 1). Under optimized conditions, **3a** was isolated in good yield directly from the reaction mixture as a dark brown powder upon cooling and filtration (Table 1). Double substitution to give the bis-carbene hydride [(IMes)₂Ru(H)₂(H₂)₂] **3b** was observed only in very small amounts even after prolonged treatment of **2** with IMes in excess.

Crystals of **3a** suitable for X-ray diffraction were obtained by slow crystallisation from a dilute mother liquor at 0 °C.^[13] The molecular structure reveals a *trans* arrangement of the two bulky ligands, as expected (Figure 1). The C–Ru–P angle amounts to 165.98(7)° indicating a significant deviation from linearity, which is in contrast to the linear arrangement in the complex **2**.^[14] The Ru–C and Ru–P distances are in the typical range observed for complexes containing the two different ligand types.^[10a] The mesitylene rings of the carbene ligand are rotated relative to each other by 6°.

For complex **3a**, a total of six peaks were located from the difference Fourier map in the coordination sphere of ruthenium. These peaks were interpreted as hydrogen atoms with distances from the central ruthenium atom ranging between 1.44(3) and 1.82(5) Å. Two hydrogen atoms (H8 and H9) have no close neighbours and can be considered as hydride ligands positioned *cis* to each other. The remaining four hydrogen atoms are arranged in pairs with interatomic distances of



Scheme 1. Formation of **3a** and **3b** from **2** and IMes (IMes = 1,3-dimesityl-1,3-dihydro-2H-imidazol-2-ylidene; Mes = Mesityl = 2,4,6-trimethylphenyl).

Table 1. Optimized conditions for the synthesis of **3a**.

IMes/Ru	H ₂ [bar]	Solvent	Time [h]	Temp. [°C]	Yield [%]
1.1/1	4	Toluene	3	RT	0
1.1/1	5	Toluene	19	55	0
2.8/1	4	Hexane	3	50	30
1/1	5	Hexane	3	55	20
1/1	5	Hexane	6	55	65

0.84(5) and 0.67(6) Å, and they are interpreted as dihydrogen ligands. One of these H₂ ligands (H4,H5) resides on the same plane as the two hydrides (H8,H9) whereas the shorter H₂ moiety (H6,H7) is almost perpendicular to it. Despite some variation in the individual values, the X-ray data suggest that the Ru–H distance is longer for the dihydrogen ligands [$d = 1.69(5)$ Å] than for the classical hydrides [$d = 1.52(3)$ Å].

A small amount of crystalline **3b** was isolated upon cooling from a reaction mixture containing IMes and **2** in a 4:1 ratio after 19 h at 55 °C. In the crystal lattice 20% of the sites were occupied by the dinitrogen complex [(IMes)₂Ru(H)₂(N₂)(H)₂] (**4**) (Figure 2). Complex **4** is most likely formed from **3b** by incorporation of adventitious nitrogen during the preparation and mounting of the crystals. In addition to the end-on dinitrogen ligand, four peaks were located from the difference Fourier map in the coordination sphere of ruthenium. They were interpreted as hydrogen atoms resulting in Ru–H distances in the range from 1.39(6) and 1.66(3) Å. Two

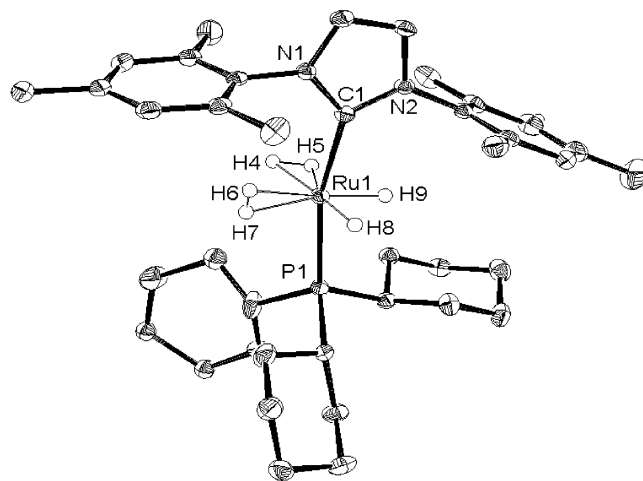


Figure 1. Molecular structure of **3a** as determined by single crystal X-ray diffraction. Selected atom distances [Å] and angles [°] (thermal ellipsoids are given on the 50% probability level): Ru1–C1 2.055(2), Ru1–P1 2.317(7), Ru1–H4 1.82(5), Ru1–H5 1.60(4), Ru1–H6 1.69(4), Ru1–H7 1.63(5), Ru1–H8 1.60(3), Ru1–H9 1.44(3); C1–Ru1–P1 165.98(7), H8–Ru1–H9 81.0(18), H9–Ru1–H5 79.9(19), H8–Ru1–H6 88.7(19).

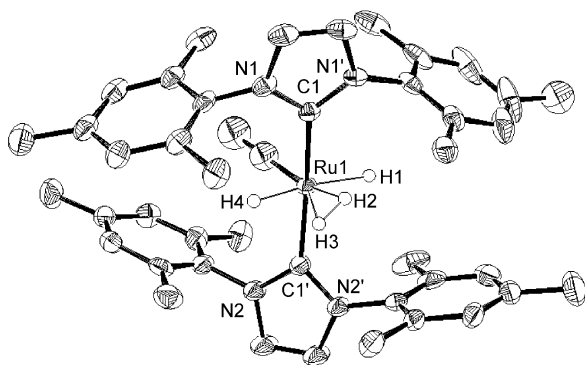


Figure 2. Molecular structure of **4** as determined by single crystal X-ray diffraction. Selected atom distances [Å] and angles [°] (thermal ellipsoids are given on the 50% probability level): H2–H3 0.90(8), C1'–Ru1 2.050(4), C1–Ru1 2.057(4), C1–Ru1–C1' 166.54(16), H2–Ru1–H3 34.0(3).

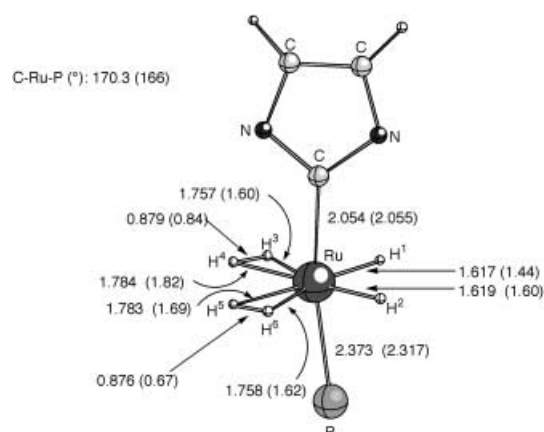


Figure 3. Comparison of calculated and crystallographically determined atom distances [Å] and angles [°] of **3a** (for clarity only the core of the complex is shown). Geometries were calculated on the BP86(RI)/TZVP level (details see ref.^[15]), figures in brackets denote the crystallographically determined values).

of the hydrogen atoms are at a distance of 0.90(8) Å from each other [the H–Ru–H angle is 34(3)°] and have been assigned as a dihydrogen ligand. The other two hydrogen atoms are *trans* to each other. The angle between the two least squares planes formed by the five-membered rings of the two *N*-heterocyclic carbene ligands is 37.5°.

Key features of the experimentally determined molecular structure of **3a** are reflected in a theoretical analysis by DFT calculations (Figure 3).^[15] Although the metal hydrogen distances are somewhat overestimated in the calculations, the ruthenium hydride distances are predicted to be significantly shorter (1.62 Å) than the Ru–H distances in the non-classical binding mode (1.75–1.87 Å) at several levels of computation. The distances and angles within the in-plane dihydrogen ligand are also very similar. The out-of-plane coordination of the second H₂ ligand is, however, not

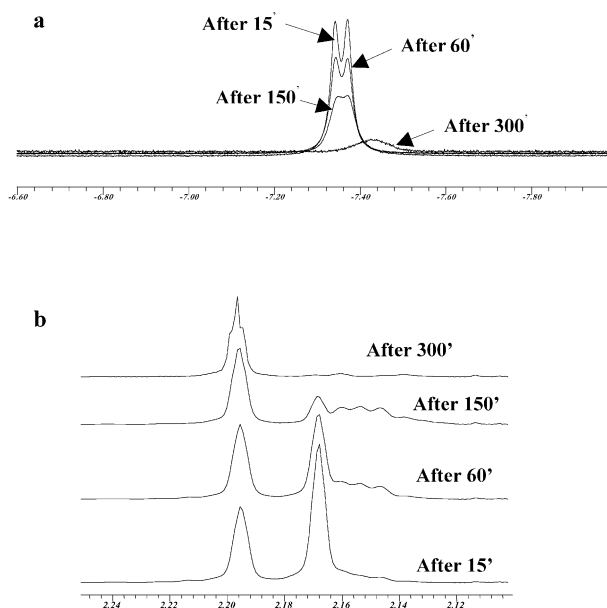
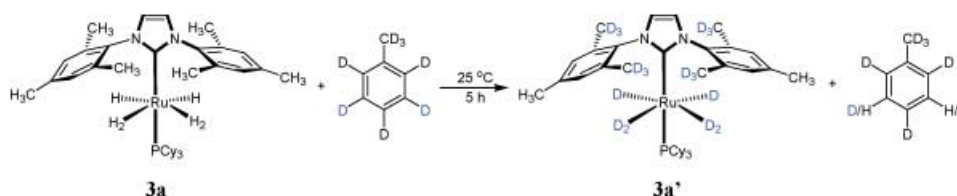


Figure 4. Significant parts of the ¹H NMR spectra for the H/D exchange in **3a**: **a**) averaged signal for the classical and non-classical hydride ligands; **b**) CH₃ groups in the IMes ligand.

indicated at this theoretical level. The calculated (CDA analysis,^[15] B3LYP/B2) dissociation energies for the IMes (–48.4 kcal/mol) and the PCy₃ (–29.0 kcal/mol) ligands are in agreement with a stronger Ru–carbene interaction.^[10b,10c]

¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectroscopic studies demonstrate that the molecular core of **3a** is retained in toluene-*d*₈ solution. In a freshly prepared sample, the six hydrogens in the coordination sphere of ruthenium give rise to an averaged signal at room temperature, appearing as a doublet (²J_{HP} = 8.32 Hz) of broad signals centred at δ = –7.35. However, the intensity of this signal decreases quickly to only 10% of its original strength after 5 hours at room temperature (Figure 4a). The signals of the *ortho*-methyl groups in the IMes ligand (δ = 2.17) disappear practically at the same rate (Figure 4b). This decay of signal intensities is accompanied by a concurrent increase in the solvent resonances.

Detailed analysis of the time-resolved ¹H and ¹³C{¹H} NMR spectra reveals that these changes result from a rapid H/D exchange between the *meta*-position of the deuterated aromatic solvent, the Ru–H moieties, and the *ortho*-methyl groups of the IMes ligand (Scheme 2, Figure 5). The incorporation of deuterium at the metal centre and the methyl positions was unambiguously demonstrated by deuterium NMR spectroscopy and by the characteristic coupling pattern in the ¹³C{¹H} NMR spectra. This activity of **3a** for the activation of simple aromatic C–H bonds is in remarkable contrast to Chaudret's complex **2**, which did not show any significant exchange with toluene-*d*₈ under the present conditions.



Scheme 2. H/D exchange process between **3a** and toluene- d_8 .

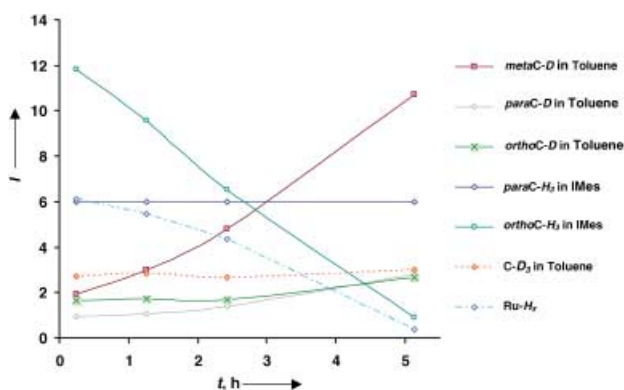
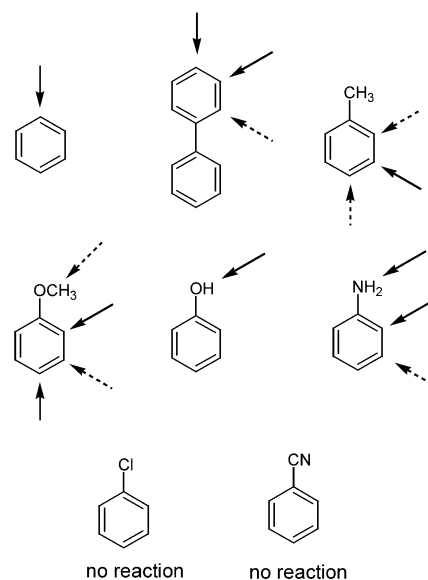


Figure 5. Time-dependent evolution of the ^1H NMR intensities I (arbitrary scale) of **3a** and toluene during the H/D exchange with **3a** in toluene- d_8 (see text for details).

Despite the rapid incorporation of deuterium in the *ortho*-methyl of the IMes ligand,^[16] the methyl groups in *para*-position and in toluene are not involved in the exchange process to a significant extent even after prolonged reaction times. There is, however, a slow secondary exchange process leading to incorporation of deuterium in the cyclohexyl ring of the PCy₃ ligand.^[17] After several weeks, approximately 75% of the hydrogens in the cyclohexyl rings were replaced with deuterium whereby the exchange occurred preferentially at C3, C4 and – to a lesser extent – C1.

In order to get further insight into the sp^2 C–H bond activation by complex **3a**, we investigated the H/D exchange with a series of other aromatic compounds. Upon dissolving **3a** in benzene- d_6 , the exchange between the complex and the solvent was even faster than with toluene- d_8 , leading to complete deuteration at the metal centre and the *ortho*-methyl groups within 5 minutes at ambient conditions. Solutions of the deuterated ruthenium complex **3a'** obtained by this method were treated with 10 equivalents of another aromatic compound (relative ratios: benzene- d_6 :**3a'**:substrate = 1000:1:10) and analyzed for decay of the substrate signals as a function of time by ^1H NMR at room temperature. Figure 6 shows the results of a typical experiment as exemplified for aniline as the aromatic substrate. The disappearance of the signals arising from the *ortho* protons upon incorporation of deuterium in the aromatic compound is accompanied by a concurrent increase of the signal intensity of the solvent. The overall reactivity pattern resulting from these investigations for



Scheme 3. Incorporation of deuterium in aromatic compounds in benzene- d_6 solutions containing **3a'**. The style of the arrows indicates the relative reactivity of the individual positions (full arrow: fast exchange; dashed arrow: slow exchange).

various aromatic compounds is summarized in Scheme 3.

As mentioned above, the H/D exchange of **3a** with benzene is very fast. Similarly, **3a'** exchanges readily with biphenyl whereby the incorporation occurs mainly in *meta* and *para* positions as further demonstrated in Figure 7. It seems tempting to assign the lower reactivity in *ortho*-position to steric hindrance, but more complex control mechanisms seem to be operating as indicated by the strong *meta* preference of the exchange with toluene.

Aromatic compounds with strongly electronegative substituents such as Cl and CN are not activated under the present conditions. Anisole is deuterated with moderate activity at the aromatic core with a slight *ortho/para* preference. Deuterium incorporation in the OCH₃ group is also noticeable, amounting to approximately 20% OCH₂D after 14 hours. Phenol, however, exchanges only at the protic position with no detectable incorporation of deuterium in the aromatic positions. In contrast, aniline shows a fast exchange in the NH₂ group and simultaneous incorporation of deuterium almost exclusively in the *ortho* position of the aromatic ring (Figures 6 and 8).

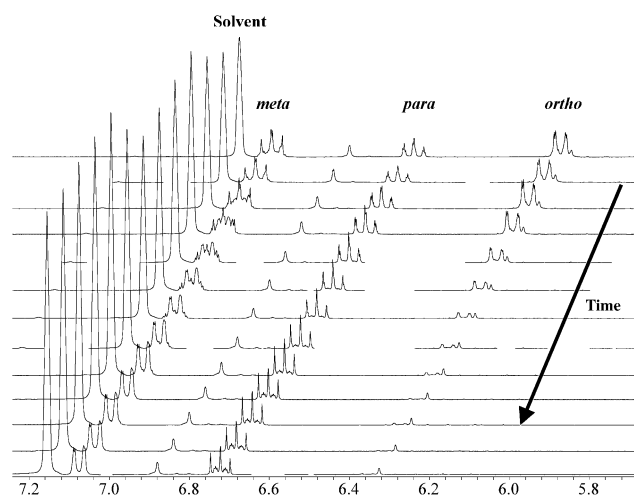


Figure 6. Staggered plot of the time dependent ^1H NMR spectra during the H/D exchange of aniline in benzene- d_6 in the presence of **3a'** (every second spectrum of the monitoring process is shown for clarity).

In summary, we have prepared the first organometallic compounds containing *N*-heterocyclic carbene ligands and dihydrogen ligands in the same coordination sphere. The non-classical ruthenium hydride [(IMes)-Ru(H) $_2$ (H $_2$) $_2$ (PCy $_3$)] **3a** exhibits a unique reactivity pattern for intra- and intermolecular activation of C–H bonds. In particular, complex **3a** effects a rapid and remarkably selective intermolecular activation of sp^2 C–H bonds in simple aromatic compounds at room temperature. This reactivity appears to be directly related to the presence of the IMes ligand in the coordination sphere of **3a**, as the related bisphosphine complex **2** does not show a similar reactivity under identical conditions. Substituents at the aromatic core of the substrate have a decisive influence on the reactivity of the exchange process, exhibiting a complex interplay of electronic and steric effects. Further studies to elucidate the mechanism of the C–H activation process and to evaluate the catalytic properties of **3a** are currently under way.

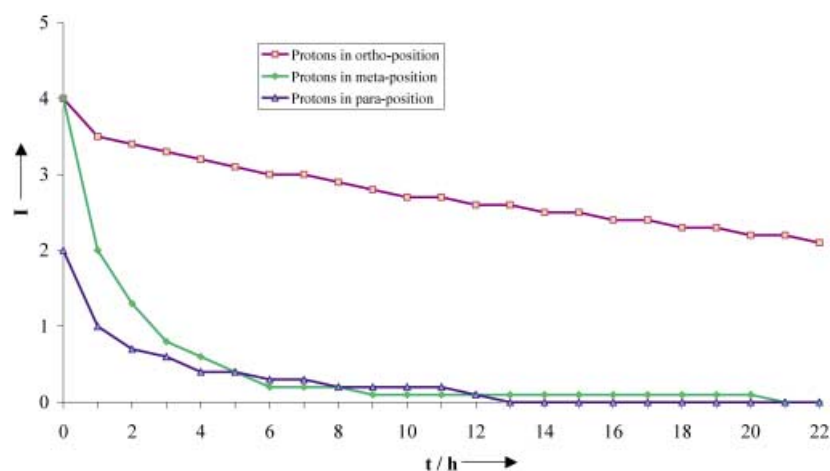


Figure 7. Time-dependent evolution of the ^1H NMR intensities I (arbitrary scale) of biphenyl in a benzene- d_6 solution of **3a'** (see text for details).

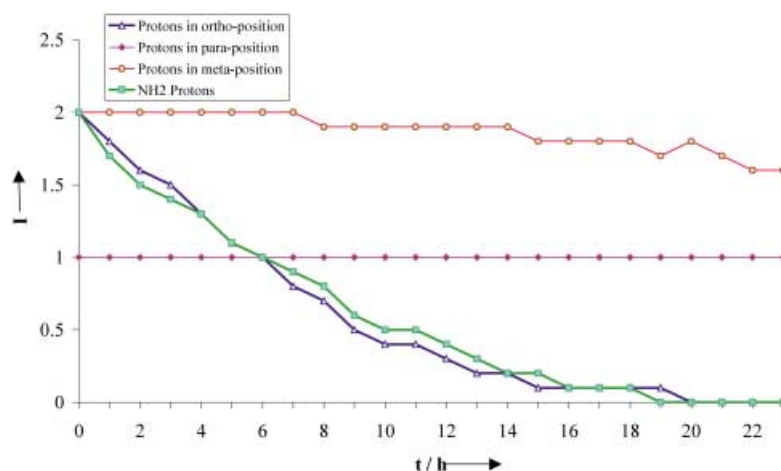


Figure 8. Time-dependent evolution of the ^1H NMR intensities I (arbitrary scale) of aniline in a benzene- d_6 solution of **3a'** (details see text).

Experimental Section

General Procedures

Reactions were conducted under Ar or H₂ atmospheres. Solvents and substrates were purchased from Aldrich and Acros and purified according to standard procedures. Preparation of the IMes ligand was carried out following a modified literature procedure.^[18] Chaudret's complex was obtained according to the direct hydrogenation route.^[7] ¹H NMR, ¹³C NMR and ³¹P NMR spectra were recorded in deuterated solvents on a Bruker DPX 300 spectrometer. ²D NMR and ¹³C NMR spectra of **3a** were performed in non-deuterated solvents on a Bruker DMX 600 spectrometer.

Preparation of the Complex (IMes)Ru(H)₂(H₂)₂(PCy₃) **3a**

Compound **2** (258 mg, 0.38 mmol), IMes (133 mg, 0.43 mmol) and hexane (15 mL) were introduced in a thick-walled glass reactor which was subsequently charged with H₂ (5 bar). The white suspension was heated under stirring to 55 °C for 6 h after which the solution had turned dark orange. After cooling to room temperature, the solution was transferred to a Schlenk tube. Complex **3a** was obtained as a dark brown powder by cooling to -20 °C for several days followed by filtration and drying under H₂ atmosphere; Yield: 157 mg (0.23 mmol, 60.5%); ¹H NMR (300 MHz, toluene-*d*₈, 25 °C): δ = -7.35 (d, 6H of Ru-H, ²J_{H,P} = 8.32 Hz), 1.0–2.0 (m, 33H of PCy₃), 2.17 (s, 12H, *o*-CH₃ of IMes), 2.19 (s, 6H, *p*-CH₃ of IMes), 6.36 (s, 2H, NCHCHN), 6.85 (s, 4H, *m*-CH of IMes); ³¹P NMR (121 MHz, toluene-*d*₈, 25 °C): δ = 78.09 (s); ¹³C NMR (150 MHz, toluene, 25 °C): δ = 199 (NCN, *J*_{P,C} = 74.4 Hz), 140.3 (NC1 of the mesitylene ring), 137.4 (*p*-C-CH₃ of IMes), 136.2 (*o*-C-CH₃ of IMes), 129.1 (*m*-CH of the IMes), 120.0 (CH of the imidazolium ring, *J*_{P,C} = 2.3 Hz), 38.2 (PCH of the Cy, *J*_{P,C} = 16.8 Hz), 30.6 (*o*-CH₂ of the Cy), 28.4 (*m*-CH₂ of the Cy, *J*_{P,C} = 9.7 Hz), δ = 27.4 (*p*-CH₂ of the Cy), 21.2 (*p*-CH₃ of the IMes), 18.8 (*o*-CH₃ of the IMes).

H/D-Exchange Experiments with **3a** and Deuterated Aromatic Compounds

Complex **3a** (13 mg; 0.018 mmol) and toluene-*d*₈ (0.6 mL) were introduced in a NMR tube under argon. The solution was analysed by ¹H NMR in intervals of 1 h for one day (see Figure 4 for details). The ²D NMR (92 MHz, toluene-*d*₈, 25 °C) after 3 h showed resonances at δ = 2.13 (*o*-Me of the mesitylene groups), 1.65 and 1.06 (Cy groups), and -7.3 (Ru-D). The same methodology was applied with benzene-*d*₆ as the solvent.

H/D-Exchange with **3a'** and Non-Deuterated Aromatic Compounds

Complex **3a** (5.4 mg; 0.0078 mmol) and benzene-*d*₆ (0.7 mL) were introduced in a NMR tube under argon. The solution was kept at room temperature for 24 hours and checked by ¹H NMR for full deuteration of **3a** to **3a'**. Then, aniline (7.2 mg; 0.078 mmol) was introduced and the solution was analysed by

¹H NMR in intervals of 1 h for one day (see Figure 6 for details). The H/D exchange experiments with other aromatic substrates were performed in the same way.

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References and Notes

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- [13] Crystal structure analyses. **3a**: brown crystals with dimensions 0.32 × 0.20 × 0.12 mm³, λ = 0.71073 Å, T = 100 K, monoclinic, P2₁/n (No. 14), a = 12.1460(7), b = 18.9333(11), c = 17.2816(10) Å, β = 106.291(2)°, V =

3814.6(4) Å³, $Z = 4$, $\rho_{\text{calc.}} = 1.205 \text{ Mg m}^{-3}$, $\mu = 0.480 \text{ mm}^{-1}$, $F(000) = 1480$, 13993 independent reflections of which 7807 with $I > 2\sigma I$ (total reflections 41072), $2\theta_{\text{max}} = 66.34^\circ$. Structure solution by Patterson method (SHELXS-97). Full matrix least squares refinement (SHELXL-97) versus F^2 . Data/restraints/parameters 13993/0/416. GOF on $F^2 = 0.92$, $R_1[I > 2\sigma(I)] = 0.058$, wR_2 (all data) = 0.125. Max./min. residual electron density: 0.7/−0.7 e Å^{−3}. Six hydrogen atoms at the ruthenium centre were located from the difference Fourier map and their positions and isotropic displacement parameters were refined. All other hydrogen atoms were forced to ride on the attached carbon atoms in geometrically idealised positions. CCDC-202653 contains the supplementary crystallographic data for this paper. These data can be obtained online free of charge (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033 or deposit@ccdc.cam.ac.uk). **3b/4**: pale yellow crystal with dimensions $0.39 \times 0.18 \times 0.18 \text{ mm}^{-3}$, $\lambda = 0.71073 \text{ Å}$, $T = 100 \text{ K}$, monoclinic, $P2_1/n$ (No. 14), $a = 14.2338(7)$, $b = 11.2474(5)$, $c = 24.3152(11) \text{ Å}$, $\beta = 92.095(2)^\circ$, $V = 3890.1(3) \text{ Å}^3$, $Z = 4$, $\rho_{\text{calc.}} = 1.216 \text{ Mg m}^{-3}$, $\mu = 0.435 \text{ mm}^{-1}$, $F(000) = 1496$, 8489 independent reflections of which 5916 with $I > 2\sigma(I)$ (total reflections 32528) $2\theta_{\text{max}} = 54^\circ$. Structure solution with Patterson method. Full matrix least squares refinement versus F^2 . Data/restraints/parameters 8489/0/423. GOF on $F^2 = 1.04$, $R_1[I > 2\sigma(I)] = 0.056$, $wR_2 = 0.1440$. Max./min. residual electron density: 1.6/−0.8 e Å^{−3}. Approximately 20% of the lattice sites in **3b** were occupied by the corresponding N₂-complex [Ru(H)₂(N₂)₂(IMes)₂] **4**, presumably formed

from reaction with adventitious N₂ during the set up of the diffraction experiment.

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- [15] Calculations on **3a** were carried out using the Gaussian98 and the Turbomole5.5 suite of programs. Gaussian98 calculations which were used as input for CDA-analysis were done on the B3LYP level of theory using the 6–31G(d) basis set for C, H, N and P and a (441/2111/31/1) valence basis for Ru associated with a non relativistic small core ECP. Turbomole calculations were carried out on the BP86 level of theory taking advantage of the RI-DFT method using the TZVP basis set together with a quasirelativistic ECP for Ru. All geometry optimisations were carried out with no constraints and all geometries were checked to be minima on the hypersurface by frequency calculations (zero imaginary frequencies). Further details and the full references for the computational methods are compiled in the Supplementary Material.
- [16] For metallation of the *ortho*-methyl groups in Ru-IMes complexes under much more forcing conditions, see: R. F. R. Jazzar, S. A. Macgregor, M. F. Mahon, S. P. Richards, M. K. Whittlesey, *J. Am. Chem. Soc.* **2002**, *124*, 4944–4945.
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