1,8-Bis(imidazolin-2-yliden-1-yl)carbazolide (bimca): A New CNC Pincer-Type Ligand with Strong Electron-Donating Properties. Facile Oxidative Addition of Methyl Iodide to Rh(bimca)(CO)†

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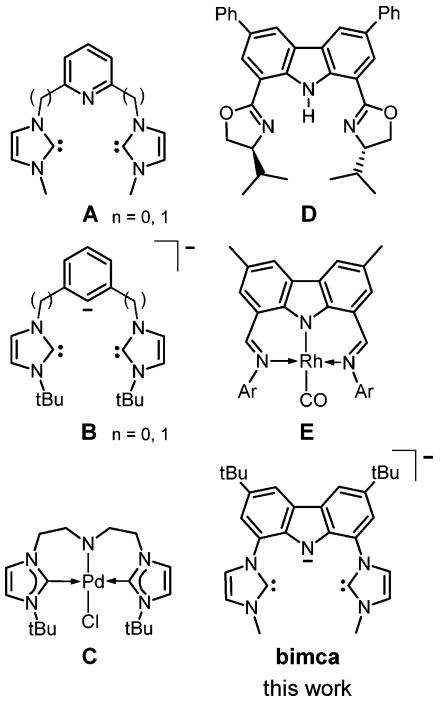
The synthesis of a new CNC pincer-type ligand based on an N-heterocyclic carbene substituted carbazole is presented. The resulting 3,6-di-*tert*-butyl-1,8-bis(3-methylimidazolin-2-yliden-1-yl)carbazolide (bimca) is a monoanionic, meridionally coordinating tridentate ligand that was generated in situ by deprotonation of the imidazolium salt (bimca)·2HI (**3a**) or (bimca)·2HBF_4 (**3b**) and characterized by NMR spectroscopy as the Li complex **4**. The successful transmetalation to rhodium upon reaction with $[Rh(CO)_2Cl]_2$ yielded Rh(bimca)(CO) (**5**). This complex shows a very small wavenumber in the IR spectrum for the ν(CO) band, thus indicating strong σ-donor and weak π-acceptor properties of the bimca ligand. The highly nucleophilic character of the Rh(I) center was proven by the formal oxidative addition of methyl iodide to Rh(bimca)(CO) (**5**), a reaction that proceeded more quickly than with any other Rh(I) complex reported so far. The complex Rh(bimca)(CH_3)I(CO) (**6**) as well as Rh(bimca)(CO) (**5**) were characterized by X-ray crystal structure analyses and show a strong distortion of the CO ligand from the Rh(bimca) plane.

Introduction

Since its first preparation by Shaw et al.,[1] the pincer-type ligand has become a valuable ligand class and their complexes play crucial roles with respect to unusual conformations, special reactivities, and catalytic applications.[2] An important feature of the pincer-type ligand is its good modifiability, mainly at the donor atoms for electronic reasons, but also at the backbone to achieve a certain geometry. Thus, a huge variety of pincer-type ligands has been prepared so far: neutral and charged, with aromatic as well as aliphatic backbones.

N-heterocyclic carbene (NHC) ligands were found to be interesting substitutes for phosphine ligands but differ in a stronger σ-donor and weaker π-acceptor character.[3] This quality is especially desired for complexes and catalysts in which a high electron density at the metal atom is advantageous. In combination with the "pincer-idea" this concept led to the synthesis of several kinds of NHC-containing pincer-type ligands: neutral **A**[4] (Chart 1) and monoanionic **B**,[4b,5] with the NHC moiety as lateral donor functions or as the backbone.[6] We were surprised that only one example of an amido-containing bis-NHC ligand has been reported so far: the synthesis of complex **C** was achieved by base-induced elimination of HCl from the respective bis-NHC-coordinated cationic

Chart 1



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† This article is dedicated to Professor Gerhard Erker on the occasion of his 60th birthday.

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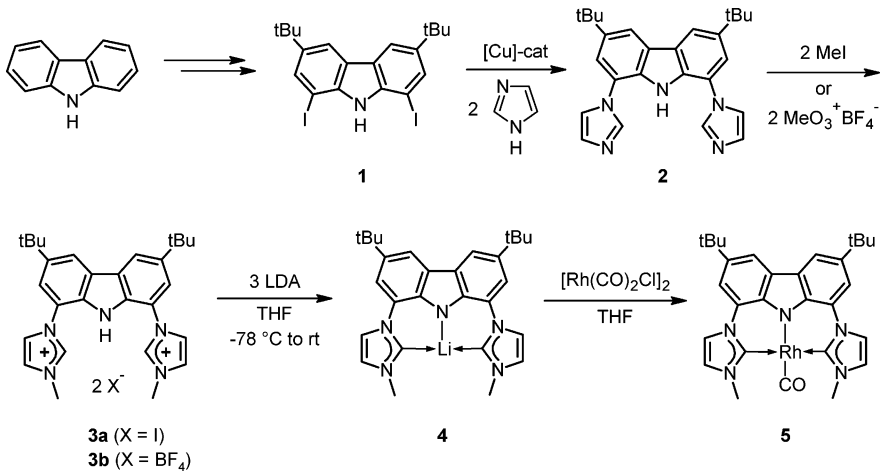
Scheme 1. Synthesis of the bimca Ligand and Its Rh(I) Complex 5



amino complex.[7] In general, pincer-type ligands with a carbazole backbone are quite rare: Nakada et al. reported a Cr complex of ligand **D** to be suitable for the asymmetric Hiyama-aldol reaction,[8] and Gibson et al. prepared complexes of type **E** with a diimino−carbazole ligand.[9] Our research is focused on the synthesis of a monoanionic bis-NHC pincer ligand with an amido donor function, but with a planar and rather fixed geometry, and it occurred to us that a carbazole backbone with substituted NHC moieties in the 1,8-positions (bimca) would be suitable for this purpose.

Results and Discussion

Ligand Synthesis. The synthesis of the bimca ligand started from 3,6-di-*tert*-butyl-1,8-diiodocarbazole (**1**), which was coupled in a copper-catalyzed Ullmann reaction with imidazole (Scheme 1). The best results were achieved with a procedure described by Buchwald using $(CuOTf)_2{\cdot}C_6H_6$ as catalyst precursor, dba and 2 equiv of 1,10-phenanthroline as ligands, and Cs_2CO_3 as base.[10] The resulting bis(imidazolyl)-substituted carbazole **2** was treated either with methyl iodide to give the bis(imidazolium) salt **3a** (X = I) or with Meerwein's salt $Me_3O^+BF_4^-$ to give compound **3b** with tetrafluoroborate as the counterions. The molecular structures of both ligand precursors could be resolved by X-ray diffraction analysis. With iodide as a counterion (Figure 1) the dicationic carbazole species is C_s symmetric with both imidazolium moieties facing each other. In the crystal structure with BF_4^- as counterions however (Figure 2), the dicationic ligand precursor is asymmetric, indicating an easy rotation of the NHC substituents. One BF_4^- counterion shows hydrogen bridges to the carbazole (N1−F1 = 2.829 Å) as well as to one water molecule that is enclosed (F3−O1 = 2.877 Å); the second BF_4^- counterion shows a hydrogen bridge also to the water molecule (F5−O1 = 2.965 Å).

Lithium 3,6-Di-*tert*-butyl-1,8-bis(3-methylimidazolin-2-ylidene-1-yl)carbazolide (Li(bimca), 4). Generation of the "free" ligand **4** was best achieved by deprotonation of **3a** or **3b** in THF solution with 3 equiv of lithium diisopropylamide (LDA) (Scheme 1). The quality of the reaction is not influenced by the counterion, and though KO^{t}Bu, KH, and methyllithium lead

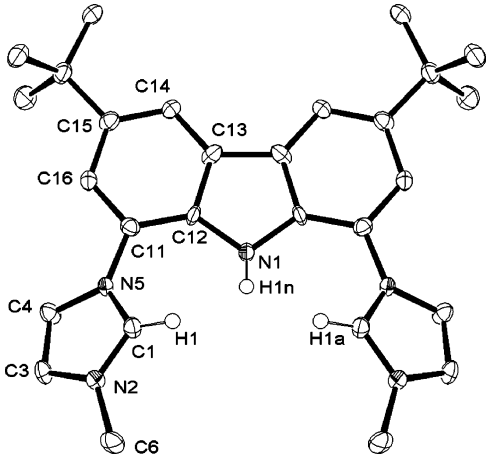


Figure 1. Molecular structure of the C_s-symmetric dicationic ligand precursor **3a**.

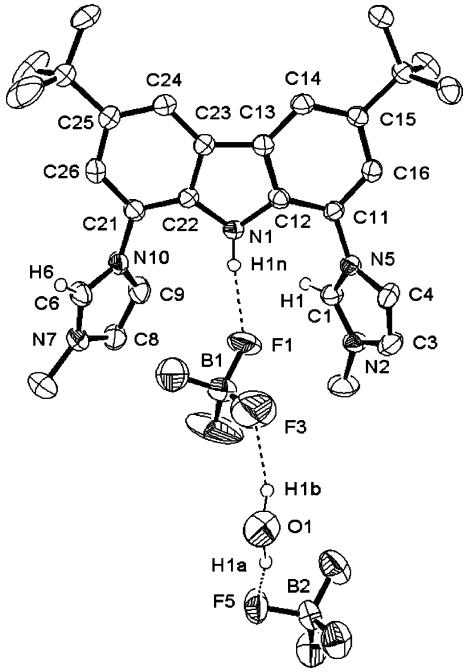


Figure 2. Molecular structure of the ligand precursor **3b**.

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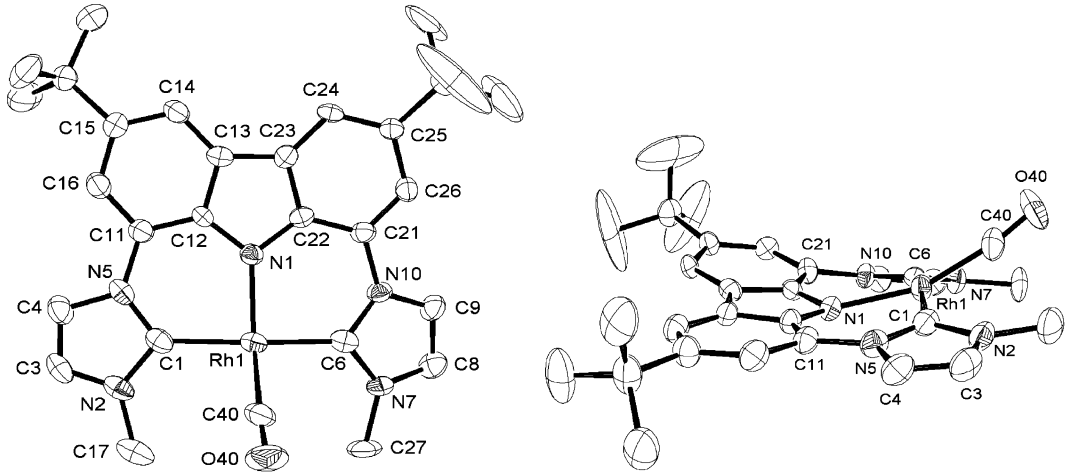

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Figure 3. ORTEP views (top and side) of the molecular structure of **5**. Selected interatomic distances (Å) and angles (deg): Rh1−N1 = 2.028(4), Rh1−C1 = 2.060(6), Rh1−C6 = 2.047(5), Rh1−C40 = 1.814(6), C40−O40 = 1.149(6); C40−Rh1−N1 = 161.0(2), C6−Rh1−C1 = 166.68(19), O40−C40−Rh1 = 170.9(6); C14−C13−C23−C24 = 9.4, C22−C21−N10−C6 = −25.3, C12−C11−N5−C1 = 7.1.

all to generation of a carbene species, the reaction with the lithium base was found to give the best results. Formation of the lithium carbene complex **4** is accompanied by a strong blue fluorescence of the yellow solution in daylight. Complex **4** is highly air and moisture sensitive but is found to be stable in solution at room temperature. However, attempts to purify **4** by separation from lithium iodide or lithium tetrafluoroborate resulted in decomposition. Therefore, we found it best to generate a solution of carbene **4** in situ for all further reactions. In the ^{1}H NMR spectrum (THF-d_8) formation of **4** is indicated by the absence of the peak of the imidazolium proton. This is confirmed by the characteristic signal for the carbene C in the ^{13}C NMR spectrum (THF-d_8) at δ 206.1—a chemical shift between that of a free unsaturated NHC (δ 210−215) and that of a lithium-coordinated NHC (δ 197).[11]

Synthesis and Properties of Rh(bimca)(CO) (5). For the preparation of the complex Rh(bimca)(CO) (**5**) a THF solution of $[Rh(CO)_2Cl]_2$ was added dropwise to an in situ generated solution of **4** in THF at −30 °C (Scheme 1). The product was precipitated by addition of pentane and extracted into benzene to remove inorganic salts. The product was isolated as an air- and moisture-sensitive yellow crystalline solid in 38% yield. In the ^{1}H NMR spectrum (THF-d_8) of **5** all proton signals of the bimca ligand are shifted downfield by 0.25−0.4 ppm compared to the signals for the complex Li(bimca) (**4**). The ^{13}C NMR spectrum (THF-d_8) shows two doublets, one for the carbonyl C atom at 199 ppm ($^1J_{RhC}$ = 70 Hz) and one for the carbene C atoms at 183 ppm ($^1J_{RhC}$ = 47 Hz), confirming the formation of a Rh(bimca)(CO) complex. The chemical shifts of the remaining bimca signals are only slightly shifted (maximum 6 ppm) either up- or downfield compared to the signals for Li(bimca) (**4**). In the IR (KBr) spectrum the strong ν(CO) band is observed at 1916 cm^{-1}. This extremely low value for a Rh−CO complex indicates a very strong π-back-donation from the metal to the carbonyl ligand caused by the strong σ-donor and weak π-acceptor properties of the bimca ligand. As a comparison, the carbazole complex **E** (Chart 1) reported by Gibson et al. shows this band at 1980 cm^{-1},[9d] cationic Rh(I)−carbonyl complexes with ligands of type **A** exhibit bands at 1982 cm^{-1} [12a] and 1968 cm^{-1},[13] and *trans*-$[RhX(CO)(NHC)_2]$ complexes have bands at 1924 cm^{-1} [14] (X = Cl$^-$) and 1943 cm^{-1} (X = I$^-$).[12b]

From a concentrated solution of **5** in a mixture of dichloromethane and DMSO (35:1) at room temperature, we were able to get yellow crystals that were suitable for X-ray crystal structure analysis. The molecular structure (Figure 3) shows a distorted-square-planar geometry around the Rh center. The bimca ligand is slightly bent and twisted in the carbazole backbone (C14−C13−C23−C24 = 9.4°), thus showing a rather high flexibility of the somehow rigid-looking backbone. In addition, the NHC rings are not coplanar with the carbazolide backbone: one ring is tilted by C12−C11−N5−C1 = 7.1° and the other even by C22−C21−N10−C6 = −25.3°. The rhodium center is situated slightly above the plane of the three coordinating bimca atoms (d = 0.23 Å). Most striking, however, is the strong distortion of the CO ligand with N1−Rh1−C40 = 161.0(2)° and a Rh1−C40−O40 angle of 170.9(6)°, which is most likely due to the steric congestion caused by the methyl substituents of the NHCs. The carbene−rhodium distances (Rh1−C6 = 2.047(5) Å and Rh1−C1 = 2.060(6) Å) and the distances of the carbonyl ligand (Rh1−C40 = 1.814(6) Å and C40−O40 = 1.149(6) Å) do not show any significant deviations from those found for other, "non-pincer" (NHC)Rh^{I} carbonyl complexes.[14,15]

Reactivity of Rh(bimca)(CO) (5). The strong distortion of the carbonyl ligand might lead to an enhanced lability which we could rule out by the following ^{13}CO exchange experiment.

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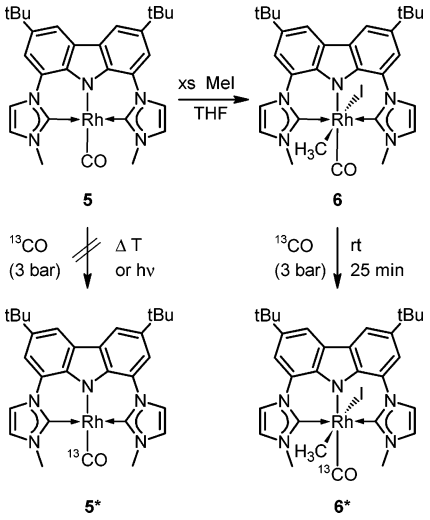
Scheme 2. Reactivity of the Rh Complexes 5 and 6



An NMR tube containing a solution of **5** in THF-d_8 was pressurized with 3 bar of ^{13}CO and the reaction monitored by ^{13}C NMR spectroscopy. At room temperature no signal of incorporated ^{13}CO could be detected. Neither irradiation of the sample with UV light nor prolonged heating at 60−70 °C led to any detectable exchange of ^{13}CO to form complex **5*** (Scheme 2).

To investigate the nucleophilicity of Rh(bimca)(CO) (**5**), we added a 10-fold excess of methyl iodide to a solution of **5** in benzene-d_6 at room temperature. This reaction is also the rate-limiting step in the Monsanto process—the carbonylation of methanol.[16]

To our surprise, an immediate reaction took place and **6** was formed as a green precipitate. Conducting the same experiment in THF-d_8 also led to an instant reaction that was accompanied by a change in color from yellow to green; however, complex **6** remained dissolved. The ^{1}H NMR (THF-d_8) spectrum revealed that compound **6** was formed as a single isomer. The signals of the carbazole backbone were shifted slightly upfield by about 0.1 ppm, whereas the signals of the NHC and its methyl group were shifted downfield by the same value. The signal of the rhodium bound methyl group could be identified as a doublet at 0.38 ppm with a $^2J_{RhH}$ coupling constant of 3.0 Hz. In the ^{13}C NMR spectrum the product could be unambiguously identified by the doublet at 0.42 ppm with a $^1J_{RhC}$ coupling constant of 20.4 Hz for the new methyl group. The signal for the carbonyl C atom was shifted upfield by 7 ppm to δ 192.5, and the $^1J_{RhC}$ coupling constant of 60.4 Hz was about 10 Hz smaller than that in complex **5**. The carbene signal was affected by an upfield shift of 15 ppm and was now detected at 167.3 ppm with a $^1J_{RhC}$ coupling of 35.5 Hz, which is again 10 Hz less than in complex **5**. The remaining signals of the bimca ligand were almost constant compared to those of the Rh(I) complex **5**.

In the IR (KBr) spectrum a clear indication for the formation of a Rh(III) species was the strong ν(CO) band at 2024 cm^{-1}, a value that is almost 110 cm^{-1} higher than that found for complex **5**. For this reaction a shift of 80−100 cm^{-1} is typically found for Rh(CO) complexes in the literature.[9d]

By slow diffusion of pentane into a THF solution of complex **6** at −35 °C we were able to get green single crystals that were suitable for X-ray structure analysis. The molecular structure of **6** (Figure 4) shows an octahedral arrangement of the coordinating atoms, in which the octahedron is tilted with respect to the carbazole plane and the Rh center is located d = 0.58 Å above the carbazole plane for steric reasons (Figure 4, side view). The CO ligand is oriented in the equatorial position but—as already observed in complex **5**—distorted from the bimca plane and points toward the apical methyl group (C40−Rh1−C41 = 86.22°). Due to steric congestion the CO ligand is tilted (Rh1−C40−O40 = 172.2(3)° and C40−Rh1−N1 = 168.27-(13)°) but is still in close contact with the NHC methyl groups (C27−O40 = 3.164 Å and C17−O40 = 3.081 Å). The iodine atom was found trans to the methyl group, as is expected on the basis of a S_N2 mechanism.

Up to 100 °C (THF-d_8) no spectroscopic evidence was found for a migratory CO insertion into the Rh−Me bond to give the corresponding Rh−acyl complex. Obviously the steric congestion is not yet sufficient to induce a migratory insertion as reported by Haynes et al. for *trans*-(NHC)$_2$RhI(CO).[12] The CO ligand, however, was found to be much more labile than in complex **5**. At a ^{13}CO pressure of 3 bar carbonyl exchange took place already at room temperature within 25 min, as a ^{13}C NMR experiment showed.

Kinetic Measurements. As previous experiments by Haynes et al.[12] and Eisenberg et al.[17] have shown, the methyl iodide addition to Rh(I) and Ir(I) complexes follows second-order

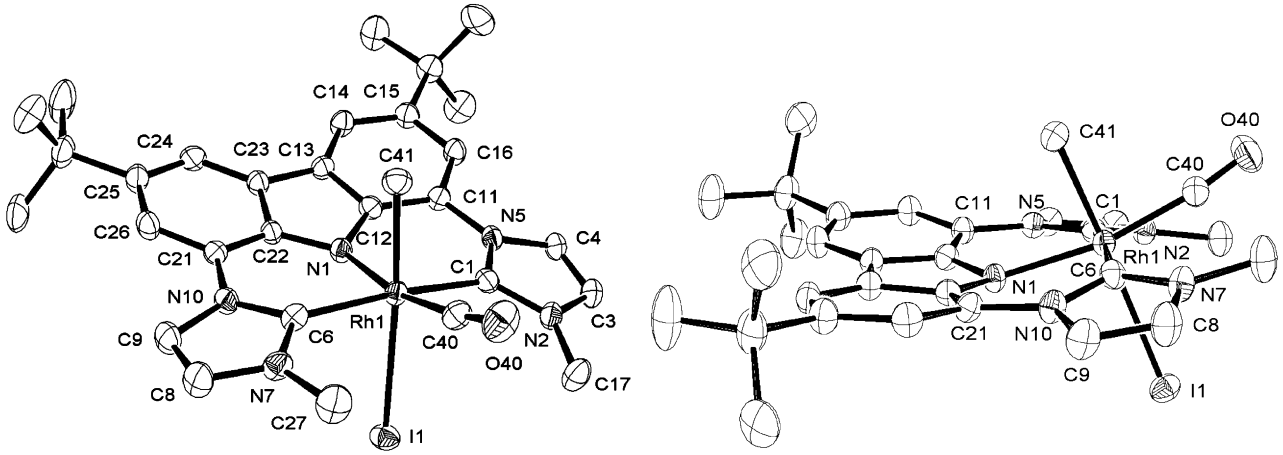


Figure 4. ORTEP views (top and side) of the molecular structure of **6**. Selected interatomic distances (Å) and angles (deg): Rh1−N1 = 2.048(2), Rh−C1 = 2.073(3), Rh1−C6 = 2.072(3), Rh1−C41 = 2.094(5), Rh−I1 = 2.8332(5), Rh1−C40 = 1.859(3), C40−O40 = 1.134(4); O40−C40−Rh1 = 172.2(3), C40−Rh1−N1 = 168.27(13), C6−Rh1−C1 = 171.66(12), N1−Rh1−C41 = 82,64(13), C40−Rh1−C41 = 86.22(15), C40−Rh1−I1 = 95.97(10), N1−Rh1−I1 = 95.36(7); C6−N10−C21−C22 = −16.2, N7−C6−Rh1−C40 = −24.8, C1−N5−C11−C12 = 12.7, N2−C1−Rh1−C40 = 34.3.

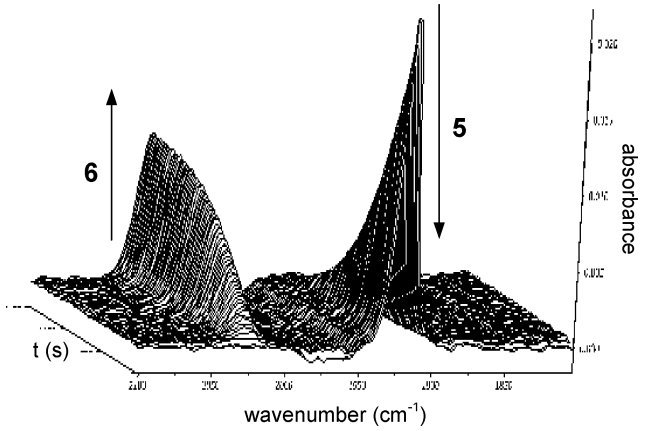


Figure 5. Series of IR spectra recorded during the reaction of **5** with MeI in THF at −78 °C.

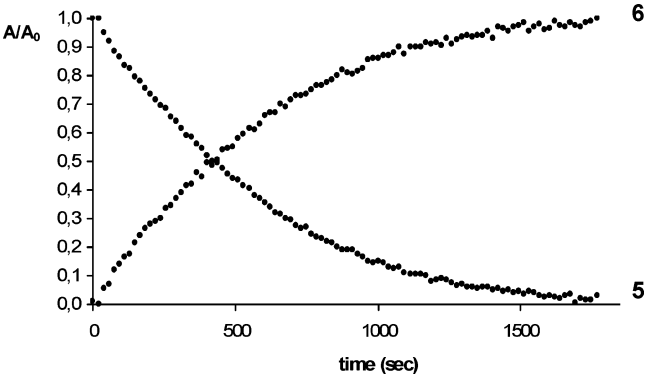


Figure 6. Kinetic plot showing growth and decay of ν(CO) bands for **5** (1921 cm^{-1}) and **6** (2022 cm^{-1}) during the reaction of **5** with MeI (0.62 M in THF, −78 °C).

kinetics and the mechanism is better described as a classical nucleophilic substitution than an oxidative addition reaction. We already found qualitatively that the methyl iodide addition proceeded much more quickly for complex **5** than was reported in literature for complex **E** (Chart 1) (80 °C, 3 h, benzene, 20 equiv of MeI).[9d] To quantify our findings, we performed in situ FT-IR spectroscopic experiments. As the reaction in THF was too fast to be monitored at room temperature, we conducted the reaction at −78 °C under pseudo-first-order conditions with a 100-fold excess of freshly distilled methyl iodide (Figures 5 and 6).

A plot of ln *A* (absorbance) versus *t* (reaction time) gives a reasonable linear fit ($R = 0.993$), and the slope provides a value for the observed rate constant $k_{obs} = 2.1 \times 10^{-3}\ s^{-1}$ and hence, for a proposed overall second-order reaction, a second-order rate constant of $k_1 = 3.4 \times 10^{-3}\ M^{-1}\ s^{-1}$.

Conclusion

We have presented a synthetic route to a novel tridentate, monoanionic, meridionally coordinating pincer-type ligand that bears two N-heterocyclic carbene moieties substituted at the 1,8-positions of a carbazole backbone. This 3,6-di-*tert*-butyl-1,8-bis(3-methylimidazolin-2-yliden-1-yl)carbazolide (bimca) ligand has strong electron-donating properties. We synthesized its Rh(I) carbonyl complex **5**, which had a very low IR ν(CO) band of 1916 cm^{-1}, indicating strong metal−CO π-back-donation. The strong nucleophilicity of the Rh center was demonstrated by the formal oxidative addition of methyl iodide to give complex **6**, a reaction known to follow a S_N2 mechanism. To the best of our knowledge, this reaction clearly proceeds more quickly with complex **5** than with the Rh(CO) complexes reported in the literature so far.[12a] Further reactivity studies of complexes **5** and **6** as well as the synthesis of other bimca complexes are the subjects of our current research.

Experimental Section

General Procedures. Unless otherwise noted, all reactions were carried out under an atmosphere of dry argon using standard Schlenk techniques or were performed in a nitrogen-filled glovebox. All solvents were dried according to standard procedures and saturated with argon prior to use. Chemicals used were obtained from commercial suppliers and used without further purification. Lithium diisopropylamide[18] and 3,6-bis-*tert*-butylcarbazole[9b] were synthesized as reported.

^1H and ^{13}C NMR spectra were recorded using a Bruker ARX 250, DRX 300, or DRX 500 spectrometer. ^1H and ^{13}C chemical shifts are reported in ppm and calibrated to TMS on the basis of the solvent as an internal standard (2.49 ppm, DMSO-d_6; 1.73 ppm, THF-d_8; 7.15 ppm, benzene-d_6). Assignments of ^{13}C NMR spectra were made with the aid of 2D correlation spectra. All NMR spectra were acquired at room temperature. Mass spectra were recorded on a JEOL JMS-700 instrument with NBA (nitrobenzyl alcohol) as matrix. Infrared spectra were recorded using a Bruker Equinox 55 FT−IR spectrometer. In situ IR studies were carried out with a Mettler Toledo React IR 4000 spectrometer in THF under a dry argon atmosphere. Melting points were determined with a Büchi B 540 melting point apparatus. Elemental analyses were performed by the Mikroanalytisches Laboratorium der Chemischen Institute der Universität Heidelberg.

1,8-Diiodo-3,6-di-*tert*-butylcarbazole (1). Dahean et al.[19] reported the synthesis of this compound; however, no analytical data were given. The compound was synthesized according to a procedure given by Nakada et al. for 3,6-diphenyl-substituted species.[8]

^1H NMR (DMSO-d_6): δ 1.37 (s, 18H, $C(CH_3)_3$), 7.81 (d, ^4J(HH) = 3.0 Hz, 2H, H-2/7), 8.24 (d, ^4J(HH) = 3.0 Hz, 2H, H-4/5), 9.62 (s, 1H, NH). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 31.7 ($C(CH_3)_3$, 34.5 ($C(CH_3)_3$), 76.7 (carb-C1/8), 117.3 (carb-C4/5), 124.2 (carb-C4a/5a), 132.9 (carb-C2/6), 140.1 (carb-C1a/8a), 144.5 (carb-C3). HRMS (FAB; *m*/*z* (%)): calcd for $C_{20}H_{23}I_2N$ 530.9920, found 530.9915 (100); calcd for $C_{19}H_{20}I_2N$ 515.9685, found 515.9676 (48). Mp: 165−168 °C.

3,6-Di-*tert*-butyl-1,8-bis(imidazol-1-yl)carbazole (2). A mixture of 3,6-di-*tert*-butyl-1,8-diiodocarbazole (**1**; 1.33 g, 2.50 mmol), imidazole (851 mg, 12.5 mmol), cesium carbonate (1.79 g, 5.50 mmol), $(CuOTf)_2 \cdot C_6H_6$ (126 mg, 250 μmol), 1,10-phenanthroline (901 mg, 5.00 mmol), and dibenzylideneacetone (dba; 60.0 mg, 250 mmol) in 10 mL of toluene was stirred in a sealed Schlenk tube at 120 °C for 72 h to give a sluggish brown suspension. After removal of the solvent in vacuo the resulting deep brown solid was extracted three times with 60 mL of warm (40 °C) water and, after drying over P_4O_{10}, extracted three times with 60 mL of pentane. The resulting off-white solid was dissolved in 100 mL of tetrahydrofuran and the remaining residue removed by filtration. Evaporation of the solvent followed by recrystallization from toluene gave the product as a white solid in 89% yield. ^1H NMR (DMSO-d_6): δ 1.42 (s, 18H, $C(CH_3)_3$), 7.17 (s, 2H, H_{imi}-4), 7.42 (d, ^4J(HH) = 3.0 Hz, 2H, H_{carb}-4/5), 7.71 (s, 2H, H_{imi}-5), 8.20 (s, 2H, H_{imi}-2), 8.34 (d, ^4J(HH) = 3.0 Hz, 2H, H_{carb}-2/7), 10.94 (s, 1H, NH). ^{13}C-

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{^{1}H} NMR (DMSO-d_6): δ 31.7 (C(CH_3)$_3$, 34.6 (C(CH_3)$_3$), 116.3 (carb-C2/7), 119.5 (carb-C4/5), 120.2 (imi-C5), 122.0 (carb-C4a/5a), 125.6 (carb-C1a/8a), 128.9 (imi-C4), 132.7 (carb-C3/6), 137.0 (imi-C2), 143.2 (carb-C1/8). IR (KBr; cm^{-1}): 3142 (m), 3107 (m), 2964 (s), 1597 (w), 1502 (vs), 1321 (w), 1260 (m), 1238 (m), 1074 (m), 1033 (w), 744 (w), 652 (w). Mp: 296−300 °C dec. MS (FAB; *m*/*z* (%)): 412.51 [M$^+$ + H] (100), 396.47 [M$^+$ − CH_3] (47). Anal. Calcd for $C_{26}H_{29}N_5$: C, 75.88; H, 7.10; N, 17.02. Found: C, 75.62; H, 7.06; N, 16.86.

3,6-Di-*tert*-butyl-1,8-bis(3-methylimidazolium)carbazole Diiodide (bimca·2HI, 3a). A mixture of 3,6-di-*tert*-butyl-1,8-bis(imidazol-1-yl)carbazole (**2**; 430 mg, 1.04 mmol) in 5 mL of acetonitrile was treated with freshly distilled methyl iodide (195 μL, 3.14 mmol) under exclusion of light and stirred at room temperature for 48 h. After the suspension turned into a clear solution, the solvent was removed and the remaining white residue dried in vacuo. The product was formed quantitatively (99%) and could be used without further purification.

^{1}H NMR (DMSO-d_6): δ 1.45 (s, 18H, C(CH_3)$_3$), 4.01 (s, 6H, N−CH_3), 7.76 (s, 2H, H_{carb}-4/5), 8.07 (d, 2H, ^3J(HH) = 3.0 Hz, H_{imi}-5), 8.25 (d, ^3J(HH) = 3.0 Hz, 2H, H_{imi}-4), 8.64 (s, 2H, H_{carb}-2/7), 9.81 (s, 2H, H_{imi}-2), 11.42 (s, 1H, NH). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 31.6 (C(CH_3)$_3$), 34.9 (C(CH_3)$_3$), 36.3 (N−CH_3), 118.9 (carb-C4a/5a), 119.5 (carb-C2/7), 121.2 (carb-C4/5), 123.4 (imi-C4), 123.9 (imi-C5), 125.3 (carb-C1/8), 132.3 (carb-C1a/8a), 137.8 (imi-C2), 143.7 (carb-C3/6). IR (KBr; cm^{-1}): 3133 (s), 3059 (s), 2961 (s), 2865 (w), 1598 (m), 1575 (m), 1551 (m), 1496 (w), 1424 (w), 1365 (m), 1295 (s), 1229 (s), 1204 (w), 1141 (m), 995 (w), 879 (w), 838 (w), 740 (w), 656 (w), 614 (m). Mp: 347−354 °C dec. MS (ESI; *m*/*z* (%)): 568.2 [M$^+$ − I] (46), 440.3 [M$^+$ − 2I] (47), 220.8 [M$^+$ −2I]/2 (100). Anal. Calcd for $C_{28}H_{35}N_5I_2$: C, 48.36; H, 5.07; N, 10.07. Found: C, 48.31; H, 5.20; N, 9.67.

3,6-Di-*tert*-butyl-1,8-bis(3-methylimidazolium)carbazole Bis(tetrafluoroborate) (bimca·2HBF$_4$, 3b). A mixture of 3,6-di-*tert*-butyl-1,8-bis(imidazol-1-yl)carbazole (**2**; 842 mg, 2.05 mmol) in 20 mL of acetonitrile was treated with Meerwein's salt ($Me_3O^+BF_4^-$; 605 mg, 4.10 mmol) and stirred at ambient temperature for 1 h. The mixture turned into a clear pale yellow solution, and the solvent was removed in vacuo. The remaining off-white residue was extracted three times with 20 mL of water and dried in vacuo. The resulting raw product was recrystallized from ethanol to give an off-white product in 78% isolated yield. ^{1}H NMR (DMSO-d_6): δ 1.47 (s, 18H, C(CH_3)$_3$), 4.01 (s, 6H, N−CH_3), 7.76 (s, 2H, H_{carb}-4/5), 8.03 (d, ^3J(HH) = 3.0 Hz, 2H, H_{imi}-5), 8.23 (d, ^3J(HH) = 3.0 Hz, 2H, H_{imi}-4), 8.64 (s, 2H, H_{carb}-2/7), 9.70 (s, 2H, H_{imi}-2), 11.45 (s, 1H, NH). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 31.6 (C(CH_3)$_3$), 34.9 (C(CH_3)$_3$), 36.3 (N−CH_3), 119.0 (carb-C4a/5a), 119.5 (carb-C2/7), 121.2 (carb-C4/5), 123.5 (imi-C4), 123.9 (imi-C5), 125.4 (carb-C1/8), 132.3 (carb-C1a/8a), 137.8 (imi-C2), 143.7 (carb-C3/6). IR (KBr; cm^{-1}): 3316 (m), 3159 (m), 2955 (s), 1598 (m), 1580 (m), 1553 (m), 1497 (m), 1427 (w), 1365 (m), 1297 (s), 1266 (m), 1231 (s), 1084 (vs), 995 (m), 880 (w), 834 (w), 739 (w), 658 (w), 619 (w), 521 (w). Mp: 318−325 °C dec. MS (ESI; *m*/*z* (%)): 528.6 [M$^+$ − BF_4] (20), 441.5 [M$^+$ − 2 BF_4] (9), 440.5 [M$^+$ − 2BF_4 − H] (27), 220.8 [M$^+$ − 2BF_4]/2 (100). Anal. Calcd for $C_{28}H_{35}N_5B_2F_8$: C, 54.66; H, 5.73; N, 11.38. Found: C, 54.44; H, 5.78; N, 11.32.

Lithium 3,6-Di-*tert*-butyl-1,8-bis(3-methylimidazolin-2-yliden-1-yl)carbazolide (Li(bimca), 4). A suspension of **3b** (10.0 mg, 16.5 μmol) in 0.5 mL of tetrahydrofuran-d_8 was treated with lithium diisopropylamide (LDA; 5.22 mg, 49.5 μmol) at room temperature and stirred for 5 min to give a pale yellow, bluish fluorescent solution of the free bis(carbene) ligand (100% conversion (NMR)). ^{1}H NMR (THF-d_8): δ 1.49 (s, 18H, C(CH_3)$_3$), 4.12 (s, 6H, N−CH_3), 7.16 (s, 2H, H_{imi}-4), 7.40 (d, ^4J(HH) = 3.0 Hz, 2H, H_{carb}-2/7), 7.77 (s, 2H, H_{imi}-5), 7.99 (d, ^4J(HH) = 3.0 Hz, 2H, H_{carb}-4/5). ^{13}C{^{1}H} NMR (THF-d_8): δ 32.9 (C(CH_3)$_3$), 35.3 (C(CH_3)$_3$), 38.4 (N-CH_3), 111.4 (carb-C4/5), 114.2 (carb-C2/7), 119.7 (imi-C4), 120.1 (imi-C5), 128.3 (carb-C4a/5a), 128.4 (carb-C1/8), 135.6 (carb-C3/6), 143.7 (carb-C1a/8a), 206.1 ($C_{carbene}$).

Rh(bimca)(CO) (5). To a solution of the in situ generated Li(bimca) (**4**; 72.4 mg, 163 μmol) in 3 mL of THF was added a solution of [Rh(CO)$_2$Cl]$_2$ (31.7 mg, 81.5 μmol) in 2 mL of tetrahydrofuran at −30 °C. The solution was warmed to room temperature over 20 min to give a reddish yellow solution of the product (100% conversion (NMR)). Addition of 6 mL of pentane and cooling to −35 °C gave the raw product as a yellow solid. Filtration and extraction of the complex with benzene to remove inorganic impurities gave a yellow powder in 38% isolated yield. ^{1}H NMR (THF-d_8): δ 1.55 (s, 18H, C(CH_3)$_3$), 4.20 (s, 6H, CH_3), 7.45 (d, ^3J(HH) = 3.0 Hz, 2H, H_{imi}-4), 7.82 (d, ^4J(HH) = 3.0 Hz, 2H, H_{carb}-2/7), 8.16 (d, ^4J(HH) = 3.0 Hz, 2H, H_{carb}-4/5), 8.23 (d, ^3J(HH) = 3.0 Hz, 2H, H_{imi}-5). ^{1}H NMR (C_6D_6): δ 1.55 (s, 18H, C(CH_3)$_3$), 3.74 (s, 6H, CH_3), 6.14 (d, ^3J(HH) = 3.0 Hz, 2H, H_{imi}-4), 7.30 (d, ^3J(HH) = 3.0 Hz, 2H, H_{imi}-5), 7.63 (d, ^4J(HH) = 3.0 Hz, 2H, H_{carb}-2/7), 8.49 (d, ^4J(HH) = 3.0 Hz, 2H, H_{carb}-4/5). ^{13}C-{^{1}H} NMR (THF-d_8): δ 32.7 (C(CH_3)$_3$), 35.5 (C(CH_3)$_3$), 40.8 (N−CH_3), 111.4 (carb-C2/7), 114.5 (carb-C4/5), 116.8 (imi-C5), 124.1 (imi-C4), 125.7 (carb-C1/8), 127.7 (carb-C4a/5a), 137.3 (carb-C1a/8a), 139.5 (carb-C3/6), 183.0 (d, ^1J(RhC) = 47 Hz, $C_{carbene}$), 199.1 (d, ^1J(RhC) = 70 Hz, CO). ^{13}C{^{1}H} NMR (C_6D_6): δ 32.5 (C(CH_3)$_3$), 35.0 (C(CH_3)$_3$), 40.3 (N−CH_3), 110.9 (carb-C2/7), 114.7 (carb-C4/5), 115.7 (imi-C5), 122.7 (imi-C4), 125.4 (carb-C1/8), 129.3 (carb-C4a/5a), 137.3 (carb-C1a/8a), 139.2 (carb-C3/6), 182.5 (d, ^1J(RhC) = 45 Hz, $C_{carbene}$), CO signal not detected. IR (KBr; cm^{-1}): 2963 (s), 2865 (m), 2018 (w), 1916 (s), 1473 (m), 1439 (m) 1402 (m), 1361 (m), 1301 (m), 1261 (s), 1100 (m), 1017 (m), 800 (m), 683 (w). IR (THF, cm^{-1}): 1921 (ν_{CO}). Mp: 188−193 °C dec. MS (FAB; *m*/*z* (%)): 569.3 [M$^+$] (17), 541.3 [M$^+$ − CO] (100). Anal. Calcd for $C_{29}H_{32}N_5ORh$: C, 61.16; H, 5.66; N, 12.30. Found: C, 61.41; H, 5.82; N, 12.09.

Rh(bimca)(CO)MeI (6). To a solution of the Rh(I) complex **5** (16.5 mg, 28.9 μmol) in 5 mL of tetrahydrofuran was added an excess of freshly distilled methyl iodide (0.20 mL, 3.2 mmol) at −78 °C. The reaction mixture was stirred for 30 min at −78 °C. The color of the solution turned from yellow to light green. Evaporation of all volatiles gave the product as an analytically pure green crystalline solid in quantitative yield (99%). ^{1}H NMR (THF-d_8): δ 0.38 (d, ^2J(RhH) = 3.0 Hz, 3H, Rh−CH_3), 1.52 (s, 18H, C(CH_3)$_3$), 4.31 (s, 6H, CH_3), 7.51 (d, ^3J(HH) = 3.0 Hz, 2H, H_{imi}-4), 7.72 (d, ^4J(HH) = 3.0 Hz, 2H, H_{carb}-2/7), 8.11 (d, ^4J(HH) = 3.0 Hz, 2H, H_{carb}-4/5), 8.34 (d, ^3J(HH) = 3.0 Hz, 2H, H_{imi}-5). ^{1}H NMR (C_6D_6): δ 0.61 (s, 3H, Rh−CH_3), 1.50 (s, 18H, C(CH_3)$_3$), 3.81 (s, 6H, CH_3), 6.13 (s, 2H, H_{imi}-4), 7.22 (s, 2H, H_{imi}-5), 7.42 (s, 2H, H_{carb}-2/7), 8.37 (s, 2H, H_{carb}-4/5). ^{13}C{^{1}H} NMR (THF-d_8): δ 0.42 (d, ^1J(RhC) = 20.4 Hz, Rh−CH_3), 32.4 (C(CH_3)$_3$), 35.4 (C(CH_3)$_3$), 42.1 (N−CH_3), 111.4 (carb-C2), 115.4 (carb-C4), 118.1 (imi-C5), 124.6 (q, carb-C1/8), 126.0 (imi-C4), 128.7 (carb-C4a/5a), 135.7 (carb-C1a/8a), 139.7 (carb-C3/6), 167.3 (d, ^1J(RhC) = 35.5 Hz, $C_{carbene}$), 192.6 (d, ^1J(RhC) = 60.4 Hz, CO (obtained from an ^{13}-CO exchange experiment (125.76 MHz)). IR (KBr; cm^{-1}): 2963 (s), 2906 (w), 2864 (w), 2024 (s), 1594 (w), 1478 (m), 1448 (m), 1405 (m), 1363 (m), 1306 (m), 1262 (s), 1101 (vs), 1017 (vs), 800 (s), 689 (m), 468 (w). IR (THF; cm^{-1}): 2022 (ν_{CO}). Mp: 175−185 °C dec. MS (FAB; *m*/*z* (%)): 683.3 [M$^+$ − CO] (11), 584.3 [M$^+$ − I] (29), 556.4 [M$^+$ − CO − I] (100), 541.3 [M$^+$ − CO − CH_3 − I] (96). Anal. Calcd for $C_{30}H_{35}N_5IORh$: C, 50.65; H, 4.96; N, 9.84. Found: C, 50.58; H, 5.14; N, 9.65.

X-ray Crystal Structure Determination. X-ray structures were obtained with a Bruker SMART CCD diffractometer for **3b** and **5** and with a Bruker APEX diffractometer for **3a** and **6**, both with a Mo Kα tube (λ = 0.710 73 Å, monochromator: highly oriented

Table 1. Crystal Data and Structure Refinement Details for 3a, 3b, 5, and 6[a]

	3a	3b	5	6
empirical formula	$C_{28.50}H_{36.50}I_{2.50}N_5$	$C_{29.50}H_{40}B_2F_8N_5O_{1.50}$	$C_{31}H_{38}N_5O_2RhS$	$C_{36}H_{47}IN_5O_3Rh$
formula wt	766.38	662.29	647.63	827.60
temp (K)	100(2)	200(2)	200(2)	200(2)
cryst syst	orthorhombic	orthorhombic	monoclinic	triclinic
space group	$Cmc2_1$	$Pbcn$	$P2_1/c$	$P\bar{1}$
Z	4	8	4	2
unit cell dimens				
a (Å)	13.594(1)	14.0380(2)	12.6115(6)	7.5073(5)
b (Å)	22.932(2)	10.9873(2)	22.2078(10	13.4334(9)
c (Å)	9.9211(8)	43.2200(5)	11.4251(5)	19.6105(13)
α (deg)	90.0	90.0	90.0	70.286(1)
β (deg)	90.0	90.0	104.611(1)	83.572(2)
γ (deg)	90.0	90.0	90.0	80.419(2)
V (Å^3)	3092.9(4)	6666.24(17)	3096.4(2)	1832.5(2)
calcd density (g/cm^3)	1.65	1.32	1.39	1.500
abs coeff (mm^{-1})	2.56	0.11	0.65	1.349
cryst color	colorless	colorless	yellow	green
cryst shape	irregular	polyhedron	polyhedron	polyhedron
θ range for data collecn (deg)	1.7−27.9	0.9−22.5	1.7−22.9	1.63−28.30
index ranges	$-17 \le h \le 17$	$-15 \le h \le 15$	$-13 \le h \le 13$	$-10 \le h \le 9$
	$-30 \le k \le 30$	$-11 \le k \le 11$	$-24 \le k \le 24$	$-17 \le k \le 17$
	$-13 \le l \le 12$	$-46 \le l \le 46$	$-12 \le l \le 12$	$-26 \le l \le 25$
no. of rflns collected	15 804	42 527	21 988	19 350
no. of indep rflns (R(int))	3803 (0.0491)	4334 (0.0780)	4265 (0.1036)	8947 (0.0390)
no. of obsd rflns ($I > 2\sigma(I)$)	3490	3298	2479	6636
abs cor	semiempirical from equivalents			
max, min transmissn	0.90, 0.88	0.98, 0.97	0.97, 0.83	0.92, 0.70
no. of data/restraints/params	3803/1/175	4334/75/469	4265/20/380	8947/42/462
goodness of fit on F^2	1.05	1.11	0.99	0.99
final R indices (I > 2σ(I))				
R1	0.044	0.051	0.040	0.038
wR2	0.109	0.122	0.076	0.077
largest diff peak, hole (e/Å^3)	2.64, −2.32	0.30, −0.35	0.38, −0.47	0.79, −0.45

[a] In all cases, the refinement method was full-matrix least squares on F^2.

graphite) as X-ray source. Determination and refinement of the crystal structures have been carried out with the Bruker SHELXTL software.[20]

Crystal data and structure refinement details for **3a**, **3b**, **5**, and **6** are given in Table 1.

Kinetic Experiment. For the oxidative addition reaction a 3.5 × 10^{-5} M solution of Rh(bimca)CO (**5**) was placed in a 10 mL reaction flask with the measurement cell and cooled to −78 °C. After the thermal equilibrium was achieved, a 100-fold excess (to employ pseudo-first-order conditions) of freshly distilled, precooled MeI was added (the extra volume has been considered) with a syringe with rapid stirring. Spectra were scanned in the metal carbonyl ν(CO) region (2200−1500 cm^{-1}) and saved at regular time intervals under computer control. After the kinetic run, absorbance versus time data for the appropriate ν(CO) frequencies were extracted offline using Microsoft Office Excel 2003 software. The decay of the ν(CO) band was well fitted by an exponential curve with a correlation coefficient of 0.993 to give the value for the observed rate constant $k_{obs} = 2.1 \times 10^{-3}$ s^{-1} and hence, for a proposed overall second-order reaction, a second-order rate constant of $k_1 = 3.4 \times 10^{-3}$ M^{-1} s^{-1}.

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Supporting Information Available: CIF files giving X-ray crystallographic data for **3a**, **3b**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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