

Photoinduced C–H Activation and Catalytic Carbonylation of Benzene – New Features of a Tris(pyrazolyl)methanesulfonato (Tpms) Rhodium(I) Complex

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Irradiation of [(Tpms)Rh(CO)(PMe₃)] (**1**) in benzene or [D₆]benzene affords the rhodium(III) compounds [(Tpms)Rh(H)(C₆H₅)(PMe₃)] (**2**) and [(Tpms)Rh(D)(C₆D₅)(PMe₃)] (**2-d₆**) respectively. The $k_{\text{H}}/k_{\text{D}}$ ratio for the formation of **2** and **2-d₆** was found to be 1.1. The complexes **2** and **2-d₆** are stable

in protic solvents. When a solution of **1** in benzene is irradiated under carbon monoxide pressure, benzaldehyde is formed catalytically with turnover numbers of up to 20. The formation of **2** and [(Tpms)Rh(H)(COC₆H₅)(PMe₃)] (**4**) under catalytic conditions allows the proposal of a catalytic cycle.

Introduction

Since the first reports on C–H bond activation in 1965,^[1] the transition-metal-catalysed activation of alkanes and arenes has become one of the most challenging fields of organometallic chemistry.^[2] Bergman was the first to observe the oxidative addition of cyclohexane to the Cp*Rh(PMe₃) fragment in 1982,^[3] which led to the development of similar complexes with ligands such as tris(pyrazolyl)borates (Tp, Tp*).[4,5] So far none of the above-mentioned complexes has been reported to catalytically functionalize hydrocarbons or arenes by C–H activation. Until now carbonylation reactions based on tripodal rhodium(I) systems like [Tp*Rh(CO)(C₂H₄)] only produced stoichiometric amounts of insertion products.^[5b] The catalytic carbonylation of arenes and alkanes is, however, known with Vaska-type catalysts like [RhCl(CO)(PPh₃)₂]^[6] and analogous compounds.^[7,8]

We have recently reported^[9] the synthesis of the novel tris(pyrazolyl)methanesulfonato ligand (Tpms), a mono-anionic tripodal nitrogen ligand. TpmsRh^I compounds show a coordination chemistry which resembles that of analogous tris(pyrazolyl)borato compounds. Moreover, they are hydrolytically stable and soluble in polar protic solvents.^[10]

We describe here the C–H activation of benzene and [D₆]benzene with [(Tpms)Rh(CO)(PMe₃)] leading to the rhodium(III) complexes [(Tpms)Rh(R)(C₆R₅)(PMe₃)] (R = H, D) that catalyse the formation of benzaldehyde from benzene and carbon monoxide.

Results and Discussion

Photoactivation of [(Tpms)Rh(CO)(PMe₃)] (**1**)

The photolysis of the bright yellow [(Tpms)Rh(CO)(PMe₃)] (**1**) offers a convenient method for the generation

of a coordinatively unsaturated intermediate which can then undergo the oxidative addition of C–H bonds. Although **1** is only moderately soluble in benzene, irradiation leads to a quantitative conversion into the C–H activation product [(Tpms)Rh(H)(C₆H₅)(PMe₃)] (**2**). However, due to its low solubility in less polar solvents we have not yet found the correct reaction conditions for the C–H activation of saturated hydrocarbons.

Preparation of [(Tpms)Rh(H)(C₆H₅)(PMe₃)] (**2**) and [(Tpms)Rh(D)(C₆D₅)(PMe₃)] (**2-d₆**)

The UV/Vis spectrum of [(Tpms)Rh(CO)(PMe₃)] (**1**) shows a band at 232 nm ($\epsilon = 17000 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$), which is typical for the Tpms ligand, and a charge transfer band at 355 nm ($\epsilon = 2000 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). In order to prevent possible photochemical reactions of the pyrazoles, **1** is irradiated in Pyrex vessels ($\lambda > 290 \text{ nm}$) which serve as a cut-off filter. The yellow suspension of **1** in benzene gradually clears as the reaction proceeds leading to the whitish hydrido compound [(Tpms)Rh(H)(C₆H₅)(PMe₃)] (**2**) (Figure 1). The reaction is complete within one hour. When the reaction is performed in a 1:1 mixture of benzene/[D₆]benzene, **2** and [(Tpms)Rh(D)(C₆D₅)(PMe₃)] (**2-d₆**) are formed in a ratio of 1:0.9 (i.e. $k_{\text{H}}/k_{\text{D}} = 1.1$). This indicates that there is only a very small kinetic isotope effect.^[11]

Both **2** and **2-d₆** are soluble in benzene, toluene, and in polar organic solvents like THF and acetone. In wet solvents like acetone no decomposition is observed within hours at ambient temperatures. However, the hydrido compound **2** reacts with a stoichiometric amount of CCl₄ to

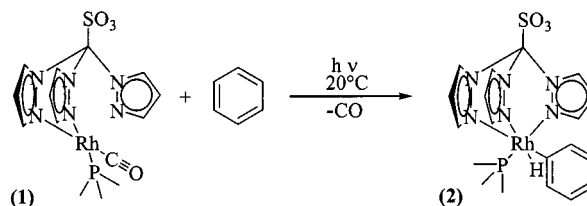


Figure 1. C–H activation of benzene with [(Tpms)Rh(CO)(PMe₃)] (**1**)

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give the corresponding chloro compound $[(\text{TpmsRh}(\text{Cl})(\text{C}_6\text{H}_5)(\text{PMe}_3)]$ (**3**) and chloroform within a few hours.

The ^1H NMR spectrum of the benzene activation product **2** shows a signal pattern consistent with a compound of C_1 symmetry. The most prominent signal is a doublet of doublets found at $\delta = -16.30$ for the hydride bound to the rhodium atom. The coupling constants to rhodium ($^1J_{\text{RhH}} = 26.0$ Hz) and phosphorous ($^2J_{\text{PH}} = 32.3$ Hz) are within the range found for similar $\text{Cp}^*[\text{12}]$ and $\text{Tp}^*[\text{13}]$ compounds. All the pyrazole protons (see Figure 2 for numbering scheme) show coupling to the hydride and the phosphorous. Due to limitations of the spectral resolution (≈ 0.2 Hz) only the *trans* couplings are observable. This allows a complete assignment of all protons by selective decoupling, COSY and NOESY-experiments (see Exp. Sect.).

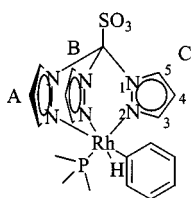


Figure 2. Schematic structure of the C_1 symmetrical complex $[(\text{TpmsRh}(\text{H})(\text{C}_6\text{H}_5)(\text{PMe}_3)]$ (**2**)

The deuteride bound to the rhodium in the $[\text{D}_6]\text{benzene}$ activation product **2-d₆** can be found as a doublet of doublets in the ^2H NMR spectrum at $\delta = -16.1$. Due to the differences in the magnetogyric ratio, the coupling constants are smaller by a factor of 6.5 ($^1J_{\text{RhD}} = 4$ Hz, $^2J_{\text{PD}} = 5$ Hz). Therefore no H–D coupling can be resolved in the ^1H NMR spectrum.

In the IR spectra of **2** and **2-d₆** the characteristic $\nu_{(\text{Rh}-\text{H})}$ band is found at $\tilde{\nu} = 2085\text{ cm}^{-1}$, whereas the $\nu_{(\text{Rh}-\text{D})}$ band can be observed at $\tilde{\nu} = 1500\text{ cm}^{-1}$. The frequency ratio caused by the different masses of H and D is close to the theoretical value of ≈ 1.41 .

The mass spectra show peaks at $[\text{M} - 1]^+$ for **2** and $[\text{M} - 2]^+$ for **2-d₆**. This indicates that the hydrido and deuterido ligands are lost under FAB conditions.

Catalytic Carbonylation of Benzene

A suspension of $[(\text{TpmsRh}(\text{CO})(\text{PMe}_3)]$ (**1**) in benzene was irradiated with a 125 W medium pressure mercury arc. The reaction was conducted in a Pyrex ($\lambda > 290\text{ nm}$) vessel equipped with Teflon seals and valves allowing us to maintain a carbon monoxide pressure of three to four atmospheres. The carbonylation proceeds without a significant induction period (Figure 3). This indicates that the primary photoprocess is fast under catalytic conditions. In the beginning the turnover frequency (TOF) is about 3 h^{-1} , which is in the same range as found for the Vaska-type compound $[\text{RhCl}(\text{CO})(\text{PMe}_3)_2]$ under similar conditions.^[7a] The analogous complex $[\text{Tp}^*\text{Rh}(\text{CO})(\text{PMe}_3)]$ ^[14] produces only sub-

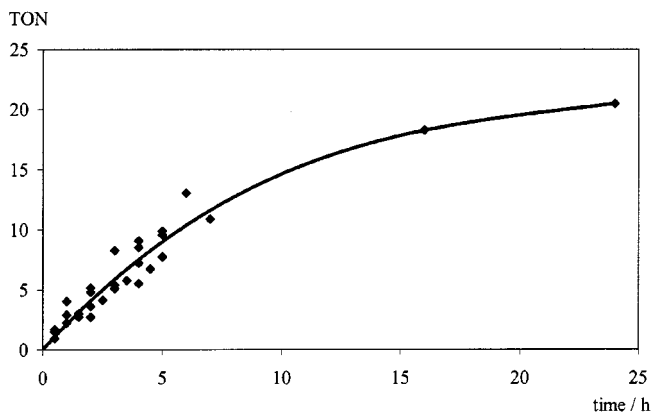


Figure 3. Time-dependence of the catalytic carbonylation of benzene

stoichiometric amounts of benzaldehyde within 5 hours under similar conditions.

The maximum turnover of 20 is reached after about 24 h. At that point only small amounts of the catalytically active hydride species can still be found in the reaction mixture. In addition secondary photoreactions of the benzaldehyde take place. This was also observed in the analogous reaction with $[\text{RhCl}(\text{CO})(\text{PMe}_3)_2]$ as catalyst.^[8]

Intermediates and Mechanism

After a short time the benzene activation product **2** and the carbon monoxide insertion product $[(\text{TpmsRh}(\text{H})(\text{COC}_6\text{H}_5)(\text{PMe}_3)]$ (**4**) can be identified by NMR spectroscopy. The most characteristic signal of **4** is a doublet of doublets for the hydrido ligand found at $\delta = -14.88$. The coupling constants as well as the spectral appearance are almost identical to those found for **2** indicating the structural relationship between **2** and **4**. This allows us to propose a catalytic cycle for the carbonylation of benzene with $[(\text{TpmsRh}(\text{CO})(\text{PMe}_3)]$ (**1**) as precursor (Figure 4).

The irradiation of the carbonyl compound **1** probably results in the formation of an unsaturated 14-electron complex, which reacts with benzene to give the hydridophenyl compound **2**. We exclude an associative mechanism as we could show that **1** does not undergo oxidative addition without irradiation. For the Vaska-type compound $[\text{RhCl}(\text{CO})(\text{PMe}_3)_2]$ an associative mechanism was proposed to be more likely than a dissociative one.^[7d]

The next step, leading to the CO insertion product **4**, again does not happen without irradiation. When complex **2** is stirred under carbon monoxide pressure without irradiation, the rhodium(I) compound **1** is recovered and no traces of **4** or benzaldehyde are observed. The reason for this is that **2** is a coordinatively saturated complex where one of the ligands has to be abstracted in order to add and insert CO. This is most likely to occur by a change of the tripod's denticity, as Tpms is known to act as a bi- or tridentate ligand in rhodium chemistry.^[10]

^1H and ^{31}P NMR studies of the reaction mixture show that **2** and **4** exist in a ratio of 3:1 throughout the catalysis,

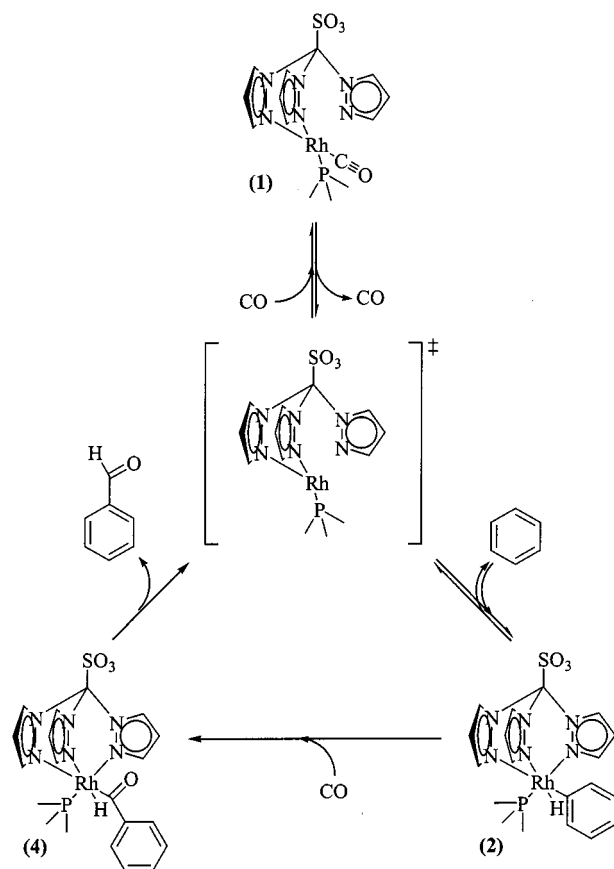


Figure 4. Proposed catalytic cycle for the photoinduced carbonylation of benzene

while only traces of **1** are found. This indicates that the Tpms ligand stabilises the catalytic intermediates **2** and **4** in a steady state at ambient temperatures. This is in clear contrast to the $[\text{RhCl}(\text{CO})(\text{PMe}_3)_2]$ catalyst where the intermediates of the catalytic cycle revert thermally to the starting material.^[15]

Conclusions

The compound $[(\text{TpmsRh}(\text{CO})(\text{PMe}_3))]$ (**1**) readily activates benzene under irradiation to give $[(\text{TpmsRh}(\text{H})(\text{C}_6\text{H}_5)(\text{PMe}_3))]$ (**2**), which is the first example of a $\text{TpmsRh}^{\text{III}}$ complex. The analogous reaction with $[\text{D}_6]\text{benzene}$ affords $[(\text{TpmsRh}(\text{D})(\text{C}_6\text{D}_5)(\text{PMe}_3))]$ (**2-d₆**). Both compounds are stable in protic solvents. The kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} = 1.1$) is similar to that found for the $[\text{Cp}^*\text{Rh}(\text{PMe}_3)_3]$ fragment.^[11a]

To the best of our knowledge, $[(\text{TpmsRh}(\text{CO})(\text{PMe}_3))]$ (**1**) is the only known catalyst with a tripodal ligand which is active in the catalytic carbonylation of benzene. The low steric bulk of the tripod and the phosphane help to keep the metal centre accessible while inhibiting intramolecular C–H activation. Therefore **1** produces efficiencies which are similar to those observed for the Vaska-type catalyst $[\text{RhCl}(\text{CO})(\text{PMe}_3)_2]$.

Compound **1** provides a push-pull system of a highly basic phosphane and the weakly donating Tpms, which can act as a bi- or tridentate ligand. This unique blend allows the stabilisation of both planar Rh^{I} and octahedral Rh^{III} complexes. This is the main reason why the hydridophenyl complex **2** and the hydridobenzoyl compound $[(\text{TpmsRh}(\text{H})(\text{COC}_6\text{H}_5)(\text{PMe}_3))]$ (**4**) are stable enough to be identified from the catalytically active reaction mixture.

Experimental Section

General Remarks: The compound $[(\text{TpmsRh}(\text{CO})(\text{PMe}_3))]$ (**1**), was synthesised as previously reported.^[10] All other reagents were commercial samples and were used as received. All reactions were carried out under nitrogen using standard Schlenk techniques unless stated otherwise. All solvents were purified and degassed by standard procedures. Filtration was done with 1 μm membrane filters (regenerated cellulose, Schleicher & Schuell). Reactions under 3–4 atm. pressure were performed in glass tubes equipped with Teflon seals and valves. All operations in glass vessels at elevated pressures should be done using effective body and face protection! Irradiation was done with a medium pressure mercury arc Philips HPK 125 (125 W, $\lambda > 230 \text{ nm}$). Turnover numbers (TON) and turnover frequencies (TOF) are based on the molar ratio of benzaldehyde/catalyst. One dimensional ^1H , ^{31}P , and ^{13}C NMR spectra were recorded with Bruker DRX 200 (at 296 K) or Bruker DRX 500 (at 300 K) spectrometers. Two dimensional NOESY and COSY as well as one dimensional ^2H , $^1\text{H}\{^1\text{H}\}$ and $^1\text{H}\{^{31}\text{P}\}$ NMR spectra were recorded with a Bruker DRX 500 spectrometer. The chemical shifts (δ) are given in ppm referenced to the solvent $[\text{D}_6]\text{benzene}$ at $\delta = 7.16$.^[16] Infrared spectra were recorded using a Bruker IFS 66 FT spectrometer. FAB mass spectra were recorded on a Finnigan MAT 8200 using a NBA matrix with addition of NaI. Elemental analyses were performed using a Perkin–Elmer CHN-2400/II elemental analyser. GC analysis was done with a HP-5890 series II chromatograph with a FID-detector and a MSD 5970 integrator. All concentrations were determined by comparison to calibration curves obtained with actual samples of benzaldehyde in benzene.

Hydridophenyltrimethylphosphane[tris(pyrazol-1-yl)methanesulfonato]rhodium(III), $[(\text{TpmsRh}(\text{H})(\text{C}_6\text{H}_5)(\text{PMe}_3))]$ (2**):** A suspension of **1** (10 mg, 0.020 mmol) in 10 mL of benzene was stirred in a Pyrex vessel in a water bath at room temperature. The mixture was irradiated for one hour. Addition of pentane precipitated 12 mg of a light grey solid. – ^1H NMR (500 MHz, C_6D_6): $\delta = -16.30$ (dd, $^1J_{\text{RhH}} = 26.0 \text{ Hz}$, $^2J_{\text{PH}} = 32.3 \text{ Hz}$, 1 H, hydrido-*H*), 0.65 (dd, $^2J_{\text{PH}} = 10.1 \text{ Hz}$, $^3J_{\text{RhH}} = 1.2 \text{ Hz}$, 9 H, $\text{P}(\text{CH}_3)_3$), 5.31 (ddd, $^3J_{\text{HH}} = 3.0 \text{ Hz}$, $^3J_{\text{HH}} = 2.0 \text{ Hz}$, $^4J_{\text{PH}} = 1.1 \text{ Hz}$, 1 H, C-pyrazolyl C⁴*H*), 5.56 (dd, $^3J_{\text{HH}} = 3.0 \text{ Hz}$, $^3J_{\text{HH}} = 2.0 \text{ Hz}$, 1 H, A-pyrazolyl C⁴*H*), 5.69 (ddd, $^3J_{\text{HH}} = 3.0 \text{ Hz}$, $^3J_{\text{HH}} = 2.0 \text{ Hz}$, $^4J_{\text{HH}} = 0.4 \text{ Hz}$, 1 H, B-pyrazolyl C⁴*H*), 6.85 (db, $^3J_{\text{HH}} = 2.0 \text{ Hz}$, 1 H, A-pyrazolyl C³*H*), 6.96 (db, $^3J_{\text{HH}} = 2.0 \text{ Hz}$, 1 H, C-pyrazolyl C³*H*), 7.05 (m, 5 H, C_6H_5), 7.10 (db, $^3J_{\text{HH}} = 2.0 \text{ Hz}$, 1 H, B-pyrazolyl C³*H*), 9.36 (ddd, $^3J_{\text{HH}} = 3.0 \text{ Hz}$, $^4J_{\text{RhH}} = 0.7 \text{ Hz}$, $^5J_{\text{PH}} = 1.5 \text{ Hz}$, 1 H, C-pyrazolyl C⁵*H*), 9.52 (dd, $^3J_{\text{HH}} = 3.0 \text{ Hz}$, $^4J_{\text{RhH}} = 0.7 \text{ Hz}$, 1 H, A-pyrazolyl C⁵*H*), 9.64 (ddd, $^3J_{\text{HH}} = 3.0 \text{ Hz}$, $^4J_{\text{RhH}} = 0.6 \text{ Hz}$, $^5J_{\text{HH}} = 0.6 \text{ Hz}$, 1 H, B-pyrazolyl C⁵*H*). – $^{13}\text{C}\{^1\text{H}\}$ NMR (500 MHz, C_6D_6): $\delta = 15.8$ [d, $^1J_{\text{PC}} = 35 \text{ Hz}$, $\text{P}(\text{CH}_3)_3$], 90.3 (s, C-SO₃), 104.7 (s, A-pyrazolyl C⁴), 104.8 (s, C-pyrazolyl C⁴), 105.0 (s, B-pyrazolyl C⁴), 121.5, 126.0, 126.1 (s, phenyl C), 126.2 (d, $J_{\text{RhC}} = 2 \text{ Hz}$, phenyl C), 135.0 (s, C-pyrazolyl C⁵), 135.3 (s, A-pyrazolyl C⁵), 135.5 (s, B-pyrazolyl C⁵), 141.2 (s, B-pyrazolyl C³), 143.0 (s,

A-pyrazolyl C^3), 143.4 (s, C-pyrazolyl C^3). – ^{31}P $\{^1\text{H}\}$ NMR (200 MHz, C_6D_6): δ = 10.3 (d, $^1J_{\text{RhP}}$ = 145 Hz). – IR (KBr): $\tilde{\nu}$ = 3176 cm^{-1} (m, pyrazolyl C–H), 3052 (w, phenyl C–H), 2963, 2909 [w, $\text{P}(\text{CH}_3)_3$ C–H], 2085 (m, Rh–H), 1569 (m, phenyl), 1521 (s, C=C), 1420 (s, P–C), 1081, 1058, 1038 (s, S=O). – MS (FAB $^+$): m/z (%) = 549 (4.3) $[\text{M} - \text{H}]^+$.

Deuteriopentadeuteriophenyltrimethylphosphane[tris(pyrazol-1-yl)methanesulfonato]rhodium(III), [(TpmsRh(D)(C₆D₅)(PMe₃))] (2-d₆): 2-d₆ was prepared in the same way as **2**, using [D₆]benzene as a solvent and irradiating for 100 minutes. Addition of pentane precipitated 12 mg of a light grey solid. – ^1H NMR (200 MHz, C_6D_6): δ = 0.64 [dd, $^2J_{\text{PH}}$ = 10.0 Hz, $^3J_{\text{RhH}}$ = 1.0 Hz, 9 H, $\text{P}(\text{CH}_3)_3$], 5.30 (ddd, $^3J_{\text{HH}}$ = 3.0 Hz, $^3J_{\text{HH}}$ = 2.0 Hz, $^4J_{\text{PH}}$ = 1.1 Hz, 1 H, C-pyrazolyl $C^4\text{H}$), 5.55 (dd, $^3J_{\text{HH}}$ = 3.0 Hz, $^3J_{\text{HH}}$ = 2.0 Hz, 1 H, A-pyrazolyl $C^4\text{H}$), 5.68 (dd, $^3J_{\text{HH}}$ = 3.0 Hz, $^3J_{\text{HH}}$ = 2.0 Hz, 1 H, B-pyrazolyl $C^4\text{H}$), 6.83 (db, $^3J_{\text{HH}}$ = 2.0 Hz, 1 H, A-pyrazolyl $C^3\text{H}$), 6.95 (db, $^3J_{\text{HH}}$ = 2.0 Hz, 1 H, C-pyrazolyl $C^3\text{H}$), 7.10 (dd, $^3J_{\text{HH}}$ = 2.0 Hz, $^3J_{\text{RhH}}$ = 0.5 Hz, 1 H, B-pyrazolyl $C^3\text{H}$), 9.37 (ddd, $^3J_{\text{HH}}$ = 3.0 Hz, $^4J_{\text{RhH}}$ = 0.7 Hz, $^5J_{\text{PH}}$ = 1.5 Hz, 1 H, C-pyrazolyl $C^5\text{H}$), 9.53 (dd, $^3J_{\text{HH}}$ = 3.0 Hz, $^4J_{\text{RhH}}$ = 0.5 Hz, 1 H, A-pyrazolyl $C^5\text{H}$), 9.65 (dd, $^3J_{\text{HH}}$ = 3.0 Hz, $^4J_{\text{RhH}}$ = 0.5 Hz, 1 H, B-pyrazolyl $C^5\text{H}$). – ^2H NMR (500 MHz, C_6D_6): δ = –16.1 (dd, $^1J_{\text{RhD}}$ = 4 Hz, $^2J_{\text{PD}}$ = 5 Hz, 1 D, deuterido-D), 7.1 (br. s, 5 D, C_6D_5). – ^{31}P $\{^1\text{H}\}$ NMR (200 MHz, C_6D_6): δ = 10 (dt, $^1J_{\text{RhP}}$ = 144 Hz, $^2J_{\text{PD}}$ = 4 Hz). – IR (KBr): $\tilde{\nu}$ = 3176 cm^{-1} (m, pyrazolyl C–H), 2963, 2909 [w, $\text{P}(\text{CH}_3)_3$ C–H], 2264 (w, phenyl C–D), 1533 (m, phenyl), 1521 (s, C=C), 1500 (m, Rh–D), 1420 (s, P–C), 1081, 1058, 1038 (s, S=O). – MS (FAB $^+$): m/z (%) = 554 (4.8) $[\text{M} - \text{D}]^+$.

Determination of the $k_{\text{H}}/k_{\text{D}}$ Ratio: A suspension of **1** (20 mg, 0.040 mmol) in a mixture of benzene (10 mL) and [D₆]benzene (10 mL) was stirred in a Pyrex vessel in a water bath at room temperature. The mixture was irradiated for 100 minutes. After the solution was evaporated, the residue was dissolved in [D₆]benzene and analysed by ^1H NMR spectroscopy. The integration ratios of the hydrido signal of **2** at δ = –16.30 (1.0 H) and the signals of the protons bound to the pyrazoles of the ligands allows the calculation of the ratio $k_{\text{H}}/k_{\text{D}}$ to be 1.1. The ratio did not change within 12 hours, which rules out a thermal equilibration of **2** with [D₆]benzene.

Chlorophenyltrimethylphosphane[tris(pyrazol-1-yl)methanesulfonato]rhodium(III), [(TpmsRh(Cl)(C₆H₅)(PMe₃))] (3): Tetrachloromethane (1 mL) was added to a solution of **2** (22 mg, 0.040 mmol) in 15 mL of benzene. The reaction mixture was stirred overnight and the solvents evaporated to dryness to yield **3** as a light grey solid (23 mg). – ^1H NMR (200 MHz, C_6D_6): δ = 0.62 [dd, $^2J_{\text{PH}}$ = 10.8 Hz, $^3J_{\text{RhH}}$ = 0.8 Hz, 9 H, $\text{P}(\text{CH}_3)_3$], 5.31 (ddd, $^3J_{\text{HH}}$ = 3.0 Hz, $^3J_{\text{HH}}$ = 2.3 Hz, $^4J_{\text{PH}}$ = 1.8 Hz, 1 H, pyrazolyl $C^4\text{H}$), 5.50 (dd, $^3J_{\text{HH}}$ = 3.0 Hz, $^3J_{\text{HH}}$ = 2.5 Hz, 1 H, pyrazolyl $C^4\text{H}$), 5.63 (dd, $^3J_{\text{HH}}$ = 3.0 Hz, $^3J_{\text{HH}}$ = 2.2 Hz, 1 H, pyrazolyl $C^4\text{H}$), 6.60 (db, $^3J_{\text{HH}}$ = 2.5 Hz, 1 H, pyrazolyl $C^3\text{H}$), 7.04 (m, 5 H, C_6H_5), 7.21 (m, 1 H, pyrazolyl $C^3\text{H}$), 7.44 (dd, $^3J_{\text{HH}}$ = 2.2 Hz, $^3J_{\text{RhH}}$ = 0.7 Hz, 1 H, pyrazolyl $C^3\text{H}$), 9.24 (ddd, $^3J_{\text{HH}}$ = 3.0 Hz, $^4J_{\text{RhH}}$ = 0.8 Hz, $^5J_{\text{PH}}$ = 1.8 Hz, 1 H, pyrazolyl $C^5\text{H}$), 9.44 (dd, $^3J_{\text{HH}}$ = 3.0 Hz, $^4J_{\text{RhH}}$ = 0.8 Hz, 1 H, pyrazolyl $C^5\text{H}$), 9.58 (dd, $^3J_{\text{HH}}$ = 3.0 Hz, $^4J_{\text{RhH}}$ = 0.8 Hz, 1 H, pyrazolyl $C^5\text{H}$). – ^{13}C $\{^1\text{H}\}$ (500 MHz, C_6D_6): δ = 12.8 [d, $^1J_{\text{PC}}$ = 35 Hz, $\text{P}(\text{CH}_3)_3$], 90.0 (s, $\text{C}-\text{SO}_3$), 105.5 (s, pyrazolyl C^4), 105.6 (s, pyrazolyl C^4), 105.7 (s, pyrazolyl C^4), 122.6, 124.2, 125.8 (s, phenyl C), 126.1 (db, J_{RhC} = 3 Hz, phenyl C), 135.0 (s, pyrazolyl C^5), 135.4 (s, pyrazolyl C^5), 135.5 (s, pyrazolyl C^5), 142.3 (s, pyrazolyl C^3), 143.4 (s, pyrazolyl C^3), 143.6 (s, pyrazolyl C^3). – ^{31}P $\{^1\text{H}\}$ NMR (200 MHz, C_6D_6): δ = 7.6 (d, $^1J_{\text{RhP}}$ = 127 Hz). – IR (KBr): $\tilde{\nu}$ = 3171 cm^{-1} (m, pyrazolyl C–H),

3059 (w, phenyl C–H), 2962, 2910 [w, $\text{P}(\text{CH}_3)_3$ C–H], 1569 (m, phenyl), 1522 (s, C=C), 1422 (s, P–C), 1099, 1070, 1054, 1021 (s, S=O). – MS (FAB $^+$): m/z (%) = 607 (7.1) $[\text{M} + \text{Na}]^+$, 549 (1.3) $[\text{M} - \text{Cl}]^+$. – $\text{C}_{19}\text{H}_{23}\text{ClN}_6\text{O}_3\text{PRhS}$ (584.8): calcd. C 39.02, H 3.96, N 14.37; found C 39.28, H 3.74, N 14.09.

Catalysis and Preparation of Benzoylhydridotrimethylphosphane[tris(pyrazol-1-yl)methanesulfonato]rhodium(III), [(TpmsRh(H)-(COC₆H₅)(PMe₃))] (4): A suspension of **1** (10 mg, 0.020 mmol) in 20 mL benzene was stirred in a Pyrex vessel equipped with Teflon seals and valves and pressurised with 3–4 atm. of carbon monoxide. The reaction mixture was irradiated for 0.5 to 24 hours in a water bath at room temperature. At regular intervals, samples for gas chromatographic analysis were taken. The solvent was finally removed under reduced pressure yielding a red brown solid, from which **4** could not be isolated as a pure compound. The crude product contains **2**, **4**, traces of **1** and traces of Rh⁰ carbonyl compounds. – ^1H NMR (200 MHz, C_6D_6): δ = –14.88 (dd, $^1J_{\text{RhH}}$ = 24.2 Hz, $^2J_{\text{PH}}$ = 35.6 Hz, 1 H, hydrido-H), 0.74 [dd, $^2J_{\text{PH}}$ = 10.6 Hz, $^3J_{\text{RhH}}$ = 1.2 Hz, 9 H, $\text{P}(\text{CH}_3)_3$], 5.6–5.9 (m, 3 H, pyrazolyl $C^4\text{H}$), 7.1 (m, 5 H, C_6H_5), 8.1–8.4 (m, 3 H, pyrazolyl $C^3\text{H}$), 9.30 (ddd, $^3J_{\text{HH}}$ = 3.1 Hz, $^4J_{\text{RhH}}$ = 0.8 Hz, $^5J_{\text{PH}}$ = 1.6 Hz, 1 H, pyrazolyl $C^5\text{H}$), 9.52 (dd, $^3J_{\text{HH}}$ = 3.1 Hz, $^4J_{\text{RhH}}$ = 0.7 Hz, 1 H, pyrazolyl $C^5\text{H}$), 9.60 (db, $^3J_{\text{HH}}$ = 3.1 Hz, 1 H, pyrazolyl $C^5\text{H}$). – ^{31}P $\{^1\text{H}\}$ NMR (200 MHz, C_6D_6): δ = 9.3 (d, $^1J_{\text{RhP}}$ = 146 Hz). – MS (FAB $^+$): m/z (%) = 577 (9.1) $[\text{M} - \text{H}]^+$, 549 (9.5) $[\text{M} - \text{CO} - \text{H}]^+$.

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