

Synthesis and Structural Features of Rhodium Complexes of Expanded Ring N-Heterocyclic Carbenes

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The rhodium complexes $[\text{Rh}(\text{NHC})(\text{COD})\text{Cl}]$ and *cis*- $[\text{Rh}(\text{NHC})(\text{CO})_2\text{Cl}]$ of seven-membered N-heterocyclic carbenes (NHC) bearing aromatic N-substituents (mesityl, xyllyl and *o*-tolyl) were synthesised, and a comparison of their steric and electronic properties with those of the analogous five- and six-membered NHC complexes was made on the basis

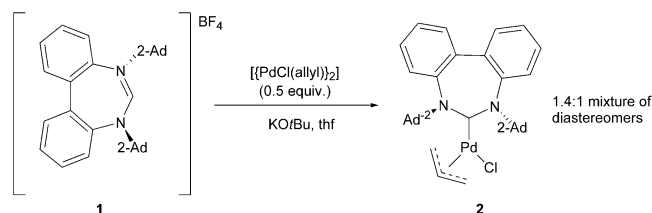
of infrared and solid-state data. The X-ray structures for the complexes $\text{Rh}(\text{6-Mes})(\text{COD})\text{Cl}$, $\text{Rh}(\text{7-Mes})(\text{COD})\text{Cl}$ and $\text{Rh}(\text{7-}o\text{Tol})(\text{COD})\text{Cl}$ were determined.

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Introduction

The structure and electronic properties of expanded ring carbenes and their effect on catalytic performance is virtually unexplored relative to their saturated and unsaturated five-membered analogues.^[1] Other than our work,^[2] the only complexes of seven-membered carbene complexes that have been reported have been the palladium(II) complexes prepared by Stahl and co-workers.^[3] The Pd^{II} complexes were synthesised by in situ deprotonation of the BF_4 salt with potassium *tert*-butoxide in the presence of the metal precursor (Scheme 1). The most distinctive feature of these complexes relative to five-membered and even six-membered carbenes is the torsional twist, which Stahl defines by two parameters: The dihedral angle between the two aryl rings of the biphenyl backbone and the torsional angle between the two $\text{N}\cdots\text{N}-\text{C}_{\text{ring}}$ planes of the carbene ring ($\text{C}_{\text{ring}}-\text{N}\cdots\text{N}-\text{C}_{\text{ring}}$). The torsion of the ring, defined by these two parameters, dictates the spatial disposition of the substituents in the coordination sphere.

A number of six-membered carbene complexes have been published and compared with their five-membered analogues in terms of their electronic and steric properties, as well as their coordination chemistry and catalytic performance.^[4] Analysis of their crystal structures shows that an increasing ring size leads to the opening of the $\text{N}-\text{C}-\text{N}$ angle and the consequential decrease in the $\text{C}_{\text{NHC}}-\text{N}-\text{C}_{\text{R}}$ angle as the main feature. This results in an increase in the steric hindrance around the metal core.



Scheme 1. Synthesis of Stahl's Pd^{II} carbene complex.

The donor abilities of carbene ligands have been studied by comparing the $\text{C}-\text{O}$ stretching frequencies for different carbonyl NHC complexes. The carbonyl stretching frequency is a common method for estimating the electron density at the metal centre, and, therefore, the donating abilities of the ligand.^[5] The IR carbonyl frequencies obtained for corresponding metal complexes with different carbene ligands provides a measure of the overall electron density donated by the carbene.

Here we report the first examples of rhodium complexes of seven-membered NHCs bearing aromatic N-substituents. By assessing the structural features of a similar group of complexes, the ligand properties and influence of five-, six- and seven-membered NHCs were examined and compared.

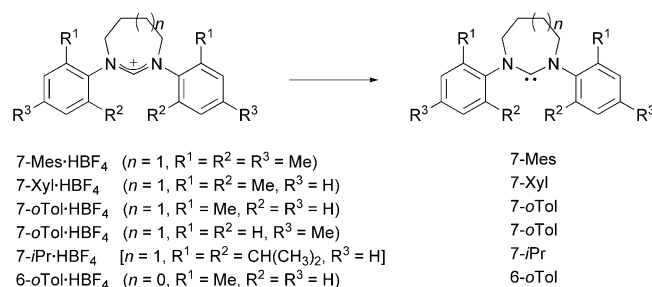
Results and Discussion

Recently we reported the synthesis of seven-membered amidinium salts with aromatic substituents, their free carbenes and corresponding silver complexes.^[2a] We have now prepared several new rhodium cyclooctadiene and bis(carbonyl) complexes, with previously described procedures.^[2b]

In addition to the previously reported carbene precursors 7-Mes $\cdot\text{HBF}_4$, 7-Xyl $\cdot\text{HBF}_4$ and 7-*i*Pr $\cdot\text{HBF}_4$, the less encumbered amidinium salts, 6-*o*Tol $\cdot\text{HBF}_4$ and 7-*o*Tol $\cdot\text{HBF}_4$ were

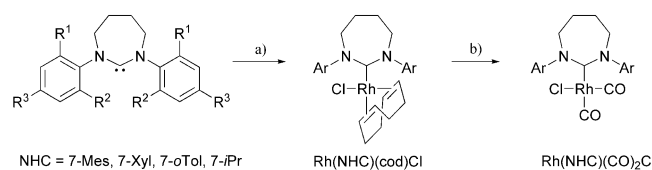
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also prepared, Scheme 2. The free carbenes were generated from the corresponding BF_4 salts by using $\text{KN}(\text{SiMe}_3)_2$ as the base and were isolated in good yields as stable crystalline solids. In contrast to the reactivity of the majority of the HBF_4 salts, deprotonation of the *ortho*-tolyl salt, $7\text{-}o\text{Tol}\cdot\text{HBF}_4$, with $\text{KN}(\text{SiMe}_3)_2$ formed the corresponding carbene $7\text{-}o\text{Tol}$ together with the base adduct $7\text{-}o\text{Tol}\cdot\text{HN}(\text{SiMe}_3)_2$ in a 55:45 ratio, whereas the six-membered equivalent, $6\text{-}o\text{Tol}\cdot\text{HBF}_4$, formed cleanly the free carbene $6\text{-}o\text{Tol}$. The above reactivity of the tolyl carbenes may be due to their reduced steric demands, which allows more ready access to the carbene core. In addition, the apparent higher basicity of the seven-membered carbenes may account for the difference in reactivity between the $7\text{-}o\text{Tol}$ and $6\text{-}o\text{Tol}$ carbenes (vide infra). A similar behaviour was previously observed by Alder et al. for tetrahydropyrimidinium salts.^[6] The authors reported a competitive nucleophilic attack of the amide anion instead of $\text{C}_{\text{NHC}}\text{-H}$ deprotonation of the azolium salt, to generate the $\text{NHC}\cdot\text{HN}(\text{SiMe}_3)_2$ adduct. Interestingly, the base adduct in this case is in equilibrium with the free carbene and the corresponding protonated base $\text{HN}(\text{SiMe}_3)_2$.



Scheme 2. Synthesis of six- and seven-membered NHCs with N-aryl substituents. Reagents and conditions: $\text{KN}(\text{SiMe}_3)_2$, thf.

Treatment of $[\text{Rh}(\text{COD})\text{Cl}]_2$ with 2 equiv. of the corresponding free carbene in thf gave the complexes $\text{Rh}(7\text{-Mes})(\text{COD})\text{Cl}$ and $\text{Rh}(7\text{-Xyl})(\text{COD})\text{Cl}$ as yellow air-stable solids in good yields (Scheme 3). The corresponding $7\text{-}o\text{Tol}$ complex, because of the instability of the free carbene, was generated by in situ deprotonation of $7\text{-}o\text{Tol}\cdot\text{HBF}_4$ with $\text{KN}(\text{SiMe}_3)_2$ followed by subsequent reaction with $[\text{Rh}(\text{COD})\text{Cl}]_2$. Attempts to produce a stable rhodium $7\text{-}i\text{Pr}$ complex failed, presumably because of the steric demands imposed by the bulky isopropyl substituents. Only the unreacted metal precursor, $[\text{Rh}(\text{COD})\text{Cl}]_2$, and the hydrolysis product of the free carbene, $7\text{-}i\text{Pr}\cdot\text{H}_2\text{O}$, were recovered from the reaction mixture.



Scheme 3. Synthesis of $\text{Rh}(\text{NHC})(\text{COD})\text{Cl}$ and $\text{Rh}(\text{NHC})(\text{CO})_2\text{Cl}$ complexes. (a) $[\text{Rh}(\text{cod})\text{Cl}]_2$, thf; (b) CO (1 atm), CH_2Cl_2 .

The carbonyl complexes $\text{Rh}(7\text{-Mes})(\text{CO})_2\text{Cl}$ and $\text{Rh}(7\text{-Xyl})(\text{CO})_2\text{Cl}$ were also prepared (Scheme 3). Treatment of dichloromethane solutions of $\text{Rh}(7\text{-Mes})(\text{COD})\text{Cl}$ and $\text{Rh}(7\text{-Xyl})(\text{COD})\text{Cl}$ with 1 atm carbon monoxide for 20 min afforded the corresponding carbonyl complexes as bright yellow solids in good yields. Their properties were compared to the previously reported analogues, 5-Mes ^[7] and 6-Mes ^[4c] carbene complexes.^[8]

^1H and ^{13}C NMR spectra of the $\text{Rh}(7\text{-Mes})(\text{COD})\text{Cl}$ and $\text{Rh}(7\text{-Xyl})(\text{COD})\text{Cl}$ complexes, recorded in CDCl_3 , show broad aromatic resonances arising from the slow rotation of the aryl rings on the NMR timescale. However, spectra recorded in $[\text{D}_6]\text{benzene}$ show sharp signals, and two distinct resonances are observed for the *ortho*-methyl groups. Hindered N–Ar rotation in $[\text{D}_6]\text{benzene}$ is also evident from the ^{13}C NMR spectra, in which two resonances are observed for the methyl carbon atoms and six for the aromatic ones (as opposed to four signals if the aromatic rings were freely rotating). For comparison, NMR spectroscopic data for the $\text{Rh}(5\text{-Mes})(\text{COD})\text{Cl}$ complex (in CDCl_3) indicate free rotation of the mesityl rings, and for $\text{Rh}(6\text{-Mes})(\text{COD})\text{Cl}$, broadened (although resolved) signals are observed for the *ortho*-methyl groups.

The ^1H NMR spectra recorded in $[\text{D}_6]\text{benzene}$ show a large downfield shift for only one of the *ortho*-methyl signals of the 7-Mes and 7-Xyl complexes, Table 1. In the more polar CDCl_3 solvent, however, the two *ortho*-methyl resonances are comparable. The above suggests that the methyl group resonating at higher frequency in $[\text{D}_6]\text{benzene}$ resides on the same side as the chlorido ligand, the signal is shifted because of hydrogen bonding with the chlorido ligand, whereas in CDCl_3 , intermolecular H-bonding with the solvent is more likely, hence similar shifts are observed for the *ortho*-methyl protons in this solvent. Indeed, close Cl–H(Me) contacts are observed in the solid-state structure of $\text{Rh}(7\text{-Xyl})(\text{COD})\text{Cl}$, vide infra.

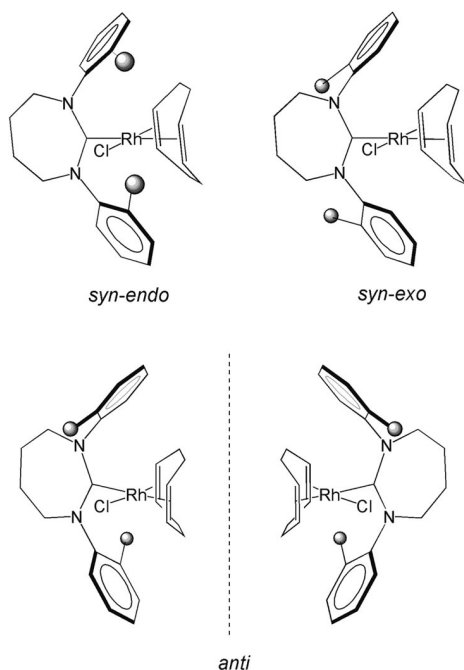
Table 1. ^1H NMR methyl shifts for the $\text{Rh}(\text{NHC})(\text{cod})\text{Cl}$ complexes.

Complex	Solvent	$\delta(\text{Me})$ [ppm]		
$\text{Rh}(7\text{-Mes})(\text{COD})\text{Cl}$	C_6D_6	3.10	2.32	2.19
$\text{Rh}(6\text{-Mes})(\text{COD})\text{Cl}$	CDCl_3	2.52	2.28	2.20
$\text{Rh}(5\text{-Mes})(\text{COD})\text{Cl}$	CDCl_3	2.53	2.27	2.25
$\text{Rh}(7\text{-Xyl})(\text{COD})\text{Cl}$	C_6D_6	3.10	2.16	
$\text{Rh}(7\text{-}o\text{Tol})(\text{COD})\text{Cl}$	CDCl_3	2.21		
$\text{Rh}(7\text{-Xyl})(\text{CO})_2\text{Cl}$	CDCl_3	2.48	2.41	
$\text{Rh}(7\text{-Mes})(\text{CO})_2\text{Cl}$	CDCl_3	2.43	2.36	2.34
$\text{Rh}(6\text{-Mes})(\text{CO})_2\text{Cl}$	CDCl_3	2.35	2.29	2.25
$\text{Rh}(5\text{-Mes})(\text{CO})_2\text{Cl}$	CDCl_3	2.35	2.23	

Similar observations were made for the carbonyl complexes. For $\text{Rh}(6\text{-Mes})(\text{CO})_2\text{Cl}$ and $\text{Rh}(7\text{-Mes})(\text{CO})_2\text{Cl}$, six aromatic and two *ortho*-methyl resonances appear in the ^{13}C NMR spectra, as well as two signals for the *ortho*-methyl groups in the ^1H NMR spectra. Both the ^1H and ^{13}C NMR spectra for complex $[\text{Rh}(5\text{-Mes})(\text{CO})_2\text{Cl}]$ show only one resonance for the *ortho*-methyl groups and four

aromatic signals (^{13}C NMR), which implies free N–Ar rotation due to the reduced steric demands of 5-Mes relative to those of the 6- and 7-Mes ligands. Interestingly, in the $\text{Rh}(7\text{-Cy})(\text{CO})_2\text{Cl}$ complex,^[2b] the seven-membered ring carbene 7-Cy (bearing cyclohexyl N-substituents) rotates freely at ambient temperature on the NMR timescale, which suggests that aromatic N-substitution generates a more encumbered ligand.

As a result of the hindered rotation of the Rh–NHC and N–Ar bonds of the *ortho*-tolyl complex $\text{Rh}(7\text{-}o\text{Tol})(\text{COD})\text{Cl}$, there are four possible rotamers, two with the *ortho*-methyl groups in a *syn* orientation and two *anti* isomers (enantiomers), Scheme 4. In a manner consistent with this, the ^1H NMR (CDCl_3) spectrum shows three sharp doublets for the *ortho*-H atoms, which corresponds to the three isomers in a 3:4.5:10 ratio, with one of the *syn* rotamers as the major isomer.



Scheme 4. Rotamers of $\text{Rh}(7\text{-}o\text{Tol})(\text{COD})\text{Cl}$.

Table 2 shows the ^{13}C NMR chemical shifts of the C_{NHC} carbon atom of the rhodium complexes. A significant downfield shift is observed for the carbene carbon atom in $\text{Rh}(7\text{-Mes})(\text{COD})\text{Cl}$ and $\text{Rh}(7\text{-Mes})(\text{CO})_2\text{Cl}$ when compared to those for $\text{Rh}(5\text{-}/6\text{-Mes})(\text{COD})\text{Cl}$ and $\text{Rh}(5\text{-}/6\text{-Mes})(\text{CO})_2\text{Cl}$. The same trend was observed for the free carbenes and the corresponding silver complexes.^[2a]

In Table 3, the carbonyl stretching frequencies of $[\text{Rh}(5\text{-Mes})(\text{CO})_2\text{Cl}]$, $[\text{Rh}(6\text{-Mes})(\text{CO})_2\text{Cl}]$, $[\text{Rh}(7\text{-Mes})(\text{CO})_2\text{Cl}]$ and $[\text{Rh}(7\text{-Xyl})(\text{CO})_2\text{Cl}]$ are listed and compared to literature values. For the six- and the seven-membered carbene complexes, electron density on the metal centre, as indicated by the carbonyl stretching frequencies, is essentially identical, which implies similar donor abilities. However, the

Table 2. ^{13}C NMR shifts [ppm] and coupling constants [Hz] for the C_{NHC} carbon atom of the rhodium complexes.

Complex	δ ($^1J_{\text{CRh}}$)
$\text{Rh}(7\text{-}o\text{Tol})(\text{COD})\text{Cl}$	222.8 (45.0)
$\text{Rh}(7\text{-Xyl})(\text{COD})\text{Cl}$	223.1 (46.3)
$\text{Rh}(7\text{-Mes})(\text{COD})\text{Cl}$	224.0 (46.7)
$\text{Rh}(6\text{-Mes})(\text{COD})\text{Cl}$	211.5 (46.9)
$\text{Rh}(5\text{-Mes})(\text{COD})\text{Cl}$	211.6 (48.2)
$\text{Rh}(7\text{-Xyl})(\text{CO})_2\text{Cl}$	212.2
$\text{Rh}(7\text{-Mes})(\text{CO})_2\text{Cl}$	213.4
$\text{Rh}(6\text{-Mes})(\text{CO})_2\text{Cl}$	202.9
$\text{Rh}(5\text{-Mes})(\text{CO})_2\text{Cl}$	205.0

higher ν_{av} values obtained for the 5-Mes complex are consistent with a reduced electron density on the metal centre and thus a less basic carbene ligand in this case.

Table 3. Infrared $\nu(\text{CO})$ for the $\text{Rh}(\text{CO})_2(\text{NHC})\text{Cl}$ complexes.^[a]

Complex	$\nu_{\text{s,as}}$ [cm^{-1}]	ν_{av} [cm^{-1}] (literature)
$\text{Rh}(5\text{-Mes})(\text{CO})_2\text{Cl}$	1995, 2080	2037.5 (2038) ^[7]
$\text{Rh}(6\text{-Mes})(\text{CO})_2\text{Cl}$	1987, 2071	2029 (2029) ^[4]
$\text{Rh}(7\text{-Mes})(\text{CO})_2\text{Cl}$	1987, 2069	2028
$\text{Rh}(7\text{-Xyl})(\text{CO})_2\text{Cl}$	1986, 2071	2028.5
$\text{Rh}(7\text{-Cy})(\text{CO})_2\text{Cl}$	2071, 1990	2030.5

[a] Measured in CH_2Cl_2 .

Solid-State Analysis

Crystals of $\text{Rh}(6\text{-}/7\text{-Mes})(\text{COD})\text{Cl}$ and $\text{Rh}(7\text{-}o\text{Tol})(\text{COD})\text{Cl}$ suitable for X-ray diffraction were obtained by layering a dichloromethane solution of the corresponding complex with hexane. The crystal structures are shown in Figure 1, and selected bond lengths and angles can be found in Table 4. The solid-state structure of the $\text{Rh}(7\text{-}o\text{Tol})(\text{COD})\text{Cl}$ complex corresponds to the *syn-exo* conformer (Scheme 4, Figure 1). Data for the $\text{Rh}(5\text{-Mes})(\text{COD})\text{Cl}$ complex have also been included in Table 4 for comparison.^[9]

It is evident from the crystallographic data that expansion of the NHC ring leads to larger N– C_{NHC} –N angles. As expected, there is a significant increase in the N–C–N angle from $107.29(12)^\circ$ in the 5-Mes rhodium complex to $117.0\text{--}118.0(4)^\circ$ in the six- and seven-membered ring carbene complexes. This leads to large changes in the $\text{C}_{\text{Ar}}\text{--N--C}_{\text{NHC}}$ angles, which are accordingly compressed from an average of $127.3(13)^\circ$ in $\text{Rh}(5\text{-Mes})(\text{COD})\text{Cl}$ to $118.8(4)^\circ$ in the six- and seven-membered NHC complexes (Table 4). Consequently, the aryl substituents on the nitrogen atoms are forced closer to the metal centre in the expanded carbenes, and virtually block two faces of the metal coordination sphere. This steric congestion may also be responsible for the longer Rh– C_{NHC} bonds observed for the 6-Mes and 7-Mes complexes than that for $\text{Rh}(5\text{-Mes})(\text{COD})\text{Cl}$ (Table 4). In contrast, the $\text{Rh}(7\text{-}o\text{Tol})(\text{COD})\text{Cl}$ complex has a much shorter Rh– C_{NHC} bond [$2.030(3)$ Å] than that for $\text{Rh}(7\text{-Mes})(\text{COD})\text{Cl}$ [$2.085(3)$ Å], which can be attributed to differences in the electronic effects of the mesityl and tolyl N-substituents. Close contacts between the chlorido

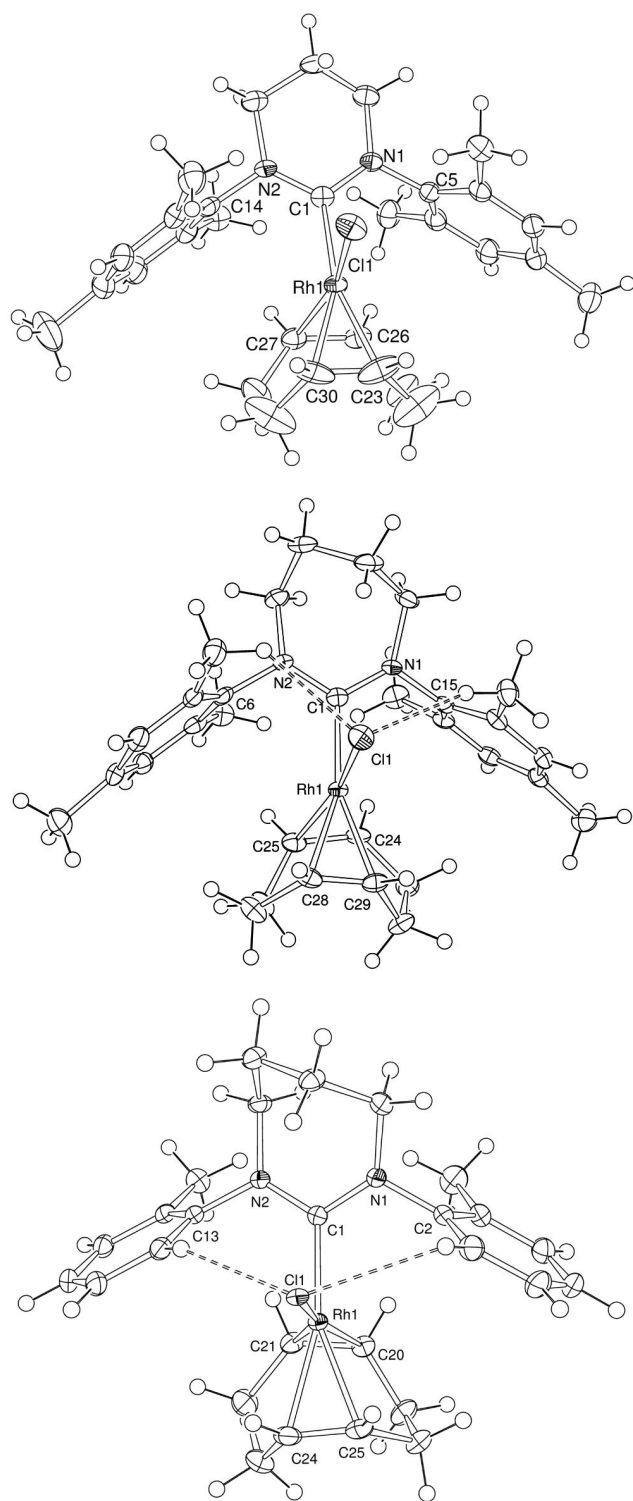


Figure 1. Solid-state molecular structures of Rh(6-Mes)(COD)Cl, Rh(7-Mes)(COD)Cl and Rh(7-*o*Tol)(COD)Cl.

ligand and the *ortho*-methyl protons were observed for the 6- and 7-Mes complexes [2.630 Å (av.) and 2.542 Å (av.), respectively]. Similarly, Rh(7-*o*Tol)(COD)Cl displays close contacts between the chlorido ligand and the *ortho*-tolyl protons, with an average Cl $\cdots$ H distance of 2.742 Å.

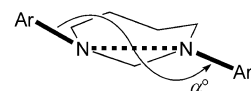


Table 4. Bond lengths [Å] and angles [°] for the Rh(NHC)(COD)-Cl complexes.

	5-Mes	6-Mes	7-Mes	7- <i>o</i> Tol
Rh–C _{NHC}	2.0513(14)	2.078(4)	2.085(3)	2.030(3)
Rh–Cl	2.3665(3)	2.3876(13)	2.3817(8)	2.4470(7)
C _{Ar} –N–C _{NHC}	127.62(13), 127.06(12)	119.5(4), 119.1(4)	119.1(2), 117.2(2)	117.1(2), 120.5(3)
N–C _{NHC} –N	107.29(12)	117.0(4)	118.0(3)	117.2(3)
C _{NHC} –Rh–Cl	91.86(4)	86.75(13)	85.27(9)	86.59(8)
tilt angle θ	59.0	83.5	87.8	81.1
α (C _{Ar} –N $\cdots$ N–C _{Ar})	28.1	8.2	28.0	46.0

The torsional angle α between the planes defined by the C_{Ar}–N $\cdots$ N–C_{Ar} atoms is a useful gauge for the spatial orientation of the aromatic N-substituents, which point directly into the coordination sphere of the metal. The 6-Mes complex has the smallest torsional angle with value of 8.2°. The 5-Mes and 7-Mes complexes display similar angles (28.1° and 28.0°, respectively), and the 7-*o*Tol complex has the largest torsional angle with a value of 46.0°.

All complexes in Figure 1 show small pyramidal distortions for the carbenic carbon atom, as measured by the deviation of the C_{NHC} carbon atom from the N–Rh–N plane. The orthogonal distance between C_{NHC} and the N–Rh–N plane is 0.11 Å for the 6- and 7-Mes carbene complexes and 0.06 Å for the 7-*o*Tol complex.

In the six- and seven-membered carbene complexes, the NHC ligand adopts an almost perpendicular arrangement with respect to the coordination plane (defined by the C_{NHC}–Rh–Cl atoms). The tilt angle θ (defined by the coordination and N–C–N planes) is 83.5° for Rh(6-Mes)(COD)-Cl, 87.8° for Rh(7-Mes)(COD)Cl and 81.1° for Rh(7-*o*Tol)(COD)Cl. However, the tilt angle θ is much smaller for Rh(5-Mes)(COD)Cl, with a value of 59.0°.

Conclusions

The sterically crowded seven-membered N-heterocyclic carbenes with aromatic N-substituents, 7-Mes, 7-Xyl and 7-*o*Tol, form stable rhodium complexes. Although by increasing further the bulk of the *ortho* substituents, as in the case of 7-*i*Pr, coordination to the rhodium centre is hindered. The donor ability of the seven-membered NHCs, on the basis of infrared data, appears to be comparable to that of their six-membered ring equivalents but greater than that of the five-membered ring NHCs.

Experimental Section

General Remarks: The solid reactants were combined together in a Schlenk tube in a glove box under a nitrogen atmosphere, and then removed from the glove box and transferred to a Schlenk line where

the solvents were added by syringe. Diethyl ether, tetrahydrofuran and hexane were distilled from sodium and benzophenone under a N₂ atmosphere. Dichloromethane was distilled from calcium hydride under a N₂ atmosphere. [Rh(COD)Cl]₂, [Rh(COD)Cl]₂ and [Pt(nbe)₃] were synthesised according to literature methods. The salts 7-Mes·HBF₄, 7-Xyl·HBF₄ and 7-*i*Pr·HBF₄ and the corresponding free NHCs were prepared according to the syntheses reported previously by us.^[2a] ¹H- and ¹³C spectra were recorded by using a Bruker Advance DPX400 spectrometer. Chemical shifts (δ) were expressed in ppm downfield from tetramethylsilane by using the residual proton as an internal standard (CDCl₃, ¹H 7.26 ppm and ¹³C 77.0 ppm; [D₆]benzene ¹H 7.15 ppm and ¹³C 128.0 ppm). Coupling constants are expressed in Hertz. HRMS were obtained on a Waters LCT Premier XE instrument and are reported as *m/z* (%). Infrared spectra were recorded by using a JASCO FT/IR-660 Plus spectrometer and analysed in solution (dichloromethane).

1,3-Bis(2-methylphenyl)-4,5,6,7-tetrahydro-3H-[1,3]diazepin-1-ium Tetrafluoroborate (7-*o*Tol·HBF₄): A suspension of *N,N'*-bis(*o*-tolyl)-formamidine (2.24 g, 10.0 mmol), K₂CO₃ (0.69 g, 5.0 mmol) and 1,4-diiodobutane (3.26 g, 10.5 mmol) in acetonitrile (30 mL) was heated to reflux overnight. Subsequently, the reaction mixture was allowed to reach ambient temperature, at which point a solution of NaBF₄ (1.40 g, 10.0 mmol) in water (20 mL) was added. The reaction mixture was stirred for 10 min, the volatiles were subsequently partially evaporated, and the product precipitated in the remaining water. The product was isolated by filtration, washed thoroughly with water, and dissolved in dichloromethane. The residual water was separated, and the dichloromethane solution dried with MgSO₄. The solution was filtered and concentrated, and ether was slowly added to precipitate 7-*o*Tol·HBF₄ as a white, crystalline material. Yield: 2.95 g (8.1 mmol, 81%). ¹H NMR (CDCl₃, 400 MHz, room temperature): δ = 7.71 (br., 2 H, *o*-CH), 7.36 (s, 1 H, NCHN), 7.28–7.22 (m, 6 H, *m,p*-CH), 4.34 (br., 4 H, N-CH₂), 2.40 (br., 4 H, N-CH₂-CH₂), 2.36 (s, 6 H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz, room temperature): δ = 156.5 (s, NCHN), 141.8 (s, *ipso*-C_{oTol}), 131.7 (s, C_{oTol}CH₃), 130.7 (s, CH_{oTol}), 129.1 (s, CH_{oTol}), 127.4 (s, CH_{oTol}), 126.5 (s, C_{oTol}CH₃), 54.3 (s, N-CH₂), 24.4 (s, NCH₂CH₂), 16.8 (s, CH₃) ppm. MS (ES): *m/z* = 279.1853 [M – BF₄]⁺. C₁₉H₂₃N₂ requires 279.1861.

1,3-Bis(2-methylphenyl)-3,4,5,6-tetrahydro-pyrimidin-1-ium Tetrafluoroborate (6-*o*Tol·HBF₄): The reaction was performed in an analogous manner to that described for 7-*o*Tol·HBF₄, on a 2.9-mmol scale. Yield: 0.99 g (2.8 mmol, 97%), white, crystalline material. ¹H NMR (CDCl₃, 400 MHz, room temperature): δ = 7.61 (d, ³J_{HH} = 8.0 Hz, 2 H, *o*-CH), 7.55 (s, 1 H, NCHN), 7.30–7.16 (m, 6 H, *m,p*-CH), 3.71 (br., 4 H, NCH₂), 2.45 (br., 2 H, NCH₂CH₂), 2.30 (s, 6 H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz, room temperature): δ = 153.7 (s, NCHN), 140.4 (s, *ipso*-C), 133.7 (s, C_{oTol}CH₃), 132.0 (s, CH_{oTol}), 130.7 (s, CH_{oTol}), 128.7 (s, CH_{oTol}), 127.9 (s, CH_{oTol}), 47.4 (s, NCH₂), 19.8 (s, NCH₂CH₂), 17.8 (s, CH₃) ppm. MS (ES): *m/z* = 265.1699 [M – BF₄]⁺. C₁₈H₂₁N₂ requires 265.1705.

Rh(5-Mes)(COD)Cl: A solution of 5-Mes (67 mg, 0.22 mmol) in dry thf (10 mL) was added to a solution of [Rh(COD)Cl]₂ (50 mg, 0.10 mmol) in dry thf (10 mL) and stirred at ambient temperature for 1 h under an argon atmosphere. The solvent was then removed in vacuo to give a dark yellow solid, which was subsequently triturated with hexanes to give 63 mg (0.11 mmol) of **1** as a bright yellow powder (57% yield). Crystals suitable for X-ray analysis were obtained by layering diethyl ether on a dichloromethane solution of the complex. ¹H NMR (400 MHz, CDCl₃, room temperature): δ = 6.96 (s, 2 H, CH_{Mes}), 6.91 (s, 2 H, CH_{Mes}), 4.40 (m, 2 H,

CH_{COD}), 3.75–3.82 (m, 4 H, NCH₂), 3.30 (m, 2 H, CH_{COD}), 2.53 (s, 6 H, CH₃), 2.27 (s, 6 H, CH₃), 2.25 (s, 6 H, CH₃), 1.70–1.72 (m, 4 H, CH_{2COD}), 1.43–1.47 (m, 4 H, CH_{2COD}) ppm. ¹³C NMR (100 MHz, CDCl₃, room temperature): δ = 211.6 (d, ¹J_{CRh} = 48.2 Hz, C_{Carbene}), 137.4 (s, C_{Mes}), 136.8 (s, C_{Mes}), 135.2 (s, C_{Mes}), 134.2 (s, C_{Mes}), 128.9 (s, CH_{Mes}), 127.3 (s, CH_{Mes}), 96.1 (s, d, ¹J_{RhC} = 7.1 Hz, CH_{COD}), 66.5 (s, d, ¹J_{RhC} = 7.5 Hz, CH_{COD}), 50.3 (s, NCH₂), 31.6 (s, CH_{2COD}), 27.1 (s, CH_{2COD}), 20.1 (s, CH₃), 18.9 (s, CH₃), 17.3 (s, CH₃) ppm. MS (ES, CH₃CN): *m/z* = 558.2354 [M – Cl + CH₃CN]⁺. C₃₁H₄₁N₃Rh requires 558.2356.

Rh(6-Mes)(COD)Cl: A solution of 6-Mes (74 mg, 0.22 mmol) in dry thf (10 mL) was added to a solution of [Rh(COD)Cl]₂ (50 mg, 0.10 mmol) in dry thf (10 mL) and stirred at ambient temperature for 1 h under an argon atmosphere. The solvent was then removed in vacuo to give a dark yellow solid, which was subsequently triturated with hexanes to give 71 mg (0.12 mmol) of Rh(6-Mes)(COD)Cl as a bright yellow powder (62% yield). Crystals suitable for X-ray analysis were obtained by layering diethyl ether on a dichloromethane solution of the complex. ¹H NMR (400 MHz, CDCl₃, room temperature): δ = 6.98 (br., 2 H, CH_{Mes}), 6.88 (br., 2 H, CH_{Mes}), 4.16 (m, 2 H, CH_{COD}), 3.27 (m, 4 H, NCH₂), 3.13 (m, 2 H, CH_{COD}), 2.52 (br. s, 6 H, *o*-CH₃), 2.28 (s, 6 H, CH₃), 2.20 (br. s, 6 H, *o*-CH₃), 2.08 (br., 2 H, CH₂), 1.39 (m, 4 H, CH_{2COD}), 1.19 (m, 4 H, CH_{2COD}) ppm. ¹³C NMR (100 MHz, CDCl₃, room temperature): δ = 211.5 (d, ¹J_{CRh} = 46.9 Hz, C_{Carbene}), 142.3 (s, C_{Mes}), 137.8 (s, C_{Mes}), 130.6 (s, CH_{Mes}), 128.5 (s, CH_{Mes}), 94.3 (d, ¹J_{CRh} = 7.4 Hz, CH_{COD}), 67.3 (d, ¹J_{CRh} = 14.7 Hz, CH_{COD}), 48.0 (s, NCH₂), 32.7 (s, CH_{2COD}), 32.0 (s, CH_{2COD}), 21.6 (s, NCH₂CH₂), 21.4 (s, CH₃), 20.6 (s, CH₃), 19.4 (s, CH₃) ppm. MS (ES): *m/z* = 531.2221 [M – Cl]⁺. C₃₀H₄₀N₂Rh requires 531.2247.

Rh(7-Mes)(COD)Cl: A solution of 7-Mes (71 mg, 0.22 mmol) in dry thf (10 mL) was added to a solution of [Rh(COD)Cl]₂ (50 mg, 0.10 mmol) in dry thf (10 mL) and stirred at ambient temperature for 1 h under an argon atmosphere. The solvent was then removed in vacuo to give a dark yellow solid, which was subsequently triturated with hexanes to give 73 mg (0.12 mmol) of **5** as a bright yellow powder (63% yield). Crystals suitable for X-ray analysis were obtained by layering diethyl ether on a tetrahydrofuran solution of the complex. ¹H NMR (400 MHz, C₆D₆, room temperature): δ = 7.06 (s, 2 H, CH_{Mes}), 6.96 (s, 2 H, CH_{Mes}), 5.00 (m, 2 H, CH_{COD}), 3.70 (m, 2 H, NCH₂), 3.18 (m, 2 H, CH_{COD}), 3.10 (s, 6 H, CH₃), 2.93 (m, 2 H, NCH₂), 2.39 (m, 2 H, NCH₂CH₂), 2.32 (s, 6 H, CH₃), 2.19 (s, 6 H, CH₃), 1.70 (m, 2 H, CH_{2COD}), 1.42–1.58 (m, 4 H, CH_{2COD}), 1.32 (m, 2 H, NCH₂CH₂) ppm. ¹³C NMR (100 MHz, C₆D₆, room temperature): δ = 224.0 (d, ¹J_{CRh} = 46.7 Hz, C_{NHC}), 143.2 (s, C_{Mes}), 136.5 (s, C_{Mes}), 135.4 (s, C_{Mes}), 133.5 (s, C_{Mes}), 129.6 (s, CH_{Mes}), 127.0 (s, CH_{Mes}), 93.2 (d, ¹J_{CRh} = 6.8 Hz, CH_{COD}), 65.9 (d, ¹J_{CRh} = 14.6 Hz, CH_{COD}), 53.6 (s, NCH₂), 31.5 (s, CH_{2COD}), 26.5 (s, CH_{2COD}), 23.5 (s, NCH₂CH₂), 20.4 (s, CH₃), 19.5 (s, CH₃), 18.5 (s, CH₃) ppm. MS (ES, CH₃CN): *m/z* = 545.2379 [M – Cl]⁺. C₃₁H₄₂N₂Rh requires 545.2403.

Rh(7-Xyl)(COD)Cl: A solution of 7-Xyl (67 mg, 0.22 mmol) in dry thf (10 mL) was added to a solution of [Rh(COD)Cl]₂ (50 mg, 0.10 mmol) in dry thf (10 mL) and stirred at ambient temperature for 1 h under an argon atmosphere. The solvent was then removed in vacuo to give a dark yellow solid, which was subsequently triturated with hexanes to give 78 mg (0.14 mmol) of **3** as a bright yellow powder (70% yield). Crystals suitable for X-ray analysis were obtained by layering hexanes on a dichloromethane solution of the complex. ¹H NMR (400 MHz, C₆D₆, room temperature): δ = 7.06 (t, ³J_{HH} = 7.4 Hz, 2 H, CH_{Xyl}), 7.05 (d, ³J_{HH} = 7.1 Hz, 4 H, CH_{Xyl}), 5.00 (m, 2 H, CH_{COD}), 3.66 (m, 2 H, NCH₂), 3.10 (m, 2 H,

CH_{COD}), 3.10 (s, 6 H, CH_3), 2.85 (m, 2 H, NCH_2), 2.33 (m, 2 H, NCH_2CH_2), 2.16 (s, 6 H, CH_3), 1.70 (m, 2 H, CH_2COD), 1.42–1.53 (m, 4 H, CH_2COD), 1.23 (m, 2 H, NCH_2CH_2) ppm. ^{13}C NMR (100 MHz, C_6D_6 , room temperature): δ = 145.5 (s, C_{Xyl}), 137.0 (s, C_{Xyl}), 133.8 (s, C_{Xyl}), 129.1 (s, CH_{Xyl}), 127.0 (s, CH_{Xyl}), 93.5 (d, $^1J_{\text{RhC}}$ = 14.8 Hz, CH_{COD}), 66.3 (d, $^1J_{\text{RhC}}$ = 6.8 Hz, CH_{COD}), 53.5 (s, NCH_2), 31.4 (s, CH_2COD), 26.6 (s, CH_2COD), 23.5 (s, NCH_2CH_2), 20.5 (s, CH_3), 18.6 (s, CH_3) ppm. ^{13}C NMR (100 MHz, CDCl_3 , room temperature): δ = 223.1 (d, $^1J_{\text{CRh}}$ = 46.3 Hz, C_{NHC}), 145.2 (s, C_{Xyl}), 136.6 (br., C_{Xyl}), 134.2 (br., C_{Xyl}), 128.8 (br., CH_{Xyl}), 126.6 (br., CH_{Xyl}), 126.5 (s, CH_{Xyl}), 93.8 (d, $^1J_{\text{RhC}}$ = 7.1 Hz, CH_{COD}), 66.3 (d, $^1J_{\text{RhC}}$ = 14.9 Hz, CH_{COD}), 54.6 (s, NCH_2), 54.4 (s, NCH_2), 31.2 (s, CH_2COD), 26.3 (s, CH_2COD), 24.0 (s, NCH_2CH_2), 19.1 (s, CH_3), 17.5 (s, CH_3) ppm. MS (ES, CH_3CN): m/z = 517.2110 [$\text{M} - \text{Cl}^+$]. $\text{C}_{29}\text{H}_{38}\text{N}_2\text{Rh}$ requires 517.2090.

Rh(7-*o*Tol)(COD)Cl: $\text{KNSi}(\text{Me}_3)_2$ (0.200 g, 1.0 mmol) and 7-*o*Tol-HBF₄ (0.361 g, 1.0 mmol) were placed into a Schlenk tube, followed by the addition of diethyl ether (10 mL). The solution was stirred for 30 min and subsequently filtered into a Schlenk tube containing a thf solution (10 mL) of $[\text{Ir}(\text{COD})\text{Cl}]_2$ (0.336 g, 0.5 mmol); an immediate colour change was observed from light to dark yellow. After the reaction mixture was stirred at room temperature for 1 h, the solvent was removed in vacuo. The precipitate was washed with hexanes and dried under vacuum to afford a brown solid. The product was dissolved in dcm (5 mL) and precipitated with diethyl ether to yield 140 mg of a yellow microcrystalline solid (0.25 mmol, 25%). ^1H NMR (500 MHz, CDCl_3 , room temperature): δ = 8.50 (d, $^3J_{\text{HH}}$ = 7.9 Hz, 2 H, CH_{Ar}), 7.32 (d, $^3J_{\text{HH}}$ = 7.8 Hz, 2 H, CH_{Ar}), 7.22 (m, 4 H, CH_{Ar}), 4.39 (m, 2 H, CH_{COD}), 4.19 (t, $^3J_{\text{HH}}$ = 12.6 Hz, 2 H, NCH_2), 3.42 (d, $^3J_{\text{HH}}$ = 13.3 Hz, 2 H, NCH_2), 2.46 (m, 2 H, NCH_2CH_2), 2.04 (m, 2 H, CH_{COD}), 2.21 (s, 6 H, CH_3), 1.77 (d, $^3J_{\text{HH}}$ = 7.7 Hz, 2 H, NCH_2CH_2), 1.42 (m, 2 H, CH_2COD), 1.23 (m, 2 H, CH_2COD), 1.19 (m, 2 H, CH_2COD), 1.04 (m, 2 H, CH_2COD) ppm. ^{13}C NMR (125 MHz, CDCl_3 , room temperature): δ = 222.8 (d, $^1J_{\text{CRh}}$ = 45.0 Hz, C_{NHC}), 146.8 (s, *ipso*- C_{Ar}), 133.5 (s, C_{Ar}), 133.0 (s, C_{Ar}), 130.0 (s, C_{Ar}), 127.4 (s, C_{Ar}), 126.6 (s, C_{Ar}), 95.3 (d, $^1J_{\text{RhC}}$ = 19.8 Hz, CH_{COD}), 66.8 (d, $^1J_{\text{RhC}}$ = 15.1 Hz, CH_{COD}), 53.3 (s, NCH_2), 31.6 (s, CH_2COD), 27.4 (s, CH_2COD), 24.0 (s, NCH_2CH_2), 18.4 (s, CH_3) ppm. MS (ES, CH_3CN): m/z = 489.1776 [$\text{M} - \text{Cl}^+$]. $\text{C}_{29}\text{H}_{38}\text{N}_2\text{Rh}$ requires 489.1790.

Rh(5-Mes)(CO)₂Cl: Complex $[\text{Rh}(5\text{-Mes})(\text{COD})\text{Cl}]$ (50 mg, 0.090 mmol) was dissolved in dichloromethane (10 mL) and stirred under an atmosphere of carbon monoxide for 30 min. The solvent was then removed in vacuo, and the resulting solid was washed with cold hexanes to remove residual 1,5-cyclooctadiene. The resulting solid was dried in vacuo to afford 38 mg (0.076 mmol) of a pale yellow solid (83% yield). ^1H NMR (400 MHz, CDCl_3 , room temperature): δ = 6.88 (s, 4 H, CH_{Mes}), 3.92 (s, 4 H, NCH_2), 2.35 (s, 12 H, CH_3), 2.23 (s, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, CDCl_3 , room temperature): δ = 205.0 (d, $^1J_{\text{RhC}}$ = 40.8 Hz, C_{NHC}), 184.2 (d, $^1J_{\text{RhC}}$ = 57.3 Hz, CO), 181.9 (d, $^1J_{\text{RhC}}$ = 74.4 Hz, CO), 135.1 (br., C_{Mes}), 137.6 (s, C_{Mes}), 133.9 (s, C_{Mes}), 128.5 (s, CH_{Mes}), 50.5 (s, NCH_2), 20.1 (s, CH_3), 17.6 (s, CH_3) ppm. IR: $\tilde{\nu}$ = 1995, 2080 (CH_2Cl_2).

Rh(6-Mes)(CO)₂Cl: Complex $[\text{Rh}(6\text{-Mes})(\text{COD})\text{Cl}]$ (50 mg, 0.088 mmol) was dissolved in dichloromethane (10 mL) and stirred under an atmosphere of carbon monoxide for 30 min. The solvent was then removed in vacuo, and the resulting solid was washed with cold hexanes to remove residual 1,5-cyclooctadiene. The resulting solid was dried in vacuo to afford 40 mg (0.078 mmol) of a pale yellow solid (88% yield). ^1H NMR (400 MHz, CDCl_3 , room

temperature): δ = 6.87 (s, 4 H, CH_{Mes}), 3.37 (m, 4 H, NCH_2), 2.35 (s, 6 H, CH_3), 2.31 (s, 6 H, CH_3), 2.29 (m, 2 H, NCH_2CH_2), 2.25 (s, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, CDCl_3 , room temperature): δ = 202.9 (d, $^1J_{\text{RhC}}$ = 40.8 Hz, C_{NHC}), 186.1 (d, $^1J_{\text{RhC}}$ = 52.5 Hz, CO), 183.7 (d, $^1J_{\text{RhC}}$ = 67.6 Hz, CO), 141.7 (s, C_{Mes}), 138.4 (s, C_{Mes}), 136.7 (s, C_{Mes}), 134.5 (s, C_{Mes}), 130.4 (s, CH_{Mes}), 129.3 (s, CH_{Mes}), 47.2 (s, NCH_2), 21.5 (s, CH_3), 21.1 (s, NCH_2CH_2), 19.9 (s, CH_3), 18.6 (s, CH_3) ppm. IR: $\tilde{\nu}$ = 1987, 2071 (CH_2Cl_2).

Rh(7-Mes)(CO)₂Cl: Complex $[\text{Rh}(7\text{-Mes})(\text{COD})\text{Cl}]$ (50 mg, 0.082 mmol) was dissolved in dichloromethane (10 mL) and stirred under an atmosphere of carbon monoxide for 30 min. The solvent was then removed in vacuo, and the resulting solid was washed with cold hexanes to remove residual 1,5-cyclooctadiene. The resulting solid was dried in vacuo to afford 40 mg (0.077 mmol) of a pale yellow solid (94% yield). ^1H NMR (400 MHz, CDCl_3 , room temperature): δ = 6.89 (s, 4 H, CH_{Mes}), 4.00 (m, 2 H, NCH_2), 3.71 (m, 2 H, NCH_2), 2.43 (s, 6 H, CH_3), 2.36 (s, 6 H, CH_3), 2.34 (m, 2 H, NCH_2CH_2), 2.23 (s, 6 H, CH_3), 2.11 (m, 2 H, NCH_2CH_2) ppm. ^{13}C NMR (100 MHz, CDCl_3 , room temperature): δ = 213.4 (d, $^1J_{\text{RhC}}$ = 40.8 Hz, C_{NHC}), 187.1 (d, $^1J_{\text{RhC}}$ = 52.5 Hz, CO), 184.5 (d, $^1J_{\text{RhC}}$ = 77.7 Hz, CO), 143.6 (s, C_{Mes}), 138.2 (s, C_{Mes}), 136.6 (s, C_{Mes}), 134.3 (s, C_{Mes}), 130.5 (s, CH_{Mes}), 129.4 (s, CH_{Mes}), 55.2 (s, NCH_2), 25.4 (s, NCH_2CH_2), 21.4 (s, CH_3), 20.5 (s, CH_3), 19.3 (s, CH_3) ppm. IR: $\tilde{\nu}$ = 1987, 2069 (CH_2Cl_2). MS (ES, CH_3CN): m/z = 506.1682 [$\text{M} - \text{Cl} - \text{CO} + \text{CH}_3\text{CN}^+$]. $\text{C}_{26}\text{H}_{33}\text{N}_3\text{ORh}$ requires 506.1679.

cis-[Rh(7-Xyl)(CO)₂Cl]: Complex $[\text{Rh}(7\text{-Xyl})(\text{COD})\text{Cl}]$ (50 mg, 0.090 mmol) was dissolved in dichloromethane (10 mL) and stirred under an atmosphere of carbon monoxide for 30 min. The solvent was then removed in vacuo, and the resulting solid was washed with cold hexanes to remove residual 1,5-cyclooctadiene. The resulting solid was dried in vacuo to afford 35 mg (0.070 mmol) of a pale yellow solid (78% yield). ^1H NMR (400 MHz, CDCl_3 , room temperature): δ = 7.12 (t, $^3J_{\text{HH}}$ = 7.0 Hz, 2 H, CH_{Xyl}), 7.05 (d, $^3J_{\text{HH}}$ = 7.5 Hz, 4 H, CH_{Xyl}), 4.04 (m, 4 H, NCH_2), 3.76 (m, 4 H, NCH_2CH_2), 2.48 (s, 6 H, CH_3), 2.41 (s, 6 H, CH_3), 2.34 (m, 4 H, CH_2COD), 2.15 (m, 4 H, CH_2COD) ppm. ^{13}C NMR (100 MHz, CDCl_3 , room temperature): δ = 212.2 (d, $^1J_{\text{RhC}}$ = 40.8 Hz, C_{NHC}), 184.5 (d, $^1J_{\text{RhC}}$ = 52.5 Hz, CO), 182.6 (d, $^1J_{\text{RhC}}$ = 77.3 Hz, CO), 144.5 (s, C_{Xyl}), 135.6 (s, C_{Xyl}), 133.3 (s, C_{Xyl}), 128.4 (s, CH_{Xyl}), 127.4 (s, CH_{Xyl}), 127.1 (s, CH_{Xyl}), 53.7 (s, NCH_2), 24.1 (s, NCH_2CH_2), 18.0 (s, CH_3), 13.1 (s, CH_3) ppm. IR: $\tilde{\nu}$ = 1986, 2071 (CH_2Cl_2). MS (ES, CH_3CN): m/z = 478.1377 [$\text{M} - \text{Cl} - \text{CO} + \text{CH}_3\text{CN}^+$]. $\text{C}_{24}\text{H}_{29}\text{N}_3\text{ORh}$ requires 478.1366.

X-ray Crystallography: Suitable crystals were selected, and a data set for $\text{Rh}(7\text{-}o\text{Tol})(\text{COD})\text{Cl}$ was measured on a Bruker-Nonius APEX II CCD camera on a κ -goniostat, while data sets for $\text{Rh}(7\text{-Mes})(\text{COD})\text{Cl}$ and $\text{Rh}(6\text{-Mes})(\text{COD})\text{Cl}$ were measured on a Bruker-Nonius KappaCCD area detector, all at the window of a Bruker-Nonius FR591 rotating anode [$\lambda(\text{Mo-K}\alpha) = 0.71073 \text{ \AA}$] driven by COLLECT^[10] and processed by DENZO^[11] software at 120 K. Structures were determined by SHELXS-97 and refined by SHELXL-97^[12] CCDC-711927 [for $\text{Rh}(7\text{-Mes})(\text{COD})\text{Cl}$], -711954 [for $\text{Rh}(7\text{-}o\text{Tol})(\text{COD})\text{Cl}$] and -711928 [for $\text{Rh}(6\text{-Mes})(\text{COD})\text{Cl}$] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): ^1H NMR spectrum from the deprotonation of 7-*o*Tol-HBF₄ with K[HMDs].

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