Bis(imino)carbazolide Complexes of Rhodium: Highly Nucleophilic Ligands Exerting a Dramatic Accelerating Effect on MeI Oxidative Addition

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Rhodium(I) complexes bearing a bis(imino)carbazolide ligand L and an additional neutral donor [LRh(C_2H_4), **2**; LRh(CO), **3**] have been prepared via a salt metathesis reaction between NaL and the dimeric rhodium precursors $[RhCl(C_2H_4)_2]_2$ and $[RhCl(CO)_2]_2$, respectively. Complex **3** was also prepared by reaction of the free ligand with $[RhCl(CO)_2]_2$, whereas a related reaction with $[RhCl(C_2H_4)_2]_2$ afforded the dinuclear Rh^I-Rh^{III} ethyl complex **4**. The X-ray crystal structure of **4** showed octahedral [bis(imino)carbazolide]Rh^{III}(Cl)Et linked to square-planar bis(ethylene)Rh^ICl via chloride bridges. Kinetic studies on the oxidative addition of MeI to **3** to form the LRh^{III}I(CO)Me complex **5** revealed a second-order rate constant of 1.66 M^{-1} s^{-1} in CH_2Cl_2 at 25 °C, which corresponds to a reaction rate approximately 50 000 times faster than that observed for $[RhI_2(CO)_2]^-$.

Introduction

The past 15−20 years have witnessed a growing understanding of the steric and electronic factors that influence the rates of key steps in homogeneous catalytic cycles. In the field of olefin polymerization, metal complexes with a coordinatively unsaturated Lewis acidic metal center are generally required,[1,2] whereas for transformations such as the carbonylation of methanol, electron-rich metal centers are necessary to favor oxidative addition of MeI to Rh^I.[3−6] In a recent study of MeI addition to rhodium complexes containing α-diimine ligands, it has been shown that RhI(CO)(2,2′-bipy) reacts with MeI ca. 7000 times faster than the carbonylation catalyst, $[RhI_2(CO)_2]^-$, but rates are moderated by introduction of bulky substituents on the diimine ligands.[7] A way of further increasing the nucleophilicity of the metal center is to replace the soft iodide ligand by a harder anionic nitrogen donor. We have recently described the synthesis of 1,8-bis(imino)carbazoles,[8,9] planar conjugated analogues of bis(imino)pyridines, where the central pyridine donor is replaced by the negatively charged N-carbazolide donor. Here we describe the synthesis of a series of bis(imino)carbazolide complexes of Rh^I and the effect of this highly nucleophilic ligand on the MeI oxidative addition reaction.

Results and Discussion

Synthesis and Characterization of Rh Complexes. The Rh^I complexes **2** and **3** were prepared using the bis(phenylimino)carbazole **1**[9] and the dimeric metal precursors $[RhCl(C_2H_4)_2]_2$ and $[RhCl(CO)_2]_2$. In a manner similar to the synthesis of bis(imino)carbazolide complexes of cobalt and iron described previously,[8] the rhodium complexes **2** and **3** were obtained in good yields via treatment of $[RhCl(C_2H_4)_2]_2$ or $[RhCl(CO)_2]_2$ with the in situ generated sodium salt derived from **1** (Scheme 1). The carbonyl derivative **3** can also be accessed by direct reaction of **1** with $[RhCl(CO)_2]_2$ at room temperature. A related reaction was observed by Siegl in the synthesis of [1,3-bis(2-pyridyilimino)isoindoline]Rh(CO), although here DABCO was employed as an external base.[10]

1 also reacted directly with $[RhCl(C_2H_4)_2]_2$, but the reaction was much slower. Monitoring the reaction by NMR spectroscopy revealed complete conversion to a new species after several hours at 70 °C in C_6D_6 solution. When the reaction was carried out on a preparative scale, a deep red, air-stable solid was isolated which, according to ^1H NMR, ^{13}C NMR, IR, and FAB-mass spectroscopy as well as elemental and crystal structure analysis, is the mixed valence dinuclear complex **4**. Prolonged heating of a C_6D_6 solution of **4** at 70 °C in an NMR tube resulted in decomposition of the complex; formation of a Rh-mirror on the walls of the

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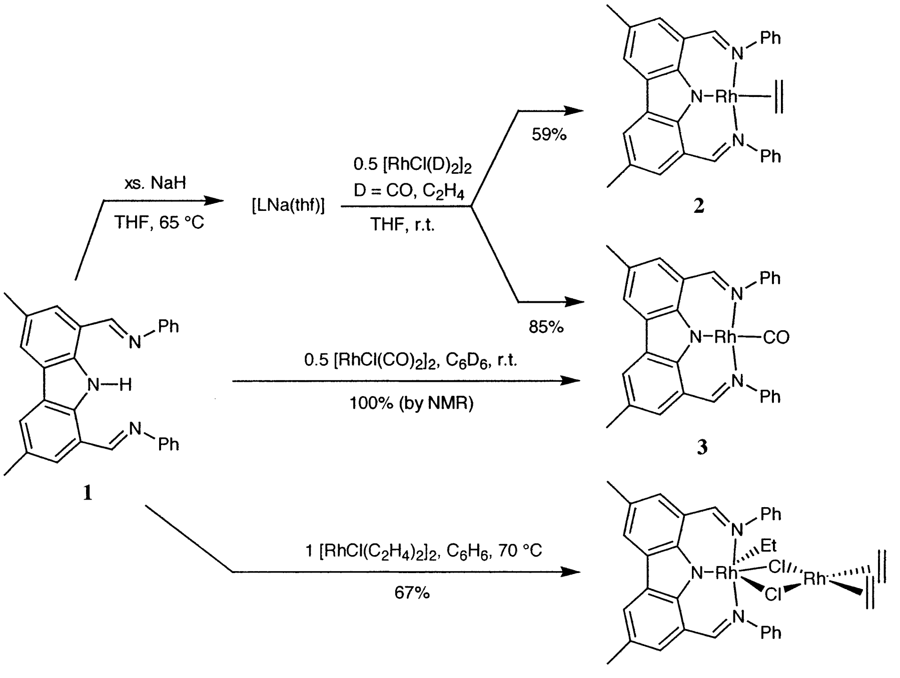
Scheme 1. Synthesis of the Bis(imino)carbazole Rh Complexes 2−4



NMR tube and the appearance of signals corresponding to free ethylene (5.24 ppm)[11] were observed.

Complexes **2**−**4** are air stable, but **2** and **3** were found to react with chlorinated solvents such as CD_2Cl_2, the ethylene adduct **2** being considerably more reactive than **3**. For a number of square-planar Rh^I complexes, oxidative addition of CH_2Cl_2 has been reported, and the resulting Rh^{III} chloroalkyl has, in some cases, been isolated and structurally characterized.[12−15] A similar reaction may occur for complexes **2** and **3** with CD_2Cl_2, but these products could not be isolated. Both complexes are believed to adopt a square-planar geometry typically observed for four-coordinate Rh^I complexes, with the C_2H_4 or CO ligand *trans* to the central anionic donor of the carbazolide ligand.[16−18] Similar ligand arrangements have also been observed for structurally characterized Rh^I complexes bearing monoanionic, tridentate [PNP] ligands with one additional phosphine or CO donor.[19] The absorption band for the bound CO in **3** was observed at 1980 cm^{-1}, which lies at the upper end of values typically observed for $Rh^I(CO)$ complexes bearing monoanionic ligands such as $[(P^iPr_2CH_2SiMe_2)_2N]$[19] (1932 cm^{-1}), $[(PPh_2CH_2SiMe_2)_2N]$[20,21] (1950 cm^{-1}), $[(P^tBu_2CH_2)_2C_6H_3]$[22] (1925 cm^{-1}), $[(PMe_2CH_2)_2C_6H_3]$[23] (1944 cm^{-1}), and 1,3-bis(2-pyridylimino)isoindoline[10] ligands (1936−1972 cm^{-1}). This suggests that the carbazolide donor is the weakest in this series of anionic carbon- and nitrogen-based donors; however, the additional phosphine and pyridine donors in these ligands will also strongly influence the electron density at the metal center and hence the CO stretching frequency.

^1H NMR spectra of **2** and **3** both gave doublet resonances for the aldimine hydrogens, with coupling to ^{103}Rh ($^3J(RhH) \approx 3.1$ Hz), confirming that both imino “arms” are bound to the Rh center.[13] The coordinated ethylene in **2** gave rise to a doublet resonance at 3.11 ppm ($^2J(RhH) = 1.6$ Hz), which is in the range typically observed for square-planar Rh^I ethylene complexes bearing neutral[24−27] and anionic[21,28] tridentate ligands. In the ^{13}C NMR spectrum of **2** a doublet signal at 54.0 ppm was observed for the bound ethylene ligand, with a typical value for the $^1J(RhC)$ coupling constant of 14.5 Hz.[24−27]

Whereas the CO donor in **3** is firmly bound to the metal center and cannot be displaced with other donors such as CH_3CN, formation of 1 equiv of free ethylene

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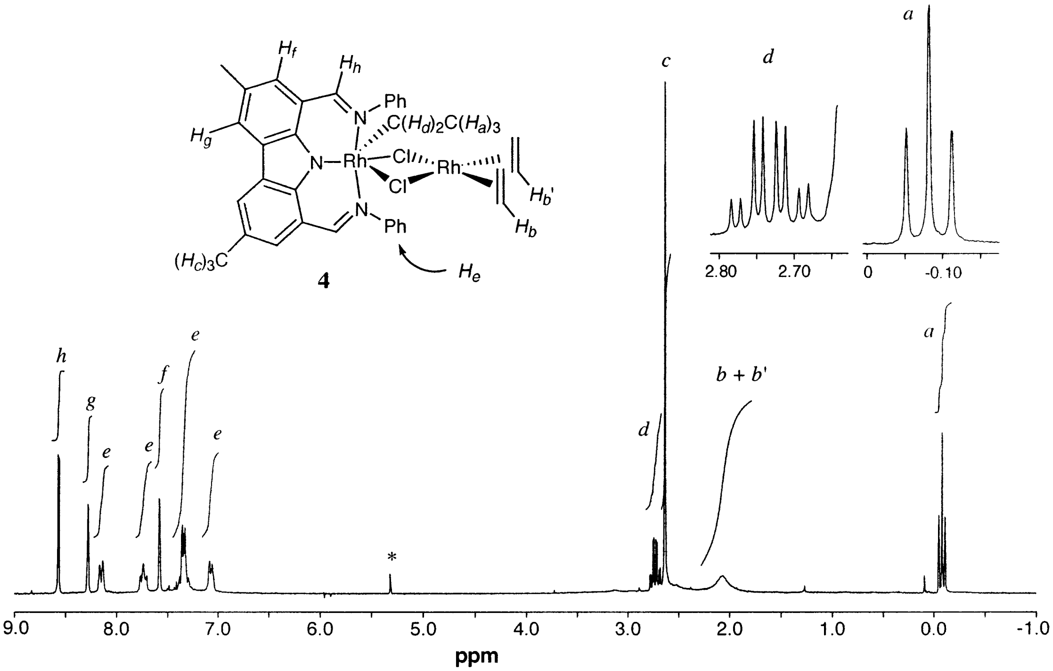

Figure 1. ^{1}H NMR spectrum of the mixed valence Rh complex **4** in CD_2Cl_2 (*).

was observed upon dissolution of **2** in CD_3CN. The Rh^I center remained bound to the carbazolide ligand, as indicated by the doublet at 8.90 ppm (^3J(RhH) = 3.0 Hz) attributable to the aldimine protons. These observations point toward the formation of a [bis(imino)-carbazolide]$Rh^I(CD_3CN)$ complex by displacement of ethylene. Furthermore, when the synthesis of **2** was carried out under an atmosphere of N_2 rather than ethylene, a mixture of products was obtained in the ratio 4:1. The major product is the ethylene adduct **2**, as shown by the doublet for the aldimine protons at 8.50 ppm. The minor product is also a bis(imino)carbazolide Rh complex, as indicated by the doublet at 8.85 ppm (^3J(RhH) = 2.9 Hz) for the aldimine protons. Addition of ethylene to the reaction mixture leads to the immediate disappearance of the signals corresponding to the minor product, and **2** is formed exclusively. Attempts to remove ethylene from **2** by heating the complex as a solid under oil-pump vacuum at 50 °C for 1 h were unsuccessful, and the starting material was recovered. These observations are consistent with the minor side product being either a three-coordinate bis(imino)-carbazolide Rh^I species or a four-coordinate $Rh^I(N_2)$ complex. Both types of complexes have previously been observed with other tridentate ligands.[15,29]

The ^{1}H NMR spectrum of **4** is shown in Figure 1. The presence of a bis(imino)carbazolide Rh species was again indicated by the doublet resonance at 8.57 ppm (^3J(RhH) = 2.5 Hz) for the aldimine proton H_h. The Rh-bound ethyl group gave rise to a triplet signal at −0.09 ppm for the CH_3 group H_a and a quartet resonance at 2.72 ppm for the methylene group H_d. The latter signal was further split into doublets due to Rh-coupling (^2J(RhH) = 3.1 Hz). The chemical shift and ^2J(RhH) coupling constant for the Rh−CH_2 group were within the range typically observed for Rh-ethyl complexes, but the signal for the ethyl-CH_3 group was located slightly upfield from the usual range of 0.28−1.32 ppm.[30−36] Anisotropic effects due to the ring-current arising from carbazole π-electrons are likely to be responsible for the observed upfield shift. (See also molecular structure of **4** in Figure 2.)

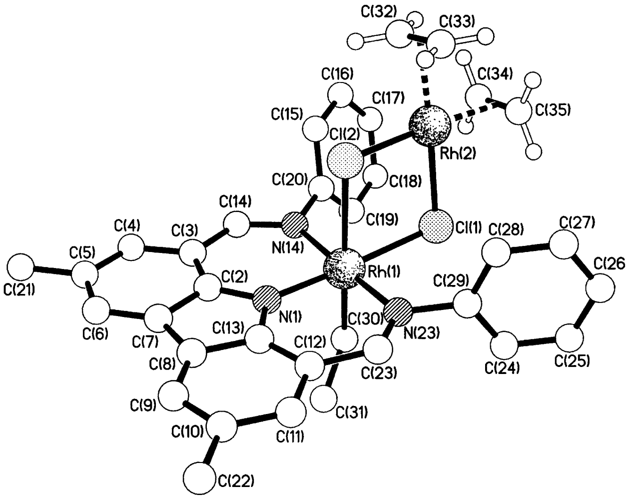

Figure 2. Molecular structure of one of the two crystallographically independent molecules present in the crystals of the mixed valence rhodium complex **4**.

The signal for the two bound ethylene molecules (protons H_b and $H_{b'}$) appeared as a broad singlet at 2.06

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Two Crystallographically Independent Molecules (A and B) Present in the Crystals of 4[a]

	mol. A	mol. B		mol. A	mol. B
Rh(1)−Cl(1)	2.418(2)	2.409(2)	Rh(1)−Cl(2)	2.658(2)	2.654(2)
Rh(1)−N(1)	1.976(7)	1.966(6)	Rh(1)−N(14)	2.083(8)	2.076(7)
Rh(1)−N(23)	2.058(8)	2.052(7)	Rh(1)−C(30)	2.050(14)	2.051(9)
Rh(2)−Cl(1)	2.390(2)	2.379(2)	Rh(2)−Cl(2)	2.384(2)	2.375(2)
Rh(2)−X(1)	1.997(14)	2.01(3)	Rh(2)−X(2)	2.003(14)	2.00(2)
C(14)−N(14)	1.319(13)	1.286(11)	C(23)−N(23)	1.293(12)	1.310(11)
N(1)−Rh(1)−C(30)	90.7(6)	91.4(3)	N(1)−Rh(1)−N(23)	89.3(3)	89.9(3)
C(30)−Rh(1)−N(23)	96.2(8)	88.4(4)	N(1)−Rh(1)−N(14)	90.8(3)	90.1(3)
C(30)−Rh(1)−N(14)	86.0(8)	92.9(4)	N(23)−Rh(1)−N(14)	177.8(3)	178.7(3)
N(1)−Rh(1)−Cl(1)	175.4(2)	173.8(2)	C(30)−Rh(1)−Cl(1)	93.9(5)	94.7(3)
N(23)−Rh(1)−Cl(1)	89.6(2)	89.1(2)	N(14)−Rh(1)−Cl(1)	90.1(2)	90.8(2)
N(1)−Rh(1)−Cl(2)	94.1(2)	92.2(2)	C(30)−Rh(1)−Cl(2)	172.1(5)	176.0(3)
N(23)−Rh(1)−Cl(2)	90.2(2)	89.7(2)	N(14)−Rh(1)−Cl(2)	87.6(2)	89.0(2)
Cl(1)−Rh(1)−Cl(2)	81.51(7)	81.64(7)	Cl(2)−Rh(2)−Cl(1)	88.07(7)	88.42(7)
X(1)−Rh(2)−X(2)	94.2(6)	92(2)	X(1)−Rh(2)−Cl(2)	89.2(6)	91(2)
X(2)−Rh(2)−Cl(2)	176.1(6)	176.4(7)	X(1)−Rh(2)−Cl(1)	177.0(6)	169(2)
X(2)−Rh(2)−Cl(1)	88.6(6)	89.0(7)	Rh(2)−Cl(1)−Rh(1)	97.66(7)	97.78(7)
Rh(2)−Cl(2)−Rh(1)	91.59(7)	91.50(7)			

[a] X(1) and X(2) are the centroids of the C(32)−C(33) and C(34)−C(35) bonds, respectively.

ppm, indicating rotation of the ethylene unit on the time scale of the ^{1}H NMR experiment. In the ^{13}C NMR spectrum, the signal for the ethylene carbons was well resolved and two doublets, at 59.3 and 60.2 ppm (^{1}J(RhC) = 13.4 and 13.0 Hz), were observed. The doublet for the methylene carbon at 18.0 ppm showed, as expected, a larger ^{1}J(RhC) coupling constant of 22.6 Hz. The reduction in symmetry from C_{2v} in the free ligand **1** to C_s in complex **4** and the hindered rotation about the N−phenyl bonds resulted in the observation of individual signals for each proton (H_e) and carbon of the imino-phenyl substituent.

Crystals of **4** suitable for X-ray analysis were grown from a concentrated solution mixture of benzene, diethyl ether, and pentane after prolonged standing at ambient temperature. The molecular structure (Figure 2) shows the presence of a chloride-bridged Rh^{III}−Rh^{I} dimer. Rh complexes with mixed valence structures of this type are quite unusual, and only a few examples bearing (PPh$_2$CH$_2$)$_2$C$_6$H$_3$,[37] benzoquinoline,[38] phenylbenzylamine,[39] and phenylazophenyl[40] ligands on the Rh^{III} center have been reported. There are two crystallographically independent molecules in the unit cell in the molecular structure of **4**. Both molecules exhibit slight disorder, there being alternate orientations of the ethyl group (70:30) in one molecule and of one of the ethylene groups (60:40) in the other.

The trivalent Rh(1) center has a slightly distorted octahedral coordination geometry with the bridging chlorides *trans* to the amido and ethyl groups. The ethyl group is pointing away toward the carbazole backbone, possibly as a result of unfavorable steric interactions with the phenyl-imino substituents. This conformation is likely to prevail in solution, as shown by the unusual upfield resonance for the ethyl-CH$_3$ group in the ^{1}H NMR spectrum of Figure 1. There are very few examples of structurally characterized Rh^{III} ethyl complexes, and the Rh−C bond lengths in these complexes lie in the range 1.991−2.107 Å, which corresponds well with the value of ca. 2.05 Å observed in **4**.[25,33−36,41−43] The short Rh−N bond to the amido nitrogen of ca. 1.97 Å may be indicative of the significant σ/π-donor capability of the carbazolide ligand. Another contributing factor may be the chelating effect of the pendant imino donors, drawing the metal center closer toward the carbazolide donor. There are no examples of structurally characterized carbazolide Rh complexes; one Rh^{III} complex bearing a imino-pyrrolide ligand has been reported recently by Brunner et al. and has a Rh−N(pyrrolide) bond length of 2.068 Å,[44] which is considerably longer than the Rh−N(carbazolide) bond in **4** and closer to the values of 2.01−2.03 Å typically obtained for Rh^{III} porphyrin complexes.[45−50] With the exception of the two phenyl substituents, the carbazolide ligand is planar to within ca. 0.07 Å, the rhodium atom lying within this plane. The two phenyl rings are steeply inclined to this plane, the torsional twists about the N(14)−C(20) and N(23)−C(29) bonds being ca. 73° and 88° respectively. In both molecules the two bridging chloride ligands are bonded to Rh(1) asymmetrically with Rh(1)−Cl(1) ca. 0.24 Å shorter than Rh(1)−Cl(2), the longer bond to Cl(2) reflecting the stronger *trans*-influence of the ethyl group compared to the carbazole amido donor. This asymmetry is also observed in the binuclear, chloride-bridged Rh^{III}−Rh^{I} complexes bearing the (PPh$_2$CH$_2$)$_2$C$_6$H$_3$ ligand.[37] The Rh(μ-Cl)$_2$Rh unit is markedly nonplanar, with a dihedral angle between the normals to the planes defined by {Rh(1), Cl(1), Cl(2)} and {Rh(2), Cl(1), Cl(2)} being ca. 11° and 8°, respectively, in the two

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independent molecules. In both molecules Rh(2) is displaced toward C(16) and away from C(27). Folded Rh(μ-Cl)$_2$Rh are also found in the aforementioned mixed valence complexes[37−40] as well as in a variety of Rh^{I} dimers such as [RhCl(CO)$_2$]$_2$,[51] Rh$_2$Cl$_2$(CO)$_2$(cod),[52] and [RhCl(PMe$_2$Ph)(CO)]$_2$.[53] According to a recent theoretical and structural analysis of square-planar complexes of the general formula L$_2$M(μ-Cl)$_2$ML$_2$, the main driving force for bending is attractive metal−metal interactions,[54] but for **4** direct Rh···Rh interactions are unlikely due to the octahedral coordination environment of Rh(1). The Rh···Rh distances of ca. 3.62 Å found in **4** are comparable with Rh···Rh separations between 3.5 and 3.6 Å in mixed valence phenylazophenyl-,[40] phenylbenzylamine-,[39] and benzoquinoline-based[38] Rh dimers. The geometry around Rh(2) is square-planar and comparable with that observed in other rhodium-bis(ethylene) complexes.[55−57] Centrosymmetrically related pairs of molecules form “tail-to-tail” π-stacked “dimers” with mean interplanar separations of their carbazole ring systems of 3.44 and 3.54 Å, respectively, for the two independent molecules. There are no other intermolecular packing interactions of note.

The mechanism of formation of **4** and the different products obtained in reaction of the free ligand **1** with either [RhCl(CO)$_2$]$_2$ or [RhCl(C$_2$H$_4$)$_2$]$_2$ to form **3** and **4**, respectively, has not been established. Two reaction pathways can be envisaged involving either heterolytic or oxidative addition of the carbazole N−H moiety to the dimeric Rh^{I} precursors. Heterolytic addition of the ligand leads directly to the Rh^{I} complexes **2** and **3** with elimination of 1 equiv HCl. The carbonyl complex **3** is stable under these conditions, whereas **2** undergoes immediate HCl addition to form a Rh^{III} ethyl species. The formation of Rh^{III} ethyl complexes by protonation of the corresponding Rh^{I} ethylene adduct with HCl and other Brønsted acids is well documented.[24,25] The reaction is in most cases believed to proceed via protonation of the metal center to form a metal hydride followed by ethylene insertion,[58−61] although direct protonation of the coordinated ethylene ligand has also been suggested in a few cases.[62,63] Complex **4** is always isolated as the final product regardless of the educt ratio. Monitoring the reaction by ^{1}H NMR spectroscopy gave no indication of any Rh hydride or other intermediates, and complex **4** was the only observable Rh species in solution.

The second possible reaction pathway involves oxidative addition of the carbazole N−H bond to the Rh^{I} precursors, generating a LRh^{III}(H)Cl(D) species (D = CO, C$_2$H$_4$). The ethylene adduct may undergo immediate ethylene insertion to form a Rh^{III} ethyl species, whereas the CO adduct may eliminate HCl to form the Rh^{I} product **3**. Oxidative addition of amines to Rh^{I} centers has attracted great interest, as it is proposed to be one of the key steps for the catalytic hydroamination of olefins.[64,65] However, confirmed oxidative additions of amines to coordinatively unsaturated metal centers are rare, possibly due to the weaker bond strength of M−N bonds compared to M−O and M−C bonds.[66,67]

From the available data it is not clear by which pathway complexes **3** and **4** are formed in the reaction of the free ligand **1** with the Rh precursors. It is interesting to note that in no case is a mononuclear bis(imino)carbazolide Rh^{III} complex observed, either as a coordinatively unsaturated complex of the type LRh(H)Cl or as an octahedral complex of the type LRh(H)Cl(D) (D = CO, C$_2$H$_4$). Coordinatively unsaturated 16-electron Rh^{III}(H)Cl complexes have been isolated and structurally characterized with “Pincer-type” (PR$_2$CH$_2$)$_2$C$_6$H$_3$ ligands and were found to be thermally stable.[22,28,29,68] The stronger σ/π-donor capability of this ligand with its C and P donors compared to the nitrogen-based bis(imino)carbazolide might be responsible for the greater stability of the Rh^{III} complex. In the case of bis(imino)carbazolide complexes, the higher oxidation state might only be stabilized by the formation of a dimer with a coordinatively saturated octahedral Rh^{III} center as in **4**; otherwise reduction to Rh^{I} could occur.

Oxidative Addition of MeI to Rh^{I} Complexes. In an NMR tube sealed with a Young's tap, 20 equiv of MeI was added to a solution of **3** in C$_6$D$_6$. At room temperature a slow conversion to the octahedral Rh^{III} derivative was observed, which could be accelerated by heating to 80 °C. After a total reaction time of 3 h the [bis(imino)carbazolide]Rh^{III}I(CO)Me complex **5** was obtained quantitatively. Complex **5** was characterized by ^{1}H NMR, ^{13}C NMR, IR, and FAB-mass spectroscopy. No spectroscopic evidence was found for a migratory CO insertion into the Rh−Me bond to give a Rh−acyl complex, in common with related Rh^{III} complexes containing tridentate [NNN] ligands.[10,21,69] By contrast, the products resulting from MeI addition to Rh^{I} carbonyl complexes containing some tridentate [PNO], [NON], or [SNS] ligands are known to undergo spontaneous migratory CO insertion.[70−72] The CO stretching frequency for **5** was observed at 2083 cm^{-1}, which is

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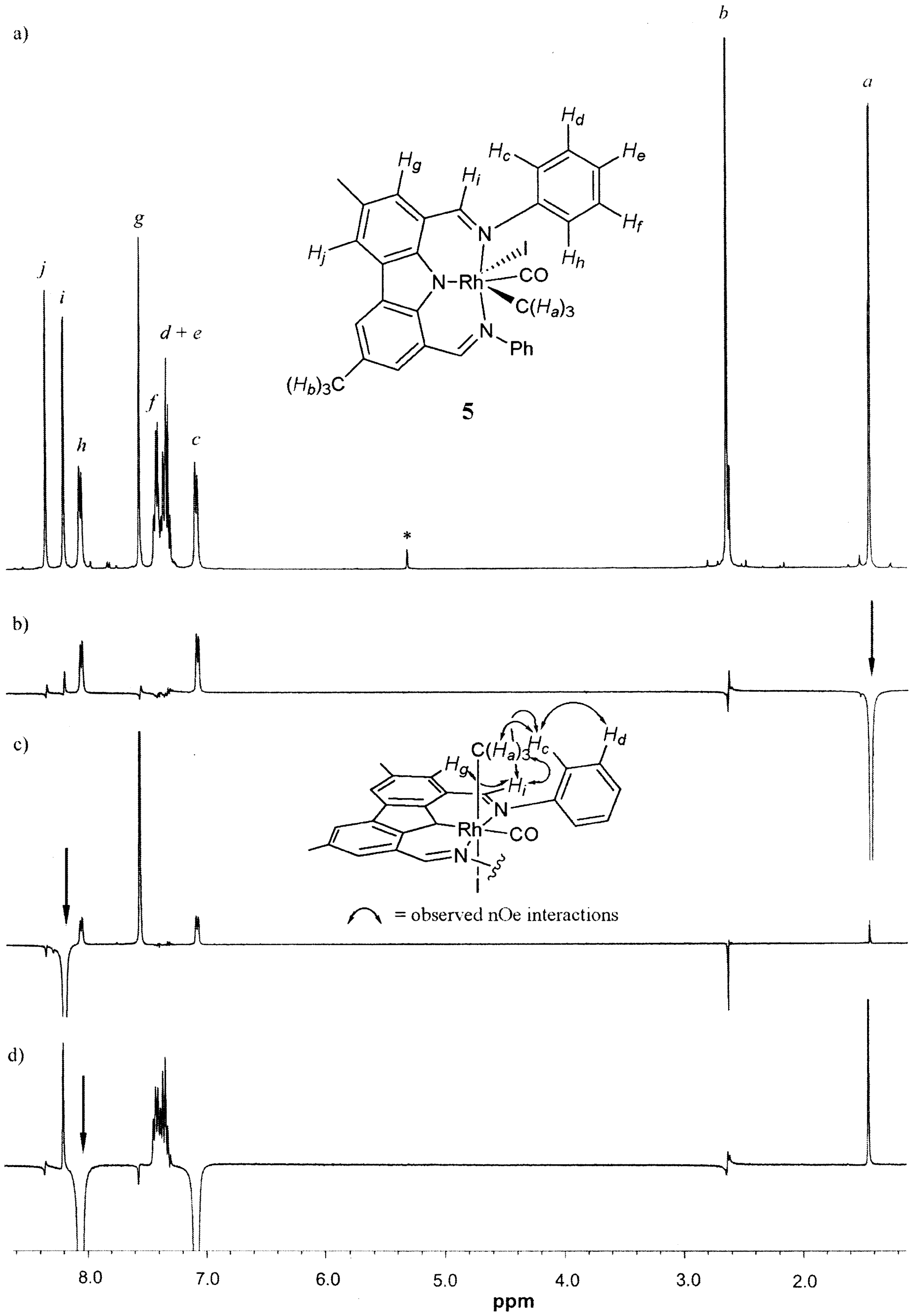
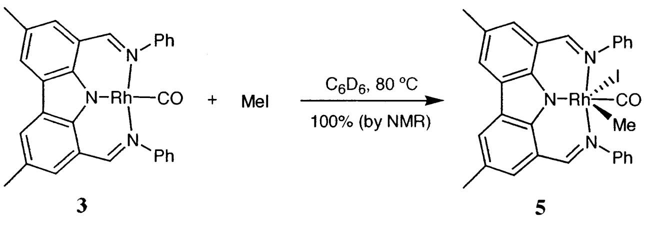


Figure 3. ^{1}H NMR (a) and NOE difference spectra (b–d) with observed NOE interactions for **5** in CD_2Cl_2 (*). (b) Irradiation of the Rh–Me resonance (H_a) at 1.44 ppm. (c) Irradiation of the aldimine resonance (H_i) at 8.20 ppm. (d) Irradiation of the *ortho*-phenyl resonance (H_h) at 8.06 ppm.

Scheme 2. Reaction of the LRh(CO) Complex 3 with MeI



considerably shifted to higher wavenumber from the value of 1980 cm^{-1} observed for **3**. A shift to higher wavenumber for ν(CO) by 80–100 cm^{-1} is characteristic of the transformation of a square-planar LRh^{I}(CO) complex to an octahedral LRh^{III}Me(CO)I species and is the result of weaker back-donation in Rh^{III} complexes compared to those bearing Rh^{I} centers.[10,21,69,70,73,74] The Rh–Me group in **5** (H_a) gave rise to the expected doublet resonances in both the ^{1}H NMR (Figure 3a) and ^{13}C NMR spectra at 1.44 ppm (^2J(RhH) = 2.2 Hz) and 9.3 ppm (^1J(RhC) = 20.9 Hz), respectively. Both chemical shifts and coupling constants are consistent with values obtained for other Rh^{III}Me(CO)I complexes.[21,70,73,74] Similar to CO complex **3**, no signal for the CO ligand was observed in the ^{13}C NMR spectrum of **5**.

COSY (^{1}H–^{1}H) and NOE difference spectra were recorded in order to fully assign the proton resonances

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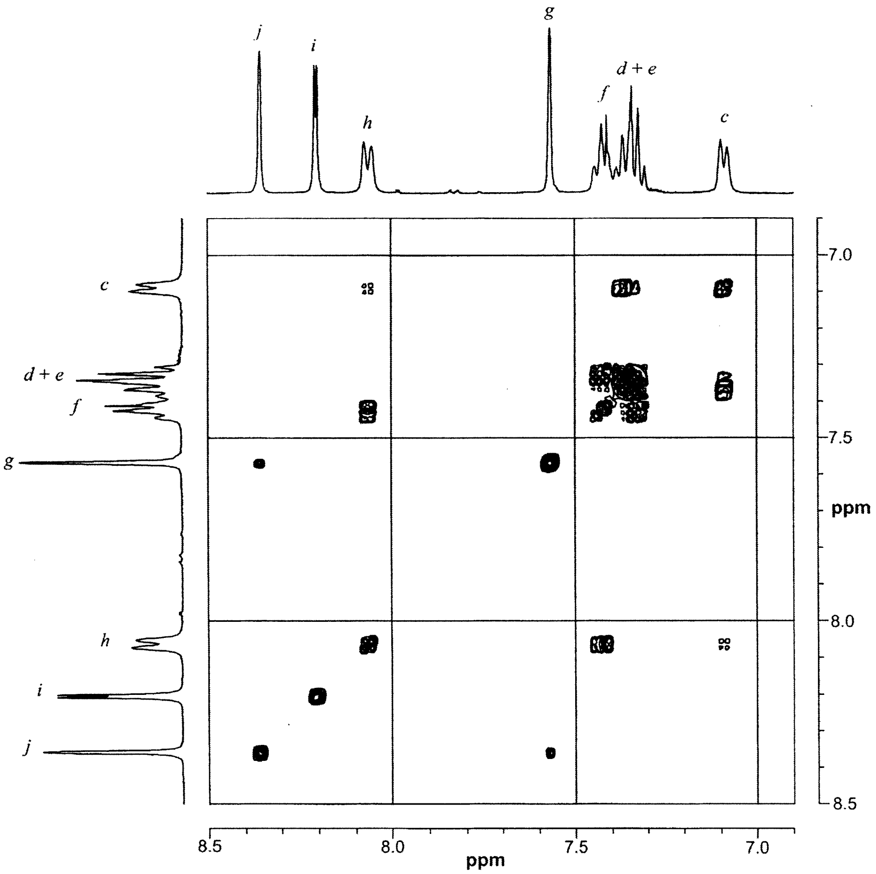

Figure 4. COSY (^{1}H−^{1}H) spectrum for **5** in CD_2Cl_2.

and establish the relative dispositions of the ligands in **5**. As shown in the ^{1}H NMR spectrum of **5** in Figure 3a, the reduced molecular symmetry of **5** (C_s) compared to **3** (C_{2v}) and hindered rotation about the N−phenyl bond resulted in the observation of individual resonances for each of the five phenyl protons (H_c−H_f, H_h) with chemical shifts similar to those obtained for the binuclear C_s-symmetric complex **4** (Figure 1). The resonances for these protons were assigned on the basis of results obtained from the COSY (^{1}H−^{1}H) spectrum shown in Figure 4 and the NOE difference spectra in Figure 3b−d.

Concerning the relative dispositions of the CO, Me, and iodide ligands in **5**, there are three possible isomers, two of which have a *cis*- and one a *trans*-relationship between the Rh−Me group and the carbazole-amide donor. These two arrangements can be distinguished with the help of the NOE difference spectra shown in Figure 3b−d. Irradiation of the Rh−Me resonance H_a resulted in an increased intensity for the signal of the aldimine proton H_i and both *ortho*-phenyl protons H_c and H_h (Figure 3b); the reverse observation is made when the aldimine resonance H_i is irradiated (Figure 3c). This establishes a *cis*-relationship between the Rh−Me group and the carbazole-amido donor, since in a *trans*-configuration no close contact between the Rh−Me group and the aldimine protons would be expected.

It is interesting to note that for the Rh−Me and aldimine groups a NOE with both *ortho*-phenyl protons H_c and H_h was observed, and irradiation of one of these resonances (H_h) also led to the saturation of the resonance for the other *ortho*-phenyl proton (H_c) (Figure 3d). This is due to a very slow rotation of the phenyl substituents around the phenyl−N bond, leading to the interconversion of H_c and H_h, as well as H_d and H_f. This rotation is slow on the normal ^{1}H NMR time scale, and five individual signals can be observed, the time scale for a NOE difference being considerably longer. Due to the slow rotation of the phenyl imino substituent, it was not possible to assign the phenyl protons in the ^{1}H NMR spectrum of **5** fully in relation to the Rh−Me group. A summary of all NOE interactions is given in Figure 3.

From the NOE difference and COSY spectra it was not possible to establish whether the CO or the iodide ligand is *trans* to the Rh−Me group. A *trans*-iodide configuration, as depicted in Figure 3, is however very likely, since oxidative addition of alkyl halides to square-planar d^8 complexes generally leads (kinetically) to *trans* adducts.[75] The same *trans* Me−Rh−I configuration has been observed for other octahedral Rh^{III}Me(CO)I complexes bearing ancillary anionic ligands after oxidative addition of MeI to square-planar Rh^I(CO) precursors.[21,69,73]

Reaction of MeI with the ethylene adduct **2** under conditions similar to those employed in the synthesis of **5** also resulted in the formation of a new Rh complex. However, no resonance corresponding to a Rh−Me group was observed in the ^{1}H NMR spectrum. Although free ethylene was observed in the reaction mixture, the Rh-containing product could not be identified.

Kinetic Studies. Kinetic experiments were carried out using FT-IR spectroscopy to monitor the oxidative

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addition of MeI to **3**. Reactions were performed in CH_2Cl_2 to provide direct comparison with data for related Rh^I complexes.[4,5,7,76] The relative instability of **3** in CH_2Cl_2 was not problematic, since under the conditions used, the decomposition of **3** is slow compared with the addition of MeI. The reaction of **3** with MeI was found to proceed as expected on the basis of the preparative study, with decay of the ν(CO) band of **3** at 1980 cm^{-1} being accompanied by the growth of a band due to **5** at 2083 cm^{-1}. In each experiment the exponential decay of the reactant showed the reaction to be first-order in **3**. Pseudo-first-order rate constants, measured over a range of MeI concentrations and temperatures, are given in the Supporting Information. A plot of k_{obs} versus [MeI] was linear, showing the reaction to be first-order in MeI and therefore second-order overall. The slope of the plot gave a value of 1.66 M^{-1} s^{-1} for the second-order rate constant at 25 °C. An Eyring plot of variable-temperature data (15−35 °C) gave activation parameters $\Delta H^{\ddagger}$ 19 (±1) kJ mol^{-1} and $\Delta S^{\ddagger}$ −179 (±4) J mol^{-1} K^{-1}. The large negative value of $\Delta S^{\ddagger}$ is consistent with a highly ordered S_N2 transition state for attack by Rh^I on MeI.

The nucleophilicity of **3** toward MeI is the highest yet measured for a Rh^I carbonyl complex. The second-order rate constant (at 25 °C) is 8 times larger than that reported recently for RhI(CO)(2,2′-bipy), which was itself the most reactive of a series of RhI(CO)(α-diimine) complexes.[7] The reactions of **3** and RhI(CO)(2,2′-bipy) have (within error) identical $\Delta H^{\ddagger}$ values but $\Delta S^{\ddagger}$ is ca. 20 J mol^{-1} K^{-1} less negative for **3**, although the reason for this difference is unclear. Complex **3** adds MeI ca. 10^3 times faster than the [PP]-ligated Rh^I complexes, $RhI(CO)(PEt_3)_2$[6] and RhI(CO)(dppe),[4,5] and ca. 5×10^4 times faster than the commercial carbonylation catalyst, $[RhI_2(CO)_2]^-$.[76] Thus the monoanionic [NNN] donor set imparts particularly high nucleophilicity on the Rh^I center. Even higher nucleophilicity toward MeI can be attained in square-planar Rh^I complexes which lack an electron-withdrawing carbonyl ligand. For instance, a Rh^I complex containing a macrocyclic ligand comprising two linked diimine units has a second-order rate constant for reaction with MeI of 2000 M^{-1} s^{-1}.[77] A number of Rh^I complexes containing tridentate N-donor ligands are also known to undergo oxidative addition reactions with C−Cl bonds.[12−15,27,78]

Conclusion

A family of rhodium complexes containing bis(imino)carbazolide ligands has been prepared and an unusual Rh^I−Rh^{III} derivative structurally characterized. Kinetic studies on the oxidative addition of MeI to (1,8-diphenylimino-3,6-dimethylcarbazolide)Rh(CO) to give (1,8-diphenylimino-3,6-dimethylcarbazolide)RhI(CO)Me revealed a second-order rate constant of 1.66 M^{-1} s^{-1} in CH_2Cl_2 at 25 °C, which corresponds to a reaction rate approximately 50 000 times faster than observed for $[RhI_2(CO)_2]^-$ under similar conditions. No evidence was found for spontaneous migratory CO insertion to give the acyl species LRh(COMe)I. The exceptional rate of oxidative addition is attributed to the anionic carbazolide ligand, which gives rise to a highly nucleophilic Rh^I center.

Experimental Section

General Considerations. All manipulations of water- and/or moisture-sensitive compounds were carried out using standard Schlenk and cannula techniques. Air-sensitive compounds were transferred in a nitrogen-filled glovebox and, unless stated otherwise, stored at room temperature. Crystal data were collected on a Siemens P4/RA diffractometer. NMR spectra were recorded on a Bruker AC-250 MHz, DRX-400 MHz, or AM-500 MHz spectrometer. ^1H and ^{13}C NMR chemical shifts were referenced to the residual proton signal and to the ^{13}C NMR signal of the deuterated solvents, respectively. Infrared spectra were obtained with thin sample films on NaCl plates or as KBr disks on a Perkin-Elmer 1760X FT-IR spectrometer. Mass spectra were recorded on a VG Autospec spectrometer. For kinetic experiments, infrared spectra were recorded using a Nicolet Magna 560 FT-IR spectrometer fitted with an MCT detector. Elemental analyses were performed by the microanalytical service of the University of North London.

Solvents and Reagents. Solvents were dried using standard procedures and used without degassing unless otherwise stated. Methyl iodide (MeI) was dried over 4 Å molecular sieves and vacuum-transferred into an ampule sealed with a Young's tap, degassed by repeated freeze−pump−thaw cycles, and stored below room temperature in the refrigerator. All other reagents are commercially available and were used without further purification.

(1,8-Diphenylimino-3,6-dimethylcarbazolide)Rh(C_2H_4) (2). Sodium hydride (190 mg, 7.9 mmol) and 1,8-diphenylimino-3,6-dimethyl-9*H*-carbazole (310 mg, 0.77 mmol) (**1**)[9] were placed in a Schlenk flask, and 30 mL of THF was added. The reaction mixture was stirred at 65 °C for 16 h. After cooling to room temperature (rt) the resulting deep orange solution was isolated by filtration and added to a solution of $[RhCl(C_2H_4)_2]_2$ (150 mg, 0.38 mmol) in THF (20 mL). The reaction mixture was stirred at rt for 16 h under an atmosphere of ethylene. The solvent was removed under reduced pressure, and the residue was extracted with toluene. The solvent was then evaporated and the residue was washed with pentane/diethyl ether (2 × 20 mL, 10:1 v/v). After drying in vacuo the product was obtained as a red, microcrystalline solid. Yield: 240 mg (59%). ^1H NMR (250 MHz, C_6D_6, rt): δ (ppm) 2.53 (s, 6H, CH_3), 3.11 (d, 4H, ^2J(RhH) = 1.6 Hz, C_2H_4), 6.86−7.00 (m, 10H, Ph-*H*), 7.23 (s, 2H, Ar-*H*), 8.32 (s, 2H, Ar-*H*), 8.50 (d, 2H, ^3J(RhH) = 3.0 Hz, N=C*H*). $^{13}C\{^1H\}$ NMR (63 MHz, C_6D_6, rt): δ (ppm) 21.5 (CH_3), 54.0 (d, ^1J(RhC) = 14.5 Hz, C_2H_4), 117.0 (Ar-*C*), 124.4 (Ar-*C*), 125.7 (Ar-*C*), 125.9 (Ar-*C*), 126.5 (Ar-*C*), 128.0 (Ar-*C*), 128.3 (Ar-*C*), 131.1 (Ar-*C*), 141.8 (Ar-*C*), 155.2 (Ar-*C*), 161.7 (N=*C*H). IR (KBr): 3058 (w), 3006 (w), 2915 (w), 2859 (w), 1637 (m, ν(C=N)), 1606 (m), 1592 (m), 1569(s), 1560 (s), 1545 (s), 1486 (s), 1449 (s), 1369 (m), 1315 (m), 1297 (m), 1249 (w), 1207 (s), 1190 (s), 1105 (w), 1025 (w), 990 (m), 852 (m), 758 (m), 707 (m), 626 (w) cm^{-1}. FAB-mass spectrum (*m*/*e*): 503 ($[M - C_2H_4]^+$). Anal. Calcd for $C_{30}H_{26}N_3Rh$: C, 67.80; H, 4.93; N, 7.91. Found: C, 67.71; H, 4.98; N, 7.93.

(1,8-Diphenylimino-3,6-dimethylcarbazolide)Rh(CO) (3). Method A: Via Salt Metathesis. Sodium hydride (210 mg, 8.7 mmol) and 1,8-diphenylimino-3,6-dimethyl-9*H*-carbazole (320 mg, 0.80 mmol) (**1**)[9] were placed in a Schlenk flask, and 30 mL of THF was added. The reaction mixture was stirred at 65 °C for 16 h. After cooling to rt the resulting deep orange solution was isolated by filtration and added to a solution of $[RhCl(CO)_2]_2$ (155 mg, 0.40 mmol) in THF (20 mL).

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The reaction mixture was stirred at rt for 16 h. The solvent was removed under reduced pressure, and the residue was extracted with toluene. The solvent was evaporated, and the residue was washed with diethyl ether/pentane (2 × 20 mL, 1:1 v/v). After drying in vacuo the product was obtained as a red, microcrystalline solid. Yield: 360 mg (85%). ^{1}H NMR (250 MHz, CD_2Cl_2, rt): δ (ppm) 2.71 (s, 6H, CH_3), 7.20−7.40 (m, 10H, Ph-*H*), 7.75 (s, 2H, Ar-*H*), 8.43 (s, 2H, Ar-*H*), 8.83 (d, 2H, ^3J(RhH) = 3.2 Hz, N═C*H*). ^{13}C{^{1}H} NMR (63 MHz, CD_2Cl_2, rt): δ (ppm) 21.6 (*C*H_3), 116.9 (Ar-*C*), 123.8 (Ar-*C*), 126.4 (Ar-*C*), 126.5 (Ar-*C*), 126.5 (Ar-*C*), 128.1 (Ar-*C*), 128.6 (Ar-*C*), 131.4 (Ar-*C*), 140.1 (Ar-*C*), 161.1 (Ar-*C*), 162.2 (N═*C*H). IR (KBr): 3061 (w), 3019 (w), 2919 (w), 2854 (w), 1980 (s, ν(CO)), 1630 (w, ν(C═N)), 1593 (m), 1574 (m), 1548 (s), 1487 (m), 1450 (m), 1366 (w), 1318 (m), 1295 (w), 1249 (w), 1209 (m), 1193 (m), 1144 (w), 1026 (w), 989 (w), 848 (w), 757 (m), 696 (m), 636 (w) cm^{-1}. FAB-mass spectrum (*m*/*e*): 531 (M$^+$), 503 ([M − CO]$^+$). Anal. Calcd for $C_{29}H_{22}N_3ORh$: C, 65.54; H, 4.17; N, 7.91. Found: C, 65.63; H, 4.27; N, 7.81.

Method B: Without Prior Ligand Deprotonation. $[RhCl(CO)_2]_2$ (9.4 mg, 0.024 mmol) and 1,8-diphenylimino-3,6-dimethyl-9*H*-carbazole (19.4 mg, 0.048 mmol) (**1**)[9] were placed into an NMR tube sealed with a Youngs Teflon stopcock, and C_6D_6 was added. This resulted in the formation of a deep red solution with vigorous liberation of CO gas. After 1.5 h at rt, a ^{1}H NMR spectrum revealed quantitative formation of the desired product **3**.

(1,8-Diphenylimino-3,6-dimethylcarbazolide)RhC_2H_5-di-μ-chloro-Rh$(C_2H_4)_2$ (4). $[RhCl(C_2H_4)_2]_2$ (261 mg, 0.67 mmol) and 1,8-diphenylimino-3,6-dimethyl-9*H*-carbazole (270 mg, 0.67 mmol) (**1**)[9] were placed into a Schlenk flask, and benzene (30 mL) was added. The resulting deep red solution was stirred at 70 °C for 6 h. After cooling to ambient temperature the solvent was removed under reduced pressure and the residue was extracted with toluene. The toluene solvent was then evaporated, and the residue was dissolved in dichloromethane (10 mL) and precipitated by the addition of pentane (50 mL). The supernatant solution was removed by filtration, and the residue was washed with pentane (2 × 20 mL). After drying in vacuo the product was obtained as a red, microcrystalline solid. Yield: 342 mg (67%). Crystals suitable for X-ray analysis were grown from a concentrated solution mixture of benzene, diethyl ether, and pentane after prolonged standing at ambient temperature. ^{1}H NMR (250 MHz, CD_2Cl_2, rt): δ (ppm) −0.09 (t, 3H, ^3J(HH) = 7.8 Hz, RhCH$_2$CH_3), 2.06 (br, 8H, C$_2H_4$), 2.63 (s, 6H, CH_3), 2.72 (dq, 2H, ^3J(HH) = 7.8 Hz, ^2J(RhH) = 3.1 Hz, RhCH_2CH$_3$), 7.06 (m, 2H, Ph-*H*), 7.34 (m, 4H, Ph-*H*), 7.58 (s, 2H, Ar-*H*), 7.73 (m, 2H, Ph-*H*), 8.13 (m, 2H, Ph-*H*), 8.27 (s, 2H, Ar-*H*), 8.57 (d, 2H, ^3J(RhH) = 2.5 Hz, N═C*H*). ^{13}C{^{1}H} NMR (63 MHz, CD_2Cl_2, rt): δ (ppm) 17.2 (RhCH$_2$*C*H$_3$), 18.0 (d, ^1J(RhC) = 22.6 Hz, Rh*C*H$_2$CH$_3$), 21.4 (*C*H$_3$), 59.3 (d, ^1J(RhC) = 13.4 Hz, *C*$_2$H$_4$), 60.2 (d, ^1J(RhC) = 13.0 Hz, *C*$_2$H$_4$), 116.4 (Ar-*C*), 123.6 (Ar-*C*), 126.32 (Ar-*C*), 126.5 (Ar-*C*), 127.4 (Ar-*C*), 128.1 (Ar-*C*), 128.7 (Ar-*C*), 132.2 (Ar-*C*), 138.9 (Ar-*C*), 156.7 (Ar-*C*), 163.5 (N═*C*H). IR (KBr): 3063 (w), 3031(w), 2997 (w), 2968 (w), 2905 (w), 2845 (w), 1635 (w, ν(C═N)), 1606 (w), 1566 (s), 1541 (m), 1488 (m), 1447 (m), 1375 (w), 1321 (m), 1303 (w), 1206 (m), 1190 (m), 1149 (m), 1027 (w), 990 (m), 853 (w), 757 (m), 695 (m), 677 (w) cm^{-1}. FAB-mass spectrum (*m*/*e*): 761 (M$^+$), 504 (LRh$^+$). Anal. Calcd for $C_{34}H_{35}Cl_2N_3Rh_2$: C, 53.56; H, 4.63; N, 5.51. Found: C, 53.66; H, 4.66; N, 5.38.

Crystal data for 4: $C_{34}H_{35}N_3Cl_2Rh_2\cdot0.5C_6H_6$, M = 801.4, triclinic, $P\bar{1}$ (no. 2), a = 11.360(1) Å, b = 18.087(1) Å, c = 18.219(2) Å, α = 75.75(1)°, β = 74.98(1)°, γ = 78.88(1)°, V = 3470.7(4) Å^3, Z = 4 (there are two crystallographically independent molecules in the asymmetric unit), D_c = 1.534 g cm^{-3}, μ(Cu Kα) = 9.33 mm^{-1}, T = 293 K, orange-red platy needles; 9494 independent measured reflections, F^2 refinement, R_1 = 0.053, wR_2 = 0.126, 6931 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \le 120°$], 762 parameters; CCDC 229816.

(1,8-Diphenylimino-3,6-dimethylcarbazolide)Rh(CO)-MeI (5). Methyl iodide (28 μL, 0.46 mmol) was added to a solution of (1,8-diphenylimino-3,6-dimethylcarbazolide)Rh(CO) (12.4 mg, 0.023 mmol) (**3**) in C_6D_6 in an NMR tube sealed with a Youngs Teflon tap. After 1.5 h at rt the reaction mixture was heated at 80 °C for another 1.5 h, after which time the volatile components were removed under reduced pressure. The resultant red solid was redissolved in CD_2Cl_2. This solution was used to obtain FAB-MS, IR, ^{1}H NMR, and ^{13}C NMR spectra, including ^{1}H-COSY and NOE difference NMR data. These data were consistent with the quantitative conversion of **3** to the complex **5**. ^{1}H NMR (250 MHz, CD_2Cl_2, rt): δ (ppm) 1.44 (d, 3H, ^2J(RhH) = 2.2 Hz, Rh-CH_3), 2.64 (s, 6H, CH_3), 7.08 (m, 2H, Ph-*H*), 7.29−7.42 (m, 6H, Ph-*H*), 7.57 (s, 2H, Ar-*H*), 8.06 (m, 2H, Ph-*H*), 8.20 (d, 2H, ^3J(RhH) = 2.6 Hz, N═C*H*), 8.36 (s, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (63 MHz, CD_2Cl_2, rt): δ (ppm) 9.3 (d, ^1J(RhC) = 20.9 Hz, Rh-*C*H$_3$), 21.4 (*C*H$_3$), 116.0 (Ar-*C*), 121.9 (Ar-*C*), 125.2 (Ar-*C*), 126.1 (Ar-*C*), 128.1 (Ar-*C*), 128.2 (Ar-*C*), 129.1 (Ar-*C*), 129.2 (Ar-*C*), 129.6 (Ar-*C*), 132.8 (Ar-*C*), 138.2 (Ar-*C*), 159.8 (Ar-*C*), 164.3 (N═*C*H). IR (thin film): 3059 (w), 3008 (w), 2906 (w), 2862 (w), 2083 (s, ν(CO)), 1633 (w,), 1604 (m), 1570 (s), 1542 (w), 1488 (m), 1450 (m), 1376 (w), 1322 (m), 1303 (w), 1251 (w), 1208 (m), 1191 (m), 1147 (w), 1026 (w), 990 (w), 953 (w), 857 (w), 759 (m), 698 (m), 633 (w) cm^{-1}. FAB-mass spectrum (*m*/*e*): 546 ([M − I]$^+$). 518 ([M − CO]$^+$ − I), 503 ([M − CO]$^+$ − MeI).

Kinetic Experiments. Samples for kinetic runs were prepared by placing the required amount of freshly distilled MeI in a 10 mL graduated flask, which was then made up to 10 mL with CH_2Cl_2. A portion of this solution was used to record a background spectrum. Another portion (typically 2.5 mL) was added to a sample of complex **3** (typically 3 μmol) in a sample vial to give a reaction solution with a complex concentration of ca. 1 mM. A portion of this solution was quickly transferred to the IR cell, and data acquisition was started. At least a 10-fold excess of MeI relative to **3** was used to maintain pseudo-first-order conditions. The IR cell (0.5 mm. path length, CaF_2 windows) was maintained at constant temperature by a thermostated jacket. FT-IR spectra were scanned in the ν(CO) region (2200−1600 cm^{-1}) and saved at regular time intervals using the Nicolet Omnic Series software. After completion of the experiment, absorbance versus time data for the appropriate ν(CO) frequencies were extracted and analyzed off-line using Kaleidagraph curve-fitting software. For each experiment, the decay of the ν(CO) band of **3** at 1980 cm^{-1} was well fitted by an exponential curve with correlation coefficient ≥ 0.999, to give the pseudo-first-order rate constant. For each set of conditions, at least two experiments were performed to check reproducibility, the k_{obs} data given being averaged values with component measurements deviating from the mean by ≤5%.

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Supporting Information Available: Tables of kinetic data (PDF) and crystallographic data (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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