First Examples of Diazepanylidene Carbenes and Their Late-Transition-Metal Complexes

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Received May 16, 2007

The synthesis of the novel seven-membered N-heterocyclic carbene (NHC) 1,3-dicyclohexyl-1,3-diazepan-2-ylidene (**3**) and its 5,6-dioxolane derivative **4** is reported and their coordination chemistry with Rh(I), Ir(I), and Pt(0) discussed. The M(cod)(**3**)Cl, where M = Rh and Ir, complexes display a high rotation barrier at room temperature about the M−C_{NHC} bond, whereas for the M$(CO)_2$(**3**)Cl and Pt$(nbe)_2$(**3**) complexes rapid rotation of the carbene ligand is observed at ambient temperature. The infrared ν(CO) values of the Rh(I) and Ir(I) derivatives M$(CO)_2$(**3**)Cl give a measure of the donor ability of the new carbene ligands. The crystal structures of the amidinium salts **3**·HPF_6 and **4**·HPF_6 together with those of M(cod)(**3**)Cl [M = Rh, Ir], Ir(cod)(**4**)Br, Ir$(CO)_2$(**3**)Cl, and Pt$(nbe)_2$(**3**) are reported. Both the salts and the coordinated carbene ligands exhibit extremely large NCN angles; for the complexes the angles are in the range 115.5(3)° [Pt(**3**)] to 122(11)° [Ir(**4**)].

Introduction

Since the isolation of the first stable, free heterocyclic carbenes,[1] there has been a wealth of new developments with respect to the types of carbenes that may be synthesized.[2] These include, for example, numerous variations on the core imidazole-type N-heterocyclic carbene[3] (such as imidazol-2-ylidines, the saturated imidazolin-2-ylidines, and benzimidazolin-2-ylidenes), triazol-3-ylidenes,[3] pyrazolin-3-ylidenes,[4] six-membered ring tetrahydropyrimidin-2-ylidenes[3] and perimidin-ylidenes,[5] cyclic alkylamino carbenes in which there is only a single heteroatom (nitrogen) in the ring,[6] acyclic and macrocyclic carbenes,[3,7] and several exciting new classes of carbenes appearing from the group of Bertrand (for example, phosphino carbenes[8] and carbocyclic carbenes[9]—stable carbenes without heteroatoms in the ring). A precursor to a rigid, expanded, seven-membered-ring N-heterocyclic carbene was first reported by Stahl and co-workers.[10] The amidinium salt **1**·HBF_4 was synthesized and coordinated to palladium(II) and the complex structurally characterized.[10a] Recently, Bertrand et al. reported a new approach for the synthesis of a range of azolium salts, protonated forms of the heterocyclic carbenes, which included the seven-membered-ring salt **2**·HBr as an example.[11]

The large expanded-ring systems provide carbenes with high basicity and extremely large NCN angles. The effect of basicity and increased NCN linearity on the ligand and complex stability and reactivity is unexplored. A completely saturated, unsubstituted, expanded-ring system is also unknown. Consequently, we report here the synthesis and full characterization of the new seven-membered-ring carbenes **3**·HPF_6 and **4**·HX (X = Br, PF_6) and their complexation to late transition metals.

Results and Discussion

Synthesis of 1,3-Diazepan-2-ylidene Carbenes 3 and 4. Our initial efforts in the area of expanded-ring N-heterocyclic carbenes (NHCs) concentrated on the synthesis of 1,3-diazepan-2-ylidene derivatives. 1,4-Bis(cyclohexylamino)butane (**5**) was

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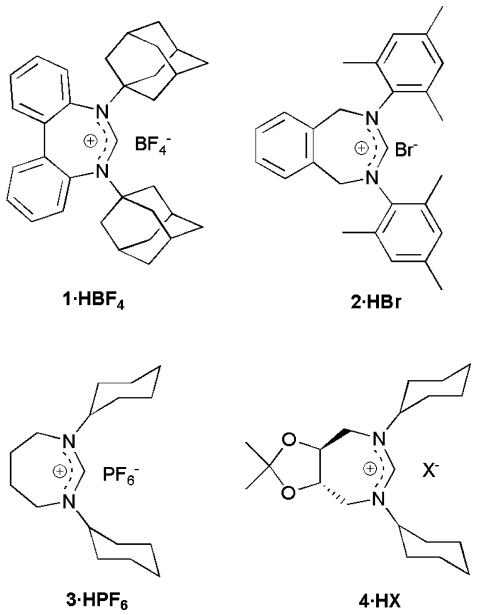
10.1021/om7004904 CCC: $37.00
Publication on Web 08/08/2007

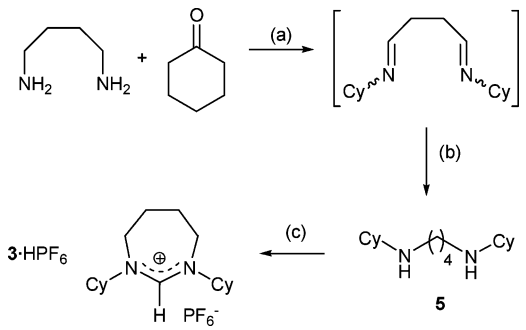


obtained in high yields by the condensation of cyclohexanone and 1,4-diaminobutane followed by reduction of the formed diimine with $NaBH_4$ (Scheme 1). Overall yields of 70% after recrystallization were obtained for the formation of the amidinium salt **3**·HPF_6 (Scheme 1) when 2 equiv of triethyl orthoformate were reacted with the bis(cyclohexylamine) in DME. The same reaction in neat triethyl orthoformate gave yields of the amidinium salt in the range of 10−20%. Our next target in the 1,3-diazepan-ylidene series was the carbene precursor **4**·HBr. We reasoned that the added strain of the dioxolane ring on the carbene backbone would result in larger NCN angles and possibly increased basicity. The diester tartrate derivative **6**, in Scheme 2, was converted via reductive amination to the bis(cyclohexylamine) **7** in high yields. For the cyclization step the formaldehyde/*N*-bromosuccinimide route was preferred, rather than the triethyl orthoformate one. Treatment of **4**·HBr with $AgPF_6$ formed its $-PF_6$ analogue, **4**·HPF_6.

Singe-crystal X-ray diffraction data were collected for salts **3**·HPF_6 and **4**·HPF_6; their ORTEP plots are shown in Figure 1. The solid-state structure of **4**·HPF_6 reveals an unusually large NCN angle at 135.90(10)° compared to a value of 127.35(15)° for the nonsubstituted seven-membered ring of **3**·HPF_6. The corresponding value of the biaryl derivative **1**·HBF_4 is even smaller at 124.2(3)°, and that of the xylene-derived salt **2**·HBr at 127.50(14)°.[11]

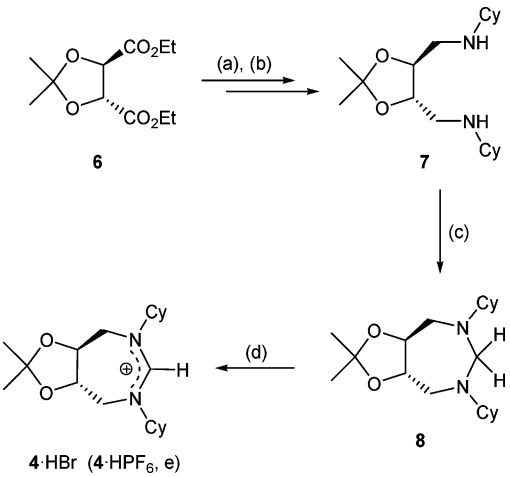
The amidinium salts **3**·HX and **4**·HX are the first saturated seven-membered rings reported and represent suitable NHC precursors. Initial attempts to prepare the free carbenes **3** and **4** using potassium *tert*-butoxide as the base afforded only the corresponding *tert*-butoxide adducts **3**·HO^{t}Bu and **4**·HO^{t}Bu (Scheme 3). In complexation studies with $[Ir(cod)Cl]_2$ these alcohol adducts did not react further even after being heated for 1 day; starting materials were recovered instead. The use of potassium hydride or a combination of potassium hydride/potassium *tert*-butoxide to deprotonate salts **3** and **4** was also unsuccessful. 1,3-Dicyclohexyl-1,3-diazepan-2-ylidene carbene (**3**) was formed only after treatment of the amidinium salt with potassium hexamethyldisilylamide $[KN(SiMe_3)_2]$ in aromatic solvents. The same base however left salt **4**·HPF_6 unchanged. The dioxolane carbene **4** was generated only after treatment of **4**·HPF_6 with the stronger amide base lithium diisopropylamide (LDA), indicating a higher basicity for **4** than its unsubstituted **3** analogue. The ^{13}C NMR spectrum of **3** (C_6D_6) shows a

Scheme 1[a]



[a] Reagents and conditions: (a) reflux in toluene; (b) $NaBH_4$ in ethanol; (c) 2 equiv of $HC(OEt)_3$, 1 equiv of NH_4PF_6, 120 °C in DME.

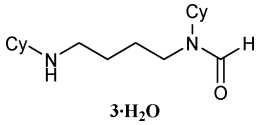
Scheme 2[a]



[a] Reagents and conditions: (a) 2 equiv of DIBAL-H (−78 °C)/2 equiv of $CyNH_2$ in toluene; (b) $NaBH_4$ in ethanol, 76% overall; (c) 1.5 equiv of CH_2O, 50 °C in MeOH; (d) 1 equiv of NBS, 0 °C in DME, 18% (steps c and d); (e) $AgPF_6$.

significantly deshielded carbene carbon shift at 251.2 ppm. This value is notably larger than those reported for tetrahydropyrimid-2-ylidenes and even acyclic carbenes, appearing in the range of 236−243 ppm.[12] A ^{13}C NMR spectrum could not be recorded for carbene **4** as it was rather unstable in solution; the formed carbene was used immediately in complexation reactions.

Complexes of 1,3-Diazepan-2-ylidene Carbenes 3 and 4. Initial complexation studies focused on the preparation of Rh(I) and Ir(I) complexes due to their ease of preparation and handling and the extensive literature of reported NHC complexes with these metals.[13] Attempts to prepare a silver(I) complex as a transmetalation agent from the reaction of the amidinium salt **3**·HX (X = Br, PF_6) with Ag_2O were unsuccessful, with the carbene hydrolysis product **3**·H_2O being isolated instead. The preferred method for the synthesis of transition-metal complexes with **3** and **4** was by direct reaction of the in situ generated carbenes with suitable metal salts.



3·H_2O

Addition of an ether solution of carbene **3** to thf solutions of $[M(cod)Cl]_2$, where M = Rh or Ir, forms cleanly the corre-

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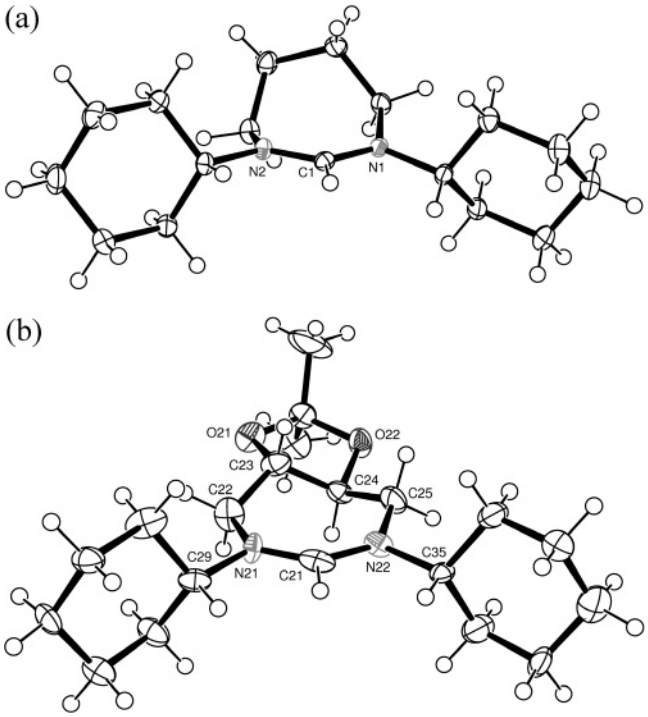
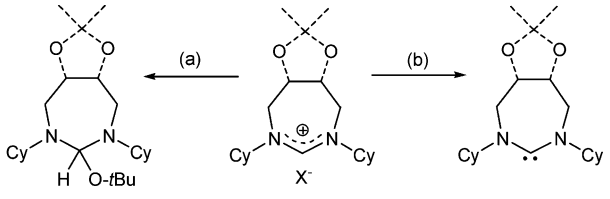


Figure 1. ORTEP ellipsoid plots at 30% probability of the amidinium cations **3**·HPF_6 (a) and **4**·HPF_6 (b). Selected bond lengths (Å) and angles (deg) for **3**·HPF_6: C(1)−N(1), 1.316(2); C(1)−N(2), 1.318(2); C(2)−N(1), 1.483(2); C(2)−C(3), 1.519(2); C(4)−C(5), 1.516(2); C(5)−N(2), 1.477(2); N(1)−C(1)−N(2), 127.35(15); C(1)−N(1)−C(2), 124.68(13); C(1)−N(1)−C(6), 118.11-(13); C(2)−N(1)−C(6), 117.07(12); C(1)−N(2)−C(5), 121.26(13); C(1)−N(2)−C(12), 119.30(13); C(5)−N(2)−C(12), 118.84(12). Selected bond lengths (Å) and angles (deg) for **4**·HPF_6: C(1)−N(2), 1.310(13); C1)−N(1), 1.313(14); C(2)−N(1), 1.476(12); C(2)−C(3), 1.520(13); C(3)−C(4), 1.461(14); C(4)−C(5), 1.476-(13); C(5)−N(2), 1.497(12); N(2)−C(1)−N(1), 135.9(10); N(1)−C(2)−C(3), 114.3(9); C(4)−C(3)−C(2), 114.1(8); C(3)−C(4)−C(5), 115.2(8); C(4)−C(5)−N(2), 112.7(9); C(1)−N(1)−C(2), 129.6(9); C(1)−N(1)−C(9), 117.3(8); C(2)−N(1)−C(9), 113.1(9); C(1)−N(2)−C(5), 127.1(9); C(1)−N(2)−C(15), 117.0(8); C(5)−N(2)−C(15), 115.0(9).

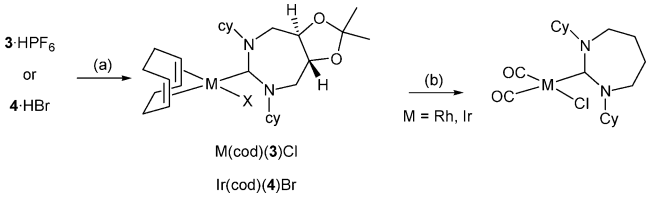
Scheme 3[a]



[a] Reagents and conditions: (a) 1 equiv of KO^{t}Bu in toluene, (b) 1 equiv of $KN(SiMe_3)_2$ in toluene for **3**, 1 equiv of $LiN(^iPr)_2$ in toluene for **4**.

sponding air-stable M(cod)(**3**)Cl complex as a yellow solid in good to high yields (Scheme 4). The in situ reaction of **4**·HBr with LDA followed by addition of $[Ir(cod)Cl]_2$ afforded complex Ir(cod)(**4**)Br, where a halogen exchange has taken place between

Scheme 4. Synthesis of Rhodium and Iridium Complexes[a]



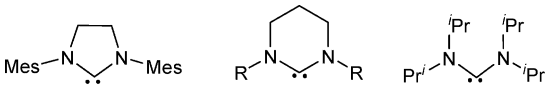
[a] Reagents and conditions: (a) 1 equiv of $KN(SiMe_3)_2$, 1/2 equiv of $[M(cod)Cl]_2$, M = Rh or Ir, in thf; (b) 1 atm of CO in CH_2Cl_2, 20 min.

Table 1. Characteristic NMR Shifts for Carbenes 3 and 4 and Their Complexes[a]

	$\delta_H(H_{Cy})$	$\delta_C(C_{NHC})$
3[b]	3.50	251.2
Rh(cod)(**3**)Cl	6.18	215.3 ($^1J_{Rh}$ = 43.7 Hz)
$Rh(CO)_2$(**3**)Cl[c]	5.34	206.2 ($^1J_{Rh}$ = 37.7 Hz)
Ir(cod)(**3**)Cl	5.74	208.3
$Ir(CO)_2$(**3**)Cl	5.11	199.8
$Pt(nbe)_2$(**3**)[b]	4.43 (br)	
4[b]	3.40	
Ir(cod)(**4**)Br[b]	6.37, 6.09	223.6

[a] Measured in $CDCl_3$, unless otherwise noted. H_{Cy} = cyclohexyl methinic proton, and C_{NHC} = carbene carbon. [b] Measured in C_6D_6. [c] Measured in toluene-d_8.

the metal chloride and LiBr present in solution. Table 1 shows characteristic NMR chemical shifts for the complexes of **3** and **4**. Upon complexation of carbene **3** the most characteristic chemical shift in the ^1H NMR ($CDCl_3$) is that for the α protons of the *N*-cyclohexyl substituents, which changes from 3.50 ppm in **3** to 6.18 ppm in the Rh(cod)(**3**)Cl complex and to 5.74 ppm in the Ir(cod)(**3**)Cl analogue. This large change in δ_H is attributed to the close proximity of the methine protons to the electron-rich metal centers. ^1H NMR spectra of the chiral iridium(I) dioxolane carbene complex Ir(cod)(**4**)Br show in addition to signals of diastereotopic methylene groups two resonances for the α *N*-cyclohexyl protons and four resonances for the olefinic protons of the coordinated 1,5-cyclooctadiene. In this case, due to the asymmetric carbene ligand, there is no plane of symmetry in the molecule as with the Rh and Ir(cod)(**3**)Cl analogues. In ^{13}C NMR ($CDCl_3$) the most notable chemical shift is that of the carbene carbon, which changes from 251.2 ppm in the free carbene to 215.3 (J_{RhC} = 43.7) and 208.3 ppm for the rhodium and iridium complexes of **3**, respectively. These values are higher than those reported for the corresponding complexes of carbenes **9**−**12**, with the exception of the acyclic carbene **13**, which shows a shift of 233.8 ppm for its rhodium complex.[14,15] The C_{NHC} chemical shift of the Ir(cod)(**4**)Br complex appears at 223.6 ppm (C_6D_6).



R = Mes (**9**) R = ^{t}Bu (**10**) R = Mes (**11**) R = ^{i}Pr (**12**) **13**

The Rh(cod)(**3**)Cl and Ir(cod)(**3**)Cl complexes were converted to the corresponding air-stable *cis*-dicarbonyl compounds $Rh(CO)_2$(**3**)Cl and $Ir(CO)_2$(**3**)Cl after treatment of their dichloromethane solutions with carbon monoxide (1 atm) for 20 min,

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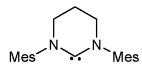
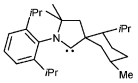
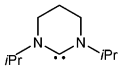
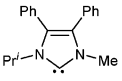
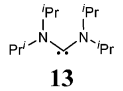
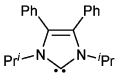
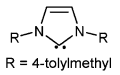
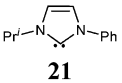
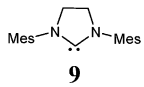
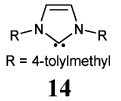
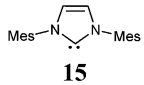
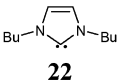
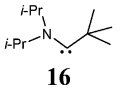
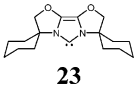
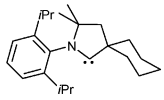
Table 2. Carbonyl Stretching Frequencies for $Rh(CO)_2(L)Cl$ and $Ir(CO)_2(L)Cl$ Complexes[a]

$Rh(CO)_2(\mathbf{L})Cl$	$\nu(CO)$[b]	$\nu_{av}(CO)$[b]	Ref.	$Ir(CO)_2(\mathbf{L})Cl$	$\nu(CO)$[b]	$\nu_{av}(CO)$[b]	Ref.
3	2071 1990	2031	-	**3**	2058 1973	2016	-
 **11**	2062 1976	2019	14a	 **18**	2055 1971	2013	6a
 **12**	2063 1982	2023	14a	 **19**	2059 1974	2017	16
 **13**	2057 1984	2021	15	 **20**	2061 1972	2017	16
 **14**	2076 1995	2036	13b	 **21**	2061 1976	2019	16
 **9**	2081 1996	2039	15	 **14**	2063 1976	2020	13b
 **15**	2076 2006	2041	15	 **22**	2062 1978	2020	13b
 **16**	2070 1989	2030	7c	 **23**	2065 1982	2024	24
 **17**	2077 1994	2036	6b				

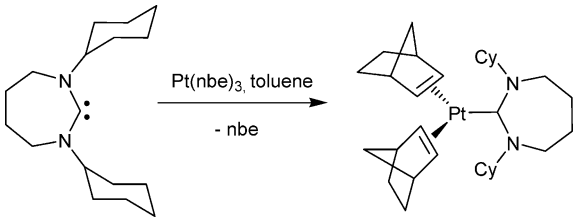
[a] IR spectra recorded in CH_2Cl_2. [b] $\nu(CO)$ and $\nu_{av}(CO)$ values in cm^{-1}.

Scheme 4. The ^1H NMR spectra of both complexes show a notable high-field shift of the methinic cyclohexyl protons when compared to those of the parent cyclooctadiene complexes (Table 1), attributed to the more electron rich metal centers.

The infrared carbonyl stretching frequencies of the rhodium and iridium carbonyl complexes *cis*-$M(CO)_2(L)Cl$ are well documented to be a good measure of the donor ability of ligand L; the more basic the ligand, the lower the observed $\nu(CO)$ values.[16] In Table 2 the carbonyl stretching frequencies of $Rh(CO)_2(\mathbf{3})Cl$ and $Ir(CO)_2(\mathbf{3})Cl$ are listed and compared to those of analogous complexes. The average carbonyl stretching frequency for the rhodium complex $Rh(CO)_2(\mathbf{3})Cl$ is 2031 cm^{-1}, suggesting a donor ability of **3** higher than that of electron-rich alkylphosphines and five-membered (saturated or unsaturated) and cyclic alkylamino carbenes, but lower than that of the tetrahydropyrimidine and acyclic carbenes **11**, **12**, and **13**. Differences between the values of $\nu_{av}(CO)$ for the $Ir(CO)_2(\mathbf{3})Cl$ complex, at 2016 cm^{-1}, and other carbene complexes were within the spectrometers' resolution limits (4 cm^{-1}), with the exception of the oxazoline-derived carbene **23**, at 2024 cm^{-1}.[16,17] For comparison, the average carbonyl stretching frequency of the $Ir(CO)_2(PCy_3)Cl$ complex is 2028 cm^{-1}.[13b]

Reaction of the in situ generated diazepanylidene carbene **3** with platinum(0) trisnorbornene forms the corresponding air-sensitive monocarbene complex $Pt(nbe)_2(\mathbf{3})$ (Scheme 5). ^1H and ^{13}C NMR spectra of $Pt(nbe)_2(\mathbf{3})$ in benzene-d_6 show broad resonances for the coordinated carbene ligand but sharp signals for the coordinated norbornenes at room temperature, consistent with a slow rotation of **3** about the Pt−C bond.

Scheme 5. Synthesis of the $Pt(nbe)_2(3)$ Complex



Solution NMR Studies. At room temperature, the rhodium and iridium complexes $M(cod)(\mathbf{3})Cl$ show a sharp ABXY pattern for the diastereotopic NCH_2 ring protons in the ^1H NMR spectrum, indicating a high rotation barrier about the metal−carbene bond. Variable-temperature ^1H NMR experiments up to 100 °C in toluene-d_8 show no line broadening for the rhodium and iridium complexes of **3**, consistent with a free energy rotation barrier greater than 74 kJ·mol^{-1}. In contrast, the room-temperature ^1H NMR spectra of the $Rh/Ir(CO)_2(\mathbf{3})Cl$ complexes show an average signal for the NCH_2 protons, indicating rapid rotation about the $M-C_{NHC}$ bond. Variable-temperature ^1H NMR spectra in the range of +20 to −90 °C in dichloromethane-d_2 confirm a fluxional behavior for the $Ir(CO)_2(\mathbf{3})Cl$ complex. At −90 °C two relatively sharp signals are observed for the NCH_2 protons in a 1:1 ratio. As the temperature is increased the signals coalesce at about −65 °C. Line shape analysis of the NMR data affords a value of 50.9 ± 3.1 kJ mol^{-1} for the enthalpy of activation ($\Delta H^{\ddagger}$).[18]

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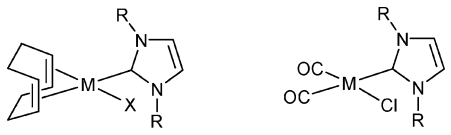
The above observations agree with those of Crabtree[13b] and Lappert et al.,[19] where high-rotation metal−carbene barriers were observed for the cyclooctadiene complexes **24** but lower rotation barriers for the biscarbonyl complexes **25**, although it



24 **25**

M = Rh, Ir; R = 4-tolylmethyl, butyl

is worth noting that the rotation barrier of the $Ir(CO)_2$(**3**)Cl complex is much lower than that of the analogous complex **25** (R = 4-tolylmethyl), with a coalescence temperature at 55 °C. Previous studies with metal−carbene complexes have shown that no electronic rotation barrier exists for the $M-C_{NHC}$ bonds, thus suggesting a steric origin of the rotation barrier.[20] Our results with the cyclooctadiene and carbonyl complexes of **3** also support a steric barrier to rotation about the $M-C_{NHC}$ bond.

Solid-State Structures of Metal Complexes. The rhodium, iridium, and platinum complexes of carbenes **3** and **4** were characterized by single-crystal X-ray diffraction studies. ORTEP drawings of the Rh(cod)(**3**)Cl and Ir(cod)(**4**)Br complexes are shown in Figure 2, and a drawing of the isostructural iridium **3** complex can been found in the Supporting Information. Bond lengths and angles are summarized in Table 3; average values are reported for the Ir(cod)(**4**)Br complex due to the presence of four nonequivalent molecules in the unit cell. In all three complexes the carbene ligand adopts a close to perpendicular arrangement with respect to the coordination plane (defined by the $C_{NHC}-M-X$ atoms). The Rh−C(1) bond distance of the Rh(cod)(**3**)Cl complex at 2.056(2) Å is close to the values reported for the corresponding pyrimidine-based carbene **12**, at 2.047(3) Å, and acyclic carbene **13**, at 2.041(2) Å, but longer than that of imidazolidine carbene complexes, with values in the range of 1.994−2.032 Å.[21] Similarly, the Ir−C(1) bond distance in the corresponding Ir(cod)(**3**)Cl complex, at 2.072-(3) Å, is close to the value reported for the iridium complex of pyrimidine carbene **11**, at 2.058(5) Å;[13d] the corresponding values for five-membered carbenes are somewhat shorter and fall within the narrow range of 2.029−2.033 Å.[13b,22]

Upon coordination of the diazepane carbene **3** to Rh or Ir the NCN angle changes from 127.35(15)° in **3**·HPF_6 to close to 120°. The corresponding value for the Ir(cod)(**4**)Br complex is 122.2(11)°. These NCN angles are considerably larger than those observed in complexes of five-membered carbenes,[23] which fall in the 103−107° range, and are even larger than for the six-membered NHCs, 115−118°.[13d,e] Although there are no reported seven-membered NHC iridium or rhodium complexes, the corresponding values for palladium complexes of **1** range

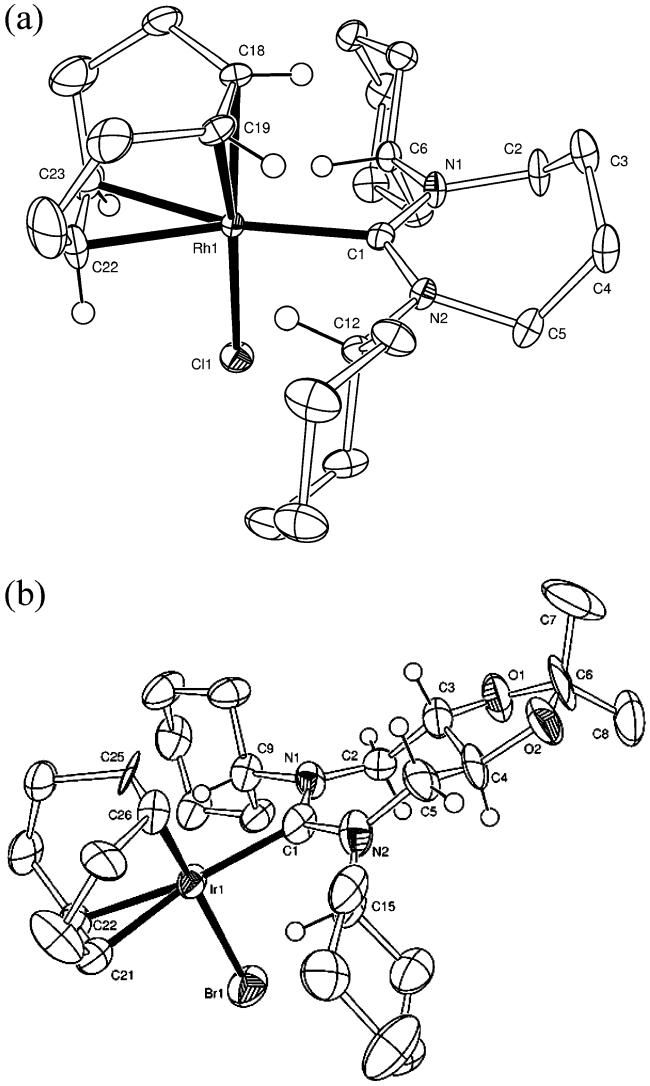


Figure 2. ORTEP ellipsoid plots at 30% probability of the molecular structures of Rh(cod)(**3**)Cl and Ir(cod)(**4**)Br.

from 113° to 117°. The very large NCN angles, in the seven-membered carbene series, lead to increased steric crowding around the metal center; the *N*-substituents are forced out toward the metal, which may have important catalytic implications. The large NCN angles may also reflect an increase in the ring strain, which in the case of carbene **1** is partially relieved by the torsional twist of the biaryl backbone. A measure of the seven-membered ring strain is the tetrahedral deviation of the ring carbon atoms. In the amidinium salt **3**·HPF_6 the C2−C5 carbon ring angles range from 111.5° to 113.3°, and in **4**·HPF_6 an even more strained ring is observed as indicated from the corresponding angle range 112.6−116.0°. Complexation of the corresponding free carbenes offers little relief to the ring strain; for example, the corresponding ring angles in Ir(cod)(**3**)Cl range from 110.4° to 114.2° and in Ir(cod)(**4**)Br from 110.1(9)° to 115.0(10)°.

The torsional angle α between the planes defined by the $C_{Cy}-N\cdots N-C_{Cy}$ atoms is a useful gauge for the spatial orientation of the cyclohexyl substituents which point directly into the metal's coordination sphere. The torsional angle α in the

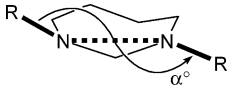


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Table 3. Selected Bond Lengths (Å) and Angles (deg) in the Rh(cod)(3)Cl, Ir(cod)(3)Cl, Ir(CO)$_2$(3)Cl, and Ir(cod)(4)Br Complexes[a]

	Rh(cod)(**3**)Cl	Ir(cod)(**3**)Cl	Ir(CO)$_2$(**3**)Cl	Ir(cod)(**4**)Br[b]
M−C$_{NHC}$	2.056(2)	2.072(3)	2.115(3)	2.088(12)
M−X	2.3935(8)	2.3747(6)	2.3649(10)	2.4929(19)
M−C(18)	2.113(2)	2.106(2)	1.893(4)	2.146(12)
M−C(19)	2.126(2)	2.120(2)	1.893(5)	2.150(12)
M−C(22)	2.188(3)	2.163(3)		2.164(12)
M−C(23)	2.219(3)	2.188(3)		2.174(11)
C=C$_{trans\text{-}X}$	1.401(3)	1.422(4)		1.428(19)
C=C$_{trans\text{-}NHC}$	1.365(4)	1.387(5)		1.366(17)
O(1)−C(18)			1.132(4)	
O(2)−C(19)			1.038(5)	
N−C$_{NHC}$−N	120.4(2)	120.4(2)	120.8(3)	122.2(11)
C$_{NHC}$−M−X	88.86(7)	89.36(7)	84.50(8)	88.88(4)
C(19)−Ir(1)−C(18)			92.22(14)	
C(19)−Ir(1)−C(1)			91.91(13)	
C(18)−Ir(1)−Cl(1)			91.61(11)	
C$_{NHC}$−N(1)−C	127.9(2)	127.1(2)	122.6(3)	127.9(10)
C$_{NHC}$−N(1)−C$_{Cy}$	117.8(2)	118.2(2)	120.7(2)	117.2(10)
C$_{Cy}$−N(1)−C	114.3(2)	114.7(2)	116.5(2)	112.9(9)
C$_{NHC}$−N(2)−C	123.5(2)	123.4(2)	125.9(3)	
C$_{NHC}$−N(2)−C$_{Cy}$	119.3(2)	119.6(2)	119.3(2)	
C−N(2)−C$_{Cy}$	115.42(19)	115.3(2)	113.9(2)	
tilt angle (θ)	89.3	89.5	86.3	88.7

[a] Abbreviations: C$_{NHC}$, carbene carbon; C=C$_{trans\text{-}X}$, double bond *trans* to halide; C=C$_{trans\text{-}NHC}$, double bond *trans* to carbene; C$_{Cy}$, cyclohexyl tertiary carbon. [b] Reported values are the average from the four molecules in the unit cell.

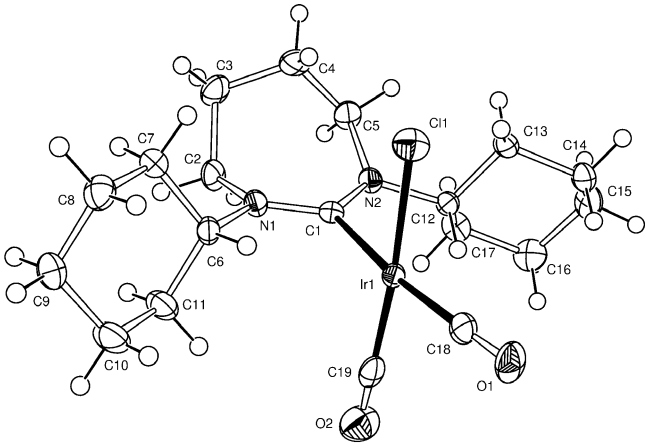

Figure 3. ORTEP ellipsoid plot at 30% probability of the molecular structure of Ir(CO)$_2$(**3**)Cl. Solvent molecules have been omitted for clarity.

amidinium salt **3**·HPF$_6$ is 23.3°, whereas in **4**·HPF$_6$ the two C$_{Cy}$−N···N planes deviate from planarity by only 3.3°. Upon coordination of **3** a small increase of the torsional angle is observed to 28.31° and 27.1° for the Ir(cod)(**3**)Cl and Rh(cod)(**3**)Cl complexes, respectively. However, for the dioxolane complex large variations in the torsional angles of the four molecules in the asymmetric unit are observed, ranging from 15.9° to 39.8°. For comparison, the torsional angle in the biaryl amidinium salt **1** is 56.2(5)°, increasing to 79.7(13)° in the palladium dimer [Pd(**1**-**HX**)Cl]$_2$.

The structure of the iridium complex *cis*-Ir(CO)$_2$(**3**)Cl is shown in Figure 3. Selected bond lengths and angles are summarized in Table 3. A longer M−C$_{NHC}$ bond is observed upon substitution of the cyclooctadiene with two carbonyl ligands, from 2.072(3) to 2.115(3) Å, respectively. The two M−CO bonds are virtually identical at 1.893(4−5) Å and close to the values reported for the analogous complex of the unsaturated carbene **23**, Table 2, at 1.897(4) and 1.892(3) Å.[24] Of note is that although the M−CO bond lengths are the same,

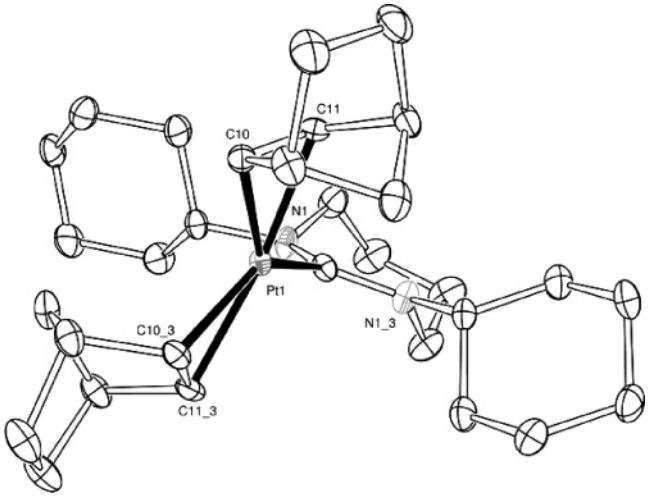

Figure 4. ORTEP ellipsoid plot at 30% probability of the molecular structure of Pt(nbe)$_2$(**3**). Solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for Pt(nbe)$_2$(**3**): C(1)−Pt(1), 2.077(4); C(11)−Pt(1), 2.140(3); C(10)−Pt(1), 2.104(3); C(10)−C(11), 1.436(4); C(1)−Pt(1)−C(11), 97.57(8); C(1)−N(1)−C(2), 120.9(3); C(10)−Pt(1)−C(10^i), 86.96(16); N(1)−C(2)−C(3), 115.8(3); C(1)−Pt(1)−C(10), 136.52(8); C(2)−C(3)−C(3^i), 109.6(3); C(10)−Pt(1)−C(11), 39.52(11); C(1)−N(1)−C(4), 119.2(2); N(1^i)−C(1)−N(1), 115.5(3); C(4)−N(1)−C(2), 115.1(2); tilt angle (θ) 84.5°.

despite having different *trans* substituents, the C−O bond *trans* to the carbene is longer by ca. 0.1 Å than the one *trans* to the chloride ligand, in line with the higher *trans* influence of the carbene ligand. A similar trend can also be observed in the structures of *cis*-Ir(CO)$_2$(**21**)Cl and *cis*-Ir(CO)$_2$(P^{t}Bu$_3$)Cl complexes.[25]

The crystal structure of the Pt(nbe)$_2$(**3**) complex shows the metal occupying the center of a trigonal planar arrangement with both olefinic carbons of the alkenes in the coordination plane (Figure 4), a characteristic coordination mode for Pt(0)(alkene)$_2$ complexes. This trigonal planar conformation around the platinum center provides a better overlap of the Pt d orbitals and the olefinic π^* systems. A C_2 crystallographic axis passes through the Pt−C(1) bond and bisects the C(3)−C(3′) bond of the carbene ligand, with the carbene ring adopting a chair conformation. Comparison of the Pt−C(1) distance at 2.077(4) Å with those of other Pt(0)(alkene)$_2$(carbene) complexes reveals a small variation from the average value of 2.05 Å.[26,27] The NCN angle of the platinum complex of **3** is notably smaller, 115.5(3)°, than the corresponding angle in its Rh(I) and Ir(I) complexes, which is approximately 120° in all three structures. The carbene tilt angle θ from the coordination plane is 84.5°. Markó and co-workers have observed that the greater the deviation of the carbene ligand from a perpendicular arrangement, the greater the strain on the remaining ligands. In the Pt(nbe)$_2$(**3**) complex an 8.5° tilt of the norbornene C=C bonds from the coordination plane is observed. The C=C bond length of the coordinated olefins is a good indicator of the extent of π-back-bonding from the metal. In the presence of strong σ

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donors, such as NHCs, long olefinic bonds are expected. In the $Pt(nbe)_2$(**3**) complex the C═C bond length of the norbornene ligands is 1.436(4) Å; this value is within the range for NHCs[28] and longer than those of $Pt(0)(alkene)_2L$ complexes, where L = phosphine ligand, with values between 1.409 and 1.422 Å.[29]

Summary

The rhodium(I), iridium(I), and platinum(0) complexes of the diazepanylidene carbene **3** have been isolated and fully characterized by NMR and IR spectroscopy and X-ray diffraction. The chiral 5,6-dioxolane carbene derivative **4** and its Ir(cod)Cl complex have also been prepared. However, the low yields of the diazepinium salt, **4**·HBr, and unstable nature of the corresponding carbene have thus far prevented us from studying further the coordination chemistry of **4**. A predominantly steric barrier to rotation of the carbene−metal fragment was found in the rhodium and iridium complexes of **3**, controlled by the size of the ancillary ligands on the metal (cyclooctadiene vs CO ligands). The IR carbonyl stretching frequencies of the $M(CO)_2$-(**3**)Cl complexes, where M = Rh and Ir, suggest a higher donor ability for carbene **3** than basic phosphines and five-membered carbenes, but acyclic and six-membered ring carbenes display a higher donor ability to **3**. The large NCN angles and high basicity found for the diazepane carbenes **3** and **4** are desirable characteristics in many catalytic applications. Further studies on the properties and catalytic applications of these diazepanylidene carbenes are currently in progress.

Experimental Section

General Remarks. All manipulations were performed using standard Schlenk techniques under an argon atmosphere, except where otherwise noted. All complexes after their formation were treated under aerobic conditions. Solvents of analytical grade were freshly distilled from sodium/benzophenone (thf, toluene, hexane) or from calcium hydride (CH_2Cl_2, MeCN). Deuterated solvents for NMR measurements were distilled from the appropriate drying agents under N_2 immediately prior to use, following standard literature methods.[30] Air-sensitive compounds were stored and weighed in a glovebox. Literature methods were employed for the synthesis of **6**.[31] All other reagents were used as received. NMR spectra were obtained on a Bruker Avance AMX 400 or 500 or a Jeol Eclipse 300 spectrometer. The chemical shifts are given as dimensionless δ values and are frequency referenced relative to the peak for TMS for ^{1}H and ^{13}C and H_3PO_4 for ^{31}P. Coupling constants *J* are given in hertz as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as "s", "d", or "m" for singlet, doublet, or multiplet, respectively. The abbreviation "br" is given for broadened signals. Mass spectra and high-resolution mass spectra were obtained in electrospray (ES) mode unless otherwise reported on a Waters Q-Tof micromass spectrometer. IR spectra were measured on a JASCO 660plus FT-IR spectrometer from 4000 to 600 cm^{-1}.

1,4-Bis(cyclohexylamino)butane (5). 1,4-Butanediamine (5 mL, 50 mmol) and cyclohexanone (10 mL, 100 mmol) were dissolved in toluene (30 mL) in a 100 mL flask equipped with a Dean−Stark apparatus. The reaction mixture was heated to 140 °C for 3 h (until 1.8 mL of water was collected in the Dean−Stark apparatus). Evaporation of toluene afforded 12.4 g of 1,4-bis-(cyclohexylimino)butane as a yellow oil (99%) which was used without further purification in the synthesis of the corresponding diamine. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.40−1.60 (m, 16H), 2.10−2.25 (m, 8H), 3.25 (m, 4H). 1,4-Bis(cyclohexylimino)butane (12.4 g, 50 mmol) was dissolved in 100 mL of dry ethanol in a 250 mL round-bottom flask, and sodium borohydride (3.77 g, 100 mmol) was added in small portions over a period of 2 h. When the gas evolution subsided, the reaction was stirred further for 1 h. The residue obtained after evaporation of the volatiles was dissolved in 100 mL of water and extracted with diethyl ether (3 × 100 mL). The combined organic fractions were washed with brine (50 mL), dried over magnesium sulfate, filtered, and concentrated under reduced pressure until white crystals started to precipitate out of the solution. The flask was stored in the fridge overnight; after filtration 9.5 g of the diamine was obtained as white crystals (75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.57 (4H, m, NCH_2), 2.35 (2H, m, NC*H*), 1.60 (14H, m, CH_2), 1.1 (10H, m, CH_2). ^{13}C NMR (400 MHz, $CDCl_3$): δ 57.3 (2C, s, N*C*H), 47.2 (2C, s, N*C*H_2), 34.0 (4C, s, *C*H_2), 28.7 (2C, s, *C*H_2), 26.5 (2C, s, *C*H_2), 25.5 (4C, s, *C*H_2). MS (ES): *m*/*z* 253.2641 (MH^+; $C_{16}H_{33}N_2$ requires 253.2644).

1,3-Dicyclohexyl-1,3-diazepan-2-ylidenium Hexafluorophosphate, 3·HPF$_6$. 1,4-Bis(cyclohexylamino)butane (3 g, 12 mmol), ammonium hexafluorophosphate (1.95 g, 12 mmol), and triethyl orthoformate (4 mL, 24 mmol) were dissolved in 150 mL of DME. The reaction was heated to 120 °C for 3 h, after which time the solvent was evaporated under reduced pressure. The remaining residue was dissolved in chloroform, and any insoluble impurities were filtered off. Evaporation of the solvent afforded 4.6 g of a white solid (94%). Recrystallization from a mixture of chloroform/diethyl ether (2:1) afforded 3.5 g of white crystals (70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (1H, s, NC*H*N), 3.60 (4H, m, NCH_2), 3.41 (2H, m, NC*H*), 2.02 (4H, m, CH_2), 1.86 (4H, m, CH_2), 1.77 (4H, m, CH_2), 1.58 (2H, m, CH_2), 1.39 (8H, m, CH_2), 1.04 (2H, m, CH_2). ^{13}C NMR (400 MHz, $CDCl_3$): δ 156.4 (1C, s, N*C*N), 57.2 (2C, s, N*C*H), 44.7 (2C, s, N*C*H_2), 31.1 (4C, s, *C*H_2), 25.5 (2C, s, *C*H_2), 25.4 (4C, s, *C*H_2), 25.2 (2C, s, *C*H_2). MS (ES): *m*/*z* 263.2495 ($M - PF_6^+$; $C_{17}H_{31}N_2$ requires 263.2487).

1,3-Dicyclohexyl-1,3-diazepan-2-ylidene Carbene (3). KNSi-$(Me_3)_2$ (100 mg, 0.6 mmol) and **3**·HPF_6 (204 mg, 0.5 mmol) were placed into a Schlenk tube followed by the addition of diethyl ether (10 mL). The solution was stirred for 30 min, subsequently filtered off into another Schlenk tube, and dried under reduced pressure to afford a colorless oil. ^{1}H NMR (C_6D_6, 500 MHz, 298 K): δ 3.51 (2H, dddd, $^3J_{HH} \cong {}^3J_{HH} = 12.0$, $^3J_{HH} \cong {}^3J_{HH} = 3.7$, NC*H*), 2.98 (4H, m, NCH_2), 1.84 (4H, m, CH_2), 1.60 (4H, m, CH_2), 1.48 (4H, m, CH_2), 1.40 (6H, m, CH_2), 1.16 (4H, m, CH_2), 0.95 (2H, ddddd, $^2J_{HH} \cong {}^3J_{HH} = 13.0$, $^3J_{HH} \cong {}^3J_{HH} \cong {}^3J_{HH} = 3.8$, C$H_2$). ^{13}C NMR (125 MHz, C_6D_6): δ 251.2 (1C, s, N*C*N), 68.6 (2C, s, N*C*H), 44.2 (2C, s, N*C*H_2), 32.5 (4C, s, *C*H_2), 27.2 (2C, s, *C*H_2), 26.4 (4C, s, *C*H_2), 26.2 (2C, s, *C*H_2).

3·HO^{t}Bu. In a glovebox **3**·HPF_6 (20 mg, 0.05 mmol), KO^{t}Bu (6 mg, 0.06 mmol), and benzene-d_6 (0.6 mL) were placed in a Young NMR tube. The mixture was left to react for 2 h, and subsequently NMR spectra were recorded. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.08 (s, 1H, NC*H*N), 3.34 (2H, m, NC*H*), 2.75 (4H, m, NCH_2), 2.15 (2H, m, CH_2), 2.00 (2H, m, CH_2), 1.62−1.88 (12H, m, CH_2), 1.34 (9H, s, C(CH_3)$_3$), 1.32 (4H, m, CH_2), 1.10 (4H, m, CH_2).

Dioxolane Bisamine 7. A solution of (4*R*,5*R*)-(−)-diethyl 2,3-*O*-isopropylidene-L-tartrate (10 mmol) in dry toluene (30 mL) was placed in an acetone/dry ice bath, and a 1 M solution of DIBAL-H

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(20 mL) in toluene was added dropwise using a syringe over a period of 1 h under nitrogen. The resulting solution was stirred at −78 °C for 3 h. After completion of the reaction, cyclohexylamine (2.3 mL, 20 mmol) was added in one portion, and the reaction mixture was allowed to warm to room temperature while being stirred overnight. To the reaction mixture was slowly added 25 mL of water, and the mixture was stirred for 15 min. The precipitate formed was filtered off, and the filtrate was washed with water (3 × 20 mL) and brine (20 mL), dried over magnesium sulfate, filtered, and concentrated under reduced pressure to afford 3.2 g of an orange oil (99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (2H, m, N=C*H*), 4.28 (2H, m, OC*H*), 2.95 (2H, m, NC*H*), 1.49−1.75 (10H, m), 1.40 (6H, s, CH_3), 1.05−1.36 (10H, m). ^{13}C NMR (400 MHz, $CDCl_3$): δ 156.7 (2C, s, N=*C*H), 110.3 (1C, s, *C*Me$_2$), 79.1 (2C, s, *C*HO), 68.4 (2C, s, N*C*H), 32.9 (s), 31.9 (s), 25.8 (s), 24.4 (s), 23.5 (4C, s, *C*H$_2$). Without further purification, the crude diimine (3.2 g, 10 mmol) was dissolved in 25 mL of dry ethanol. Subsequently, sodium borohydride (750 mg, 20 mmol) was added in small portions over a period of 2 h. When the gas evolution had subsided, the reaction was stirred further for another hour. The residue obtained after evaporation of ethanol was dissolved in 100 mL of water and extracted with 3 × 25 mL of diethyl ether. The combined organic layers were washed with brine (25 mL), dried over magnesium sulfate, filtered, and concentrated under reduced pressure to afford 4.9 g of **7** as a white waxy solid (75.6%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.78 (2H, m, OC*H*), 2.74 (4H, m, NCH_2), 2.35 (2H, m, NC*H*), 1.81 (4H, m, CH_2), 1.66 (4H, m, CH_2), 1.55 (2H, m, CH_2), 1.32 (6H, s, CH_3), 1.18 (6H, m, CH_2), 1.01 (4H, m, CH_2). ^{13}C NMR (400 MHz, $CDCl_3$): δ 107.7 (1C, s, *C*Me$_2$), 81.0 (2C, s, *C*HO), 56.0 (2C, s, N*C*H), 48.5 (2C, s, N*C*H$_2$), 32.5 (s), 32.4 (s), 26.2 (s), 25.1 (s), 24.0 (4C, s, *C*H$_2$). MS (ES): *m*/*z* 325.2853 (MH^+; $C_{19}H_{37}N_2O_2$ requires 325.2855).

Diazepinium Salt 4·HBr. The dioxolane diamine **7** (500 mg, 1.54 mmol) was dissolved in methanol (30 mL) and treated with an aqueous formaldehyde solution (36.5%, 0.2 mL, 2.26 mmol). The reaction mixture was stirred at 50 °C in a pressure tube overnight. Evaporation of the solvent afforded **8** as a pale yellow oil (504 mg, 1.5 mmol) which was used without further purification in the next step. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95−1.25 (m, 10H), 1.32 (s, 6H), 1.55−1.85 (m, 10H), 2.45 (m, 2H), 2.55 (m, 2H), 3.15 (m, 2H), 3.55 (s, 1H), 3.88 (m, 2H). **8** (504 mg, 1.5 mmol) was dissolved in dimethoxyethane, and *N*-bromosuccinimide (274 mg, 1.54 mmol) was added in small portions at 0 °C. The reaction mixture was stirred for 3 h at room temperature. A pale yellow precipitate formed, which was filtered off, washed with hexane, and dried in vacuo to yield 100 mg (18%) of the bromide salt as a pale yellow powder. ^{1}H NMR (250 MHz, $CDCl_3$): δ 9.42 (1H, s, NC*H*N), 4.45 (2H, m, OC*H*), 3.74 (4H, m, NCH_2), 3.08 (2H, m, NC*H*), 2.10−1.40 (16H, m, CH_2), 1.40 (6H, s, CH_3), 1.05 (4H, m, CH_2). ^{13}C NMR (100 MHz, DEPT, $CDCl_3$): δ 157.3 (1C, s, N*C*HN), 113.3 (1C, s, *C*Me$_2$), 76.5 (2C, s, O*C*H), 69.4 (2C, s, N*C*H), 46.9 (2C, s, N*C*H$_2$), 31.0 (2C, s, *C*H$_2$), 30.9 (2C, s, *C*H$_2$), 26.8 (2C, s, *C*H$_3$), 25.0 (2C, s, *C*H$_2$), 24.93 (2C, s, *C*H$_2$), 24.88 (2C, s, *C*H$_2$). MS (ES): *m*/*z* 335.2704 (M − Br^+; $C_{20}H_{35}N_2O_2$ requires 335.2699).

Diazepinium Salt 4·HPF$_6$. The dioxolane diamine 7 (500 mg, 1.54 mmol), ammonium hexafluorophosphate (250 mg, 1.54 mmol), and triethyl orthoformate (0.5 mL, 3.1 mmol) were dissolved in 25 mL of DME. The reaction was heated to 90 °C and left running overnight. Subsequently, the volatiles were evaporated under reduced pressure, the slurry obtained was dissolved in chloroform (30 mL), and the insoluble impurities were filtered off. Evaporation of the solvent produced a yellow oil which was recrystallized from chloroform/diethyl ether (2:1) to afford 70 mg of white crystals (10%). ^{1}H NMR (250 MHz, $CDCl_3$): δ (1H, s, NC*H*N), (2H, m, OC*H*), (4H, m, NCH_2), (2H, m, NC*H*), (16H, m, CH_2), (6H, s, CH_3), (4H, m, CH_2).

4·HO^{t}Bu. In a glovebox 4·HBr (19 mg, 0.05 mmol), KO^{t}Bu (6 mg, 0.06 mmol), and benzene-d_6 (0.6 mL) were placed in a Young NMR tube. The mixture was left to react for 2 h, and subsequently NMR spectra were recorded, confirming quantitative conversion of **4**·HBr to the title compound. ^{1}H NMR (400 MHz, C_6D_6): δ 4.95 (1H, s, NC*H*N), 4.76 (1H, ddd, $^3J_{HH} \cong {}^3J_{HH} = 9.0$, $^3J_{HH} = 6.5$, OC*H*), 4.25 (1H, ddd, $^3J_{HH} \cong {}^3J_{HH} = 9.0$, $^3J_{HH} = 4.52$, OC*H*), 3.57 (1H, dd, $^2J_{HH} = 10.5$, $^3J_{HH} = 6.5$, NCH_2), 3.25 (2H, m, NCH_2), 3.00 (1H, dd, $^3J_{HH} \cong {}^2J_{HH} = 9.0$, NC$H_2$), 2.61 (2H, m, NC*H*), 2.07 (2H, dd, $^3J_{HH} \cong {}^3J_{HH} = 14.6$, C$H_2$), 1.96 (1H, d, $^3J_{HH} = 12.1$, CH_2), 1.89 (1H, d, $^3J_{HH} = 12.1$, CH_2), 1.79 (4H, m, CH_2), 1.67 (3H, s, OCCH_3), 1.64 (3H, s, OCCH_3), 1.61 (2H, d, $^3J_{HH} = 14.6$, CH_2), 1.30 (17H, m, C(CH_3)$_3$, CH_2), 1.05 (2H, m, $^3J_{HH} = 3.5$, CH_2). ^{13}C NMR (100 MHz, C_6D_6): δ 109.8 (1C, s, *C*Me$_2$), 100.4 (1C, s, *C*(CH$_3$)$_3$), 81.0 (1C, s, *C*HO), 80.1 (1C, s, *C*HO), 73.6 (1C, s, N*C*HN), 63.3 (1C, s, N*C*H), 62.5 (1C, s, N*C*H), 46.0 (1C, s, N*C*H$_2$), 43.8 (1C, s, N*C*H$_2$), 38.1 (1C, s), 33.0 (1C, s), 32.4 (1C, s), 32.3 (1C, s), 31.5 (1C, s), 29.3 (3C, s, C(*C*H$_3$)$_3$), 28.3 (1C, s), 28.0 (1C, s), 27.3 (1C, s), 27.1 (1C, s), 27.0 (1C, s), 26.8 (1C, s), 26.8 (1C, s).

Rh(cod)(3)Cl. KNSi(Me$_3$)$_2$ (140 mg, 0.7 mmol) and **3**·HPF$_6$ (285 mg, 0.7 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 another Schlenk tube containing a 10 mL thf solution of [Rh(cod)Cl]$_2$ (0.35 mmol). An immediate color change was observed from light to dark yellow. After the reaction was stirred at room temperature for 1 h, the volatiles were removed in vacuo. The yellow solid obtained was washed with hexane (2 × 20 mL) and dried. Crystals suitable for X-ray diffraction were obtained by layering a dichloromethane solution of the compound with hexane. Yield: 66% (0.200 g). Anal. Found (Calcd) for $C_{25}H_{42}ClRhN_2$: C, 58.87 (58.99); H, 8.37 (8.32). ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 6.18 (2H, dddd, $^3J_{HH} \cong {}^3J_{HH} = 11.5$, $^3J_{HH} \cong {}^3J_{HH} = 3.2$, NC*H*), 4.78 (2H, m, C$H_{cod}$), 3.34 (2H, m, NC$H_2$), 3.21 (2H, m, NC$H_2$), 3.17 (2H, m, C$H_{cod}$), 2.29 (6H, m, C$H_2$), 1.87 (2H, m, C$H_2$), 1.79 (10H, m, C$H_2$), 1.69 (4H, m, C$H_2$), 1.52 (6H, m, C$H_2$), 1.26 (2H, dddd, $^2J_{HH} \cong {}^3J_{HH} = 12.0$, $^3J_{HH} \cong {}^3J_{HH} = 3.7$, C$H_2$), 1.08 (2H, ddddd, $^2J_{HH} \cong {}^3J_{HH} = 13.0$, $^3J_{HH} \cong {}^3J_{HH} \cong {}^3J_{HH} = 3.8$, C$H_2$); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 215.3 (1C, d, $^1J_{Rh} = 43.7$, N*C*N), 93.9 (2C, d, $^1J_{Rh} = 6.8$, $C_{C=C}$), 66.8 (2C, d, $^1J_{Rh} = 5.4$, $C_{C=C}$), 65.8 (2C, s, N*C*H), 42.7 (2C, N*C*H$_2$), 31.8 (2C, s, *C*H$_2$), 31.2 (2C, s, *C*H$_2$), 30.3 (2C, s, *C*H$_2$), 27.9 (2C, s, *C*H$_2$), 25.6 (2C, s, *C*H$_2$), 25.3 (2C, s, *C*H$_2$), 24.9 (4C, s, *C*H$_2$). MS (ES, MeCN): *m*/*z* 473.2382 (M − Cl^+; $C_{25}H_{42}N_2Rh$ requires 473.2403), 514.2619 (M + MeCN − Cl^+).

Rh(CO)$_2$(3)Cl. Carbon monoxide was slowly bubbled for 30 min through a solution of Rh(cod)(3)Cl (100 mg, 0.075 mmol) in dichloromethane (10 mL). A color change from yellow to pale yellow was observed during the reaction. The volatiles were removed under reduced pressure, and the obtained solid was washed with cold hexane (2 × 30 mL) and dried. Yield: 84% (0.065 g). Anal. Found (Calcd) for $C_{19}H_{30}ClRhN_2O_2$: C, 50.06 (49.96); H, 6.61 (6.62). ^{1}H NMR (toluene-d_8, 500 MHz, 298 K): δ 5.34 (2H, dddd, $^3J_{HH} \cong {}^3J_{HH} = 11.9$, $^3J_{HH} \cong {}^3J_{HH} = 3.4$, NC*H*), 2.91 (4H, m, NCH_2), 2.30 (2H, m, CH_2), 1.68 (6H, m, CH_2), 1.55 (4H, m, CH_2), 1.40 (6H, m, CH_2), 1.16 (2H, dddd, $^2J_{HH} \cong {}^3J_{HH} = 12.2$, $^3J_{HH} \cong {}^3J_{HH} = 3.5$, C$H_2$), 1.08 (2H, dddd, $^2J_{HH} \cong {}^3J_{HH} = 12.1$, $^3J_{HH} \cong {}^3J_{HH} = 3.7$, C$H_2$), 0.91 (2H, ddddd, $^2J_{HH} \cong {}^3J_{HH} = 13.1$, $^3J_{HH} \cong {}^3J_{HH} \cong {}^3J_{HH} = 3.6$, C$H_2$). ^{13}C NMR (toluene-$d_8$, 125 MHz, 298 K): δ 206.2 (1C, d, $^1J_{Rh} = 37.7$, N*C*N), 188.2 (1C, d, $^1J_{Rh} = 54.1$, *C*O), 184.9 (1C, d, $^1J_{Rh} = 75.5$, *C*O), 67.6 (2C, s, N*C*H), 44.1 (2C, N*C*H$_2$), 30.8 (2C, s, *C*H$_2$), 30.1 (2C, s, *C*H$_2$), 26.1 (2C, s, *C*H$_2$), 25.8 (2C, s, *C*H$_2$), 25.7 (4C, s, *C*H$_2$). MS (ES, CH_3CN): *m*/*z* 462.1648 (M − Cl^+; $C_{19}H_{30}N_2O_2Rh$ requires 462.1628).

Ir(cod)(3)Cl. KNSi(Me$_3$)$_2$ (0.200 g, 1.0 mmol) and **3**·HPF$_6$ (0.408 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 10 mL thf solution of $[Ir(cod)Cl]_2$ (0.336 g, 0.5 mmol); an immediate color 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 hexane and dried under vacuum to afford 450 mg of a brown solid. The product was purified by chromatography on silica gel with dichloromethane as the mobile phase. The product was eluted as a yellow band in the first fraction ($R_f = 0.6$). The product fractions were pooled and evaporated to dryness to yield a yellow solid. Crystals suitable for X-ray diffraction were obtained by layering hexane on a dichloromethane solution of the compound. Yield: 62% (370 mg). Anal. Found (Calcd) for $C_{25}H_{42}ClIrN_2$: C, 49.91 (50.19); H, 7.01 (7.08). ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 5.74 (2H, dddd, $^3J_{HH} \cong {}^3J_{HH} = 11.4$, $^3J_{HH} \cong {}^3J_{HH} = 3.1$, NC*H*), 4.33 (2H, m, C$H_{cod}$), 3.39 (2H, m, NC$H_2$), 3.26 (2H, m, NC$H_2$), 2.86 (2H, m, C$H_{cod}$), 2.11 (6H, m, C$H_2$), 1.3 − 1.9 (20H, m, C$H_2$), 1.27 (4H, m, C$H_2$), 1.03 (2H, m, C$H_2$). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 208.3 (1C, s, N*C*N), 78.4 (2C, s, $C_{C=C}$), 65.3 (2C, s, $C_{C=C}$), 50.6 (2C, s, N*C*H), 43.4 (2C, N*C*H$_2$), 32.5 (2C, s, *C*H$_2$), 31.3 (2C, s, *C*H$_2$), 30.2 (2C, s, *C*H$_2$), 28.5 (2C, s, *C*H$_2$), 25.5 (2C, s, *C*H$_2$), 25.1 (2C, s, *C*H$_2$), 24.8 (4C, s, *C*H$_2$). MS (ES, CH_3CN): *m*/*z* 488.1728 (M − cod$^+$; $C_{17}H_{30}N_2{}^{191}Ir^{35}Cl$ requires 488.1704), 561.2658 (M − Cl$^+$).

Ir(CO)$_2$(3)Cl. Ir(cod)(**3**)Cl (100 mg, 0.17 mmol) was placed in a round-bottom flask, and subsequently, 10 mL of dichloromethane was added. Into the yellow solution carbon monoxide was bubbled for 30 min, after which the color changed to light yellow, the volatiles were subsequently removed under reduced pressure, and the crude solid was washed with cold hexane. Yield: 82% (78 mg). Anal. Found (Calcd) for $C_{17}H_{30}ClN_2O_2Ir$: C, 41.62 (41.79); H, 5.46 (5.54). ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 5.11 (2H, m, NC*H*), 3.39 (4H, m, NCH_2), 1.99 (2H, m, CH_2), 1.89 (2H, m, CH_2), 1.76 (6H, m, CH_2), 1.69 (2H, m, CH_2), 1.59 (2H, m, CH_2), 1.34 (8H, m, CH_2), 1.02 (2H, m, CH_2). ^{1}H NMR (toluene-d_8, 500 MHz, 298 K): δ 5.18 (2H, dddd, $^3J_{HH} \cong {}^3J_{HH} = 11.6$, $^3J_{HH} \cong {}^3J_{HH} = 3.5$, NC*H*), 2.63 (4H, m, NCH_2), 1.96 (2H, m, CH_2), 1.53 (2H, m, CH_2), 1.44 (4H, m, CH_2), 1.39 (4H, m, CH_2), 1.14 (6H, m, CH_2), 0.93 (2H, m, CH_2), 0.89 (2H, m, CH_2), 0.65 (2H, m, CH_2). ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ 199.8 (1C, s, N*C*N), 180.2 (1C, s, *C*O), 168.2 (1C, s, *C*O), 66.1 (2C, s, N*C*H), 44.0 (2C, N*C*H$_2$), 30.6 (2C, s, *C*H$_2$), 29.8 (2C, s, *C*H$_2$), 29.0 (2C, s, *C*H$_2$), 24.7 (2C, s, *C*H$_2$), 24.5 (2C, s, *C*H$_2$), 24.4 (2C, s, *C*H$_2$). ^{13}C NMR (toluene-d_8, 125 MHz, 298 K): δ 200.5 (1C, s, N*C*N), 180.8 (1C, s, *C*O), 169.2 (1C, s, *C*O), 65.9 (2C, s, N*C*H), 43.4 (2C, N*C*H$_2$), 29.6 (2C, s, *C*H$_2$), 28.8 (2C, s, *C*H$_2$), 24.6 (2C, s, *C*H$_2$), 24.4 (2C, s, *C*H$_2$), 24.3 (2C, s, *C*H$_2$), 24.2 (2C, s, *C*H$_2$). MS (ES, CH_3CN): *m*/*z* 488.1728 (M − 2CO$^+$; $C_{17}H_{30}N_2{}^{191}Ir^{35}Cl$ requires 488.1704).

Ir(cod)(4)Br. LiN(^{i}Pr)$_2$ (6 mg, 0.05 mmol) and **4**·HBr (19 mg, 0.05 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 another Schlenk tube containing a 10 mL thf solution of $[Ir(cod)Cl]_2$ (17 mg, 0.025 mmol). After the reaction was stirred at room temperature for 1 h, the volatiles were removed in vacuo. The yellow solid obtained was washed with hexane (2 × 20 mL) and dried. Crystals suitable for X-ray diffraction were obtained by layering a dichloromethane solution of the complex with hexane. ^{1}H NMR (400 MHz, C_6D_6): δ 6.37 (1H, dddd, $^3J_{HH} \cong {}^3J_{HH} = 12.1$, $^3J_{HH} \cong {}^3J_{HH} = 3.1$, NC*H*), 6.09 (1H, dddd, $^3J_{HH} \cong {}^3J_{HH} = 11.5$, $^3J_{HH} \cong {}^3J_{HH} = 3.5$, NC*H*), 5.16 (1H, ddd, $^3J_{HH} \cong {}^3J_{HH} = 8.0$, $^3J_{HH} = 3.0$, OC*H*), 5.01 (1H, ddd, $^3J_{HH} \cong {}^3J_{HH} = 8.0$, $^3J_{HH} = 5.1$, OC*H*), 3.58 (2H, ddd, $^3J_{HH} = 13.1$, $^3J_{HH} = 6.0$, $^3J_{HH} = 3.5$), 3.39 (1H, ddd, $^3J_{HH} = 11.0$, $^3J_{HH} = 8.5$, $^3J_{HH} = 3.0$), 3.27 (1H, ddd, $^3J_{HH} = 11.0$, $^3J_{HH} = 8.5$, $^3J_{HH} = 3.0$), 3.17 (1H, ddd, $^3J_{HH} \cong {}^3J_{HH} = 7.0$, $^3J_{HH} = 2.0$), 3.07 (1H, m), 3.00 (1H, m), 2.53 (1H, m), 2.37 (2H, m), 2.30 − 1.30 (33H, m). ^{13}C NMR (100 MHz, C_6D_6): δ 223.6 (1C, s, N*C*HN), 113.6 (1C, s,

Table 4. Crystal Data and Refinement Results for All Samples

	3·HPF$_6$	**4**·HPF$_6$	Rh(COD)(**3**)Cl	Ir(COD)(**3**)Cl	Ir(CO)$_2$(**3**)Cl	Ir(COD)(**4**)Br	Pt(nbe)$_2$(**3**)
empirical formula	$C_{17}H_{31}F_6N_2P$	$C_{20}H_{35}F_6N_2O_2P$	$C_{25}H_{42}ClN_2Rh$	$C_{25}H_{42}ClIrN_2$	$C_{19}H_{30}ClIrN_2O_2$	$C_{28.75}H_{47.75}BrIrN_2O_2$	$C_{31}H_{50}N_2Pt$
fw	408.41	480.47	508.97	598.26	546.10	725.55	645.82
cryst syst, space group	monoclinic, $P2_1/c$	monoclinic, $P2_1$	monoclinic $P2_1/c$	monoclinic $P2_1/c$	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$	orthorhombic, *Pbcn*
a/Å	10.8504(3)	10.2267(4)	13.075(3)	13.0652(2)	9.274(5)	20.584(4)	11.7981(3)
b/Å	9.7539(4)	14.7526(7)	11.031(2)	11.0159(2)	16.763(5)	12.814(3)	11.0902(2)
c/Å	18.4811(5)	15.9420(7)	16.955	16.9846(3)	13.187(5)	27.659(6)	21.1619(5)
α/deg	90	90	90	90	90	90	90
β/deg	95.123(2)	91.736(2)	102.86(3)	102.660(1)	91.532(5)	109.39(3)	90
γ/deg	90	90	90	90	90	90	90
vol/Å^3	1948.11(11)	2404.07(18)	2383.9(8)	2385.1(1)	2049.3(15)	6882(2)	2768.89(11)
Z, calcd density/Mg m^{-3}	4, 1.392	4, 1.327	4, 1.418	4, 1.666	4, 1.770	8, 1.401	4, 1.549
abs coeff/mm^{-1}	0.200	0.179	0.842	5.724	6.660	5.064	5.089
F(000)	864	1016	1072	1200	1072	2898	1312
cryst description	colorless slab	colorless slab		yellow rhombus			colorless plate
cryst dimensions/mm^3	0.40 × 0.36 × 0.16	0.40 × 0.26 × 0.10	0.45 × 0.30 × 0.22	0.42 × 0.12 × 0.08	0.25 × 0.20 × 0.20	0.25 × 0.20 × 0.08	0.14 × 0.12 × 0.04
θ range/deg	3.04−27.48	4.85−27.48	3.08−27.0 0	3.08−27.50	3.28−27.0 0	2.94−25.50	3.17−27.48
no. of reflns collected/unique	21673/4452	31833/22144	9619/5169	29089/5459	8708/4447	53504/25075	21679/3173
R_{int}	0.0401	0.0644	0.0290	0.0240	0.0234	0.0950	0.0354
no. of data/restraints/params	4452/0/236	22144/562/693	5169/0/262	5459/0/262	4447/0/227	25075/19/1233	3173/0/155
final *R* indices [$F^2 > 2\sigma(F^2)$]: R1, wR2	0.0404, 0.0908	0.0879, 0.1949	0.0316, 0.0689	0.0216, 0.0500	0.0228, 0.0564	0.0563, 0.1389	0.0224, 0.0451
R indices (all data): R1, wR2	0.0640, 0.1018	0.2011, 0.2674	0.0404, 0.0726	0.0258, 0.0516	0.0242, 0.0571	0.0705, 0.1466	0.0326, 0.0490
largest diff peak and hole/e Å^{-3}	0.484, −0.419	0.429, −0.399	0.947, −0.550	0.859, −1.225	0.768, −0.878	1.048, −1.677	0.985, −0.985

CMe_2), 82.1 (1C, $C_{C=C}$), 81.1 (1C, $C_{C=C}$), 80.6 (1C, $C_{C=C}$), 79.9 (1C, $C_{C=C}$), 66.3 (1C, O*C*H), 68.2 (1C, s, O*C*H), 54.3 (1C, s), 50.8 (1C, s), 47.9 (1C, s), 46.9 (1C, s), 46.7 (1C, s), 35.3 (1C, s), 33.4 (2C, s), 33.0 (1C, s), 32.1 (1C, s), 31.7 (1C, s), 30.0 (1C, s), 29.1 (1C, s), 27.4 (1C, s), 27.3 (1C, s), 27.0 (1C, s), 26.8 (1C, s), 26.5 (2C), 26.2 (1C, s), 26.1 (1C, s). MS (ES, CH_3CN): *m*/*z* 676.3452 ($M + CH_3CN - Br^+$; $C_{30}H_{49}N_3O_2$ requires 676.3454).

Pt(nbe)$_2$(3). $KNSi(Me_3)_2$ (10 mg, 0.05 mmol) and **3**·HPF_6 (20 mg, 0.05 mmol) were placed into a flamed Schlenk tube followed by addition of diethyl ether (5 mL). The solution was stirred for 30 min and subsequently filtered into another Schlenk tube containing a 4 mL thf solution of platinum tris(norbornene) (23 mg, 0.05 mmol). After the reaction mixture was stirred at room temperature for 1 h, the volatiles were removed in vacuo. The residue was dissolved in dry hexane and filtered through a cannula, fitted with a glass filter paper, to another Schlenk tube. Crystals of the title compound were grown after the hexane solution was allowed to stand in the fridge for 2 days. Yield: 82% (32 mg). ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 4.43 (2H, br, NC*H*), 3.05 (2H, br, nbe), 2.93 (4H, br, NCH_2), 2.70 (2H, br, nbe), 2.25 (2H, br, nbe), 2.0 − 1.0 (30H, br), 0.80 (4H, br, nbe), 0.32 (2H, br, nbe), 0.15 (2H, br, nbe). ^{13}C NMR (C_6D_6, 100 MHz, 298 K): δ 64.2 (br), 55.2 (br), 45.2 (br), 43.9 (br), 30.6−33.5 (br), 26.2 (br).

X-ray Crystallography. Suitable crystals were selected, and data for **3**·HPF_6, **4**·HPF_6, Ir(COD)(**3**)Cl, Rh(COD)(**3**)Cl, Ir(COD)(**4**)Br, $Ir(CO)_2$(**3**)Cl, and Pt(nbe)$_2$(**3**) were measured on a Bruker Nonius KappaCCD area detector at the window of a Bruker Nonius FR591 rotating anode ($\lambda_{Mo\,K\alpha}$ = 0.71073 Å) driven by COLLECT[32] and processed by DENZO[33] software at 120 K. The structures were determined in SHELXS-97 and refined using SHELXL-97.[34] Crystal data and refinement results for all samples are collated in Table 4. Crystallographic data for all compounds have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 642719−642725. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Rd., Cambridge CB2 1EZ, U.K. (fax (+44) 1223 336033, e-mail deposit@ccdc.cam.ac.uk).

Acknowledgment. We thank the EPSRC for funding, including that for the National Crystallography Service, Johnson Matthey plc for the loan of hydrated $RhCl_3$, and Dr. Niek Buurma from Cardiff University for help with the kinetic measurements.

Supporting Information Available: X-ray crystallographic data as CIF files for the compounds **3**·HPF_6, **4**·HPF_6, Rh(COD)(**3**)Cl, Ir(COD)(**3**)Cl, Ir(COD)(**4**)Br, $Ir(CO)_2$(**3**)Cl, and Pt(nbe)$_2$(**3**), tables and figures giving rate constants and an Eyring plot associated with the variable-temperature proton measurements, and figures showing infrared and NMR spectra and the variable-temperature proton measurements for Ir(COD)(**3**)Cl. This material is available free of charge via the Internet at http://pubs.acs.org.

OM7004904

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