ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

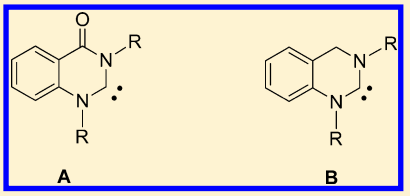
A New Mixed Amino−Amido N-Heterocyclic Carbene Based on Anthranilic Acid

Abdelaziz Makhloufi, Michaela Wahl, Walter Frank, and Christian Ganter*

Institut für Anorganische Chemie und Strukturchemie, Heinrich-Heine-Universität Düsseldorf, Universitätsstrasse 1, D-40225 Düsseldorf, Germany

Supporting Information

ABSTRACT: The synthesis of a new mixed amino−amido N-heterocyclic carbene (type **A**) starting from anthranilic acid is presented. A new straightforward synthetic approach to related diaminocarbenes of type **B** is also described. Both NHCs react with group 6 elements to form heteroureas and coordinate to L_2ClM fragments (M = Rh, Ir; L_2 = COD, $(CO)_2$). IR spectroscopic analysis of the carbonyl complexes reveals that the diamino-NHC is a better donor ligand (TEP: 2054 cm^{-1}) compared to the amino−amido NHC (TEP: 2060 cm^{-1}). In line with this behavior, a carbene dimerization to give the corresponding olefin is observed only for derivatives of type **A**. X-ray structure determinations are reported for two Rh complexes of ligand **A** and its cationic precursor.



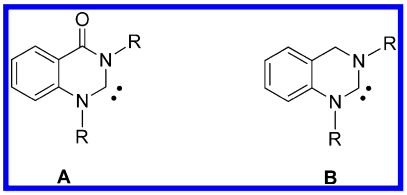
INTRODUCTION

N-Heterocyclic carbenes (NHCs) have developed into a well-recognized class of compounds with applications as ligands for organometallic complexes and organocatalysts within the last twenty years.[1] The modification of the electronic nature of NHCs continues to stimulate active current research, and a number of different backbone structures and substitution patterns have been reported within this context.[2] In diaminocarbenes the nitrogen lone pairs provide electron density for the stabilization of the carbene carbon atom, whereas this electron-donating effect is drastically diminished in the case of diamidocarbenes.[3] Accordingly, when regarded as ligands in transition metal complexes, the former are classified as superb σ-donors, while for the latter a π-acceptor interaction also contributes significantly to the metal−carbene bonding. Additionally, the diamido substitution pattern leads to a smaller singlet−triplet gap and endows the diamidocarbenes with some electrophilic reactivity in addition to the typical nucleophilic behavior of NHCs. Mixed amino−amido-type NHCs show properties intermediate between those described above.[4] In continuation of our efforts to develop new backbone structures for electron-poor NHCs[5] we present here a new amino−amido carbene **A**, which is easily derived from anthranilic acid. A related diamino NHC **B** based upon the same scaffold was also accessed to enable a comparison of electronic properties. Our report is stimulated by a very recent publication by Zhang and Shi,[6] who described an alternative synthetic approach to the diamino carbenes **B**.

RESULTS AND DISCUSSION

Synthesis of Anthranilic Acid-Based NHCs 6. The cyclic amidinium salts **5** were identified as precursors for the new carbene structure **A**, and they were synthesized as depicted in Scheme 1. The basic heterocyclic scaffold quinazolin-4-one **3** was assembled by the condensation of anthranilic acid **1** and formamide **2** at elevated temperature according to a protocol described by Sherill.[7] Introduction of the substituent at the amide nitrogen atom was achieved by treatment of **3** with KOH and an excess of alkylation reagent (MeI, EtI, BzBr) in acetonitrile at elevated temperature, affording the neutral derivatives **4** in good yield.

Chart 1. Types of N-Heterocyclic Carbenes Reported in This Contribution



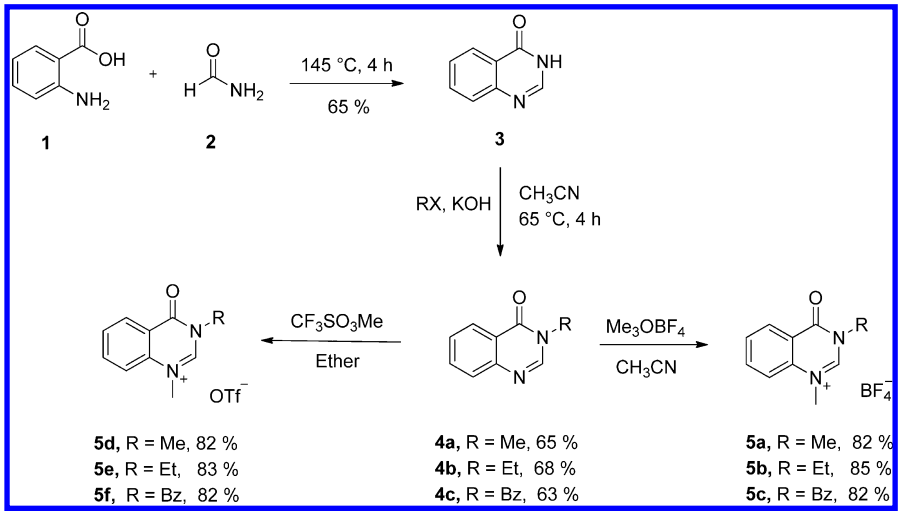
More powerful alkylation reagents were required for the conversion of derivatives **4** to the respective amidinium salts **5**. Thus, treatment of **4** with either methyltriflate in ether or Meerwein's salt (Me_3O BF_4) in acetonitrile at room temperature provided the desired cations with tetrafluoroborate (**5a**−**c**) or triflate (**5d**−**f**) anions as colorless crystalline solids in high yield.

The ^1H and ^{13}C resonances for the amidinium moiety NCHN were detected at 9.84−10.12 and 153.9−154.5 ppm, respectively. Crystals of the tetrafluoroborate salt **5a**-(BF_4) were obtained by diffusion of ether into a THF solution and examined by X-ray diffraction analysis. The molecular structure of the cation is depicted in Figure 1 together with selected geometrical data. The molecule is entirely flat and shows bond lengths and angles that are comparable to those in related amidinium carbene precursors.[3a,8] The C1−N1 bond involving the amide-type nitrogen N1 is significantly longer (1.321(4) Å)

Received: November 28, 2012
Published: January 22, 2013

   dx.doi.org/10.1021/om301152n | *Organometallics* 2013, 32, 854−861

Scheme 1. Preparation of Quinazoline-4-ones and Cationic Carbene Precursors



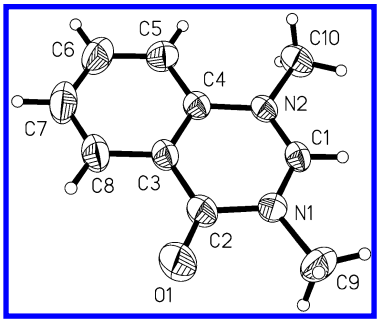


Figure 1. Structure of the cation in the crystal of compound **5a**-(BF_4). Bond lengths [Å] and angles [deg]: O1−C2 1.210(4), N1−C1 1.321(4), N1−C2 1.408(5), N2−C1 1.297(4), N2−C4 1.409(4), C2−C3 1.441(5), C3−C4 1.381(5); C1−N1−C2 121.2(3), C1−N2−C4 120.0(3), N2−C1−N1 124.4(3), N1−C2−C3, 115.3(3), C4−C3−C2 120.8(3), C3−C4−N2 118.3(3).

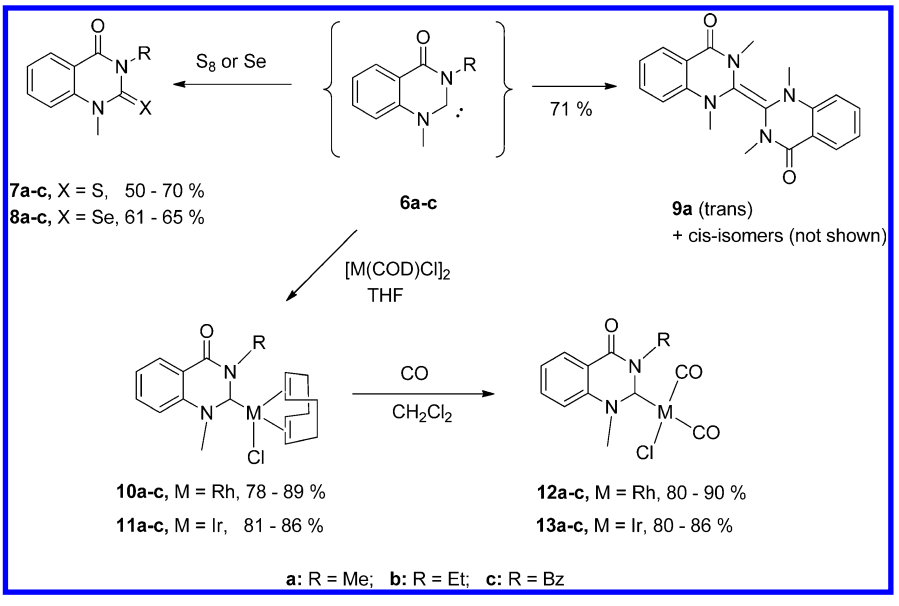
than the C1−N2 bond to the amine-type nitrogen N2 (1.297(4) Å).

The amino−amido carbenes **6** were then successfully generated in situ by deprotonation of the amidinium salts **5** with NaHMDS in THF at −80 °C and trapped by elemental sulfur or selenium, resulting in the formation of the heteroureas **7** and **8** (Scheme 2). When **6a** was generated in the absence of a scavenging reagent, the corresponding olefin **9a** arising from carbene dimerization was isolated in 71% yield after workup as a mixture of cis and trans isomers (ca. 1:1 ratio), as evident from two signal sets in the ^{1}H and ^{13}C NMR spectra.

After the successful trapping of the in situ generated carbene, the preparation of metal complexes was studied. NHC precursors **5a−c** were deprotonated with KOtBu in THF at −80 °C in the presence of $[(COD)MCl]_2$ (M = Rh, Ir), resulting in the metal complexes **10a−c** and **11a−c** (Scheme 2).

All (COD)metal complexes were isolated in high yield after column chromatography and were fully characterized. For the (COD)Rh complexes **10** doublet resonances were observed in the ^{13}C NMR spectra for the carbene C atoms as a result of a $^{1}J_{C-Rh}$ coupling of ca. 50 Hz. Suitable crystals of complexes **10a**

Scheme 2. Reactions of Carbenes 6



dx.doi.org/10.1021/om301152n | Organometallics 2013, 32, 854−861

and **10c** were examined by X-ray diffraction (Figures 2 and 3). **10c** crystallizes in the monoclinic space group $P2_1/c$ with two

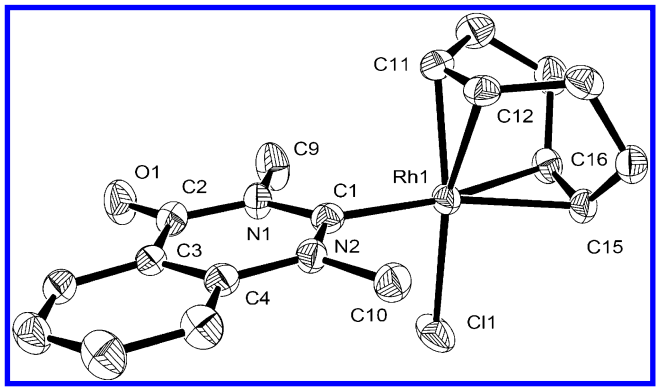


Figure 2. Molecular structure of compound **10a** in the solid state. H atoms are omitted for clarity. Displacement factors are shown at the 30% probability level. Selected bond lengths [Å] and angles [deg]: Rh1−C1 2.030(4), Rh1−C11 2.111(4), Rh1−C12 2.128(3), Rh1−C15 2.190(3), Rh1−C16 2.228(3), Rh1−Cl1 2.3710(10), O1−C2 1.224(4), N1−C2 1.397(5), N1−C1 1.382(5), N2−C1 1.341(4), N2−C4 1.408(4), C2−C3 1.447(5), C3−C4 1.394(5); C1−Rh1−Cl1 87.37(10), N2−C1−N1 116.3(3).

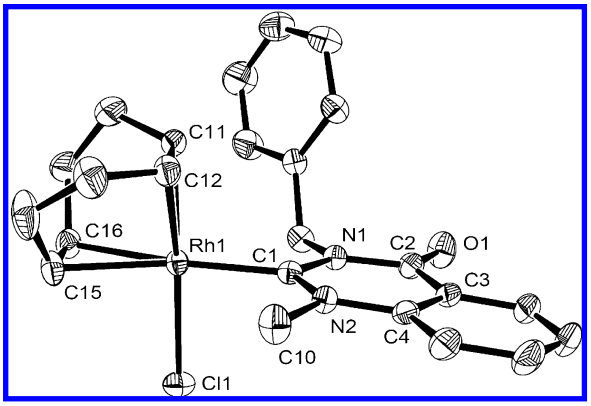


Figure 3. Molecular structure of compound **10c** in the solid state. Only one of two independent molecules in the asymmetric unit is shown. H atoms are omitted for clarity. Displacement factors are shown at the 30% probability level. Selected bond lengths [Å] and angles [deg]: Rh1−C1 2.026(4), Rh1−C11 2.131(2), Rh1−C12 2.125(2), Rh1−C15 2.221(2), Rh1−C16 2.218(2), Rh1−Cl1 2.3780(6), O1−C2 1.216(3), N1−C2 1.404(3), N1−C1 1.375(3), N2−C1 1.345(3), N2−C4 1.402(3), C2−C3 1.452(3), C3−C4 1.392(3); C1−Rh1−Cl1 87.27(6), N2−C1−N1 116.1(2).

independent molecules in the asymmetric unit, which show identical geometrical parameters within experimental uncertainty. In both structures, the plane of the essentially flat carbene ligand is in a perpendicular arrangement to the coordination plane of the rhodium atom. Bond lengths and angles are not significantly affected by the exchange of a methyl (**10a**) for a benzyl group (**10c**); they coincide for both structures within the 3σ range. In complex **10a**, the Rh1−C1 bond of 2.030(4) Å and the Rh−C distances to the olefinic carbon atoms of the COD ligand cis (ca. 2.12 Å) and trans (ca. 2.20 Å) to the carbene are within the range usually observed for complexes of this type.[1b,c,4g,h,9] More specifically, the Rh−C distance is identical to that for the complex with the 1,3-dimethylimidazol-2-ylidene ligand,[10] while it is 3 pm shorter than that reported by Zhang and Shi for a related complex containing a ligand of type **18** (vide infra).[6] Within the six-membered heterocycle of the NHC ligand, the C(carbene)−N bond lengths show comparable differences, as described above for the precursor molecule **5a**: the longer C1−N1(amide) bond of 1.382(5) Å reflects the reduced interaction of this amide-type nitrogen with the carbene center compared to the amine-type N atom with a C1−N2 distance of 1.341(4) Å. In both carbene complexes the C1−N bonds are significantly elongated by ca. 5 pm compared to the amidinium precursor, while the N−C−N angle decreases by 8°.

The Tolman electronic parameter (TEP) is a commonly applied measure of the donor properties of NHC ligands,[1c] and it can be easily calculated from the CO stretching vibrations of suitable NHC−metal carbonyl complexes.[2e,11] Therefore, in order to classify the new carbenes **6**, the dicarbonyl complexes **12** and **13** were prepared by passing a slow stream of CO through dichloromethane solutions of the (COD)metal complexes **10** and **11** (Scheme 2). Complexes **12** and **13** were characterized in solution by NMR, mass spectrometry, and IR. The stretching vibrations of the carbonyl ligands are listed in Table 1 together with the TEP values derived thereof.

Table 1. CO Streching Vibrations (CH_2Cl_2 solution) and δ ^{13}C of the Carbene C Atom for Carbonyl Complexes 12, 13, 23, and 24

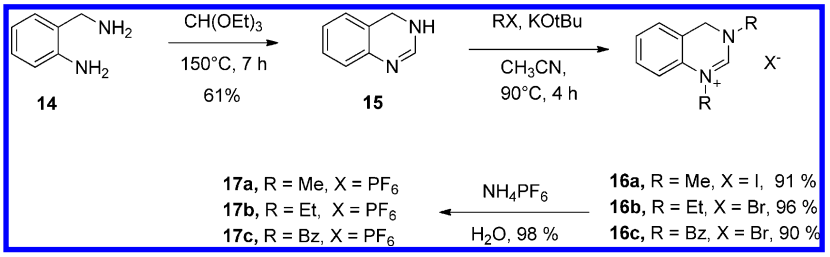
complex	ligand	ν(CO) (cm^{-1})	δ ^{13}C (ppm)	TEP (cm^{-1})
12a	**6a**	2089, 2010	219	2060
12b	**6b**	2088, 2010	219	2059
12c	**6c**	2089, 2012	213	2061
13a	**6a**	2075, 1994	210	2060
13b	**6b**	2075, 1993	210	2060
13c	**6c**	2075, 1995	213	2061
23a	**18a**	2075, 2003	198	2051
23b	**18b**	2075, 2002	214	2051
23c	**18c**	2082, 2005	208	2055
24a	**18a**	2062, 1986	201	2051
24b	**18b**	2071, 1989	218	2056
24c	**18c**	2070, 1989	208	2056

Synthesis of Diamino NHC Derivatives 18. In order to assess the influence of the keto group attached to the scaffold of NHC **6**, the synthesis of related diamino NHCs **18** was targeted. The appropriate amidinium salt precursors **16** are straightforwardly available from 2-aminobenzylamine **14**, which was cyclized by treatment with triethylorthoformate at elevated temperature, affording the dihydrochinazoline **15** in 61% yield.[12] Reaction of **15** in acetonitrile with alkylating reagents (MeI, EtI, BzBr) in the presence of KOtBu provided the desired amidinium salts **16** as colorless crystalline solids in excellent yield (Scheme 3), which were fully characterized by NMR spectroscopy, mass spectrometry (ESI-MS), and elemental analysis. Zhang and Shi reported recently the syntheses of several dihydrochinazolinium salts via imine formation from aromatic aldehydes.[6] Their approach allows the preparation of derivatives with different substituents attached to the nitrogen atoms including aryl groups. However, sophisticated starting materials and/or Pd-catalyzed coupling reactions are required. Notably, the protocol described here provides the dihydrochinazolinium salts in two steps commencing from cheap convenient starting materials.

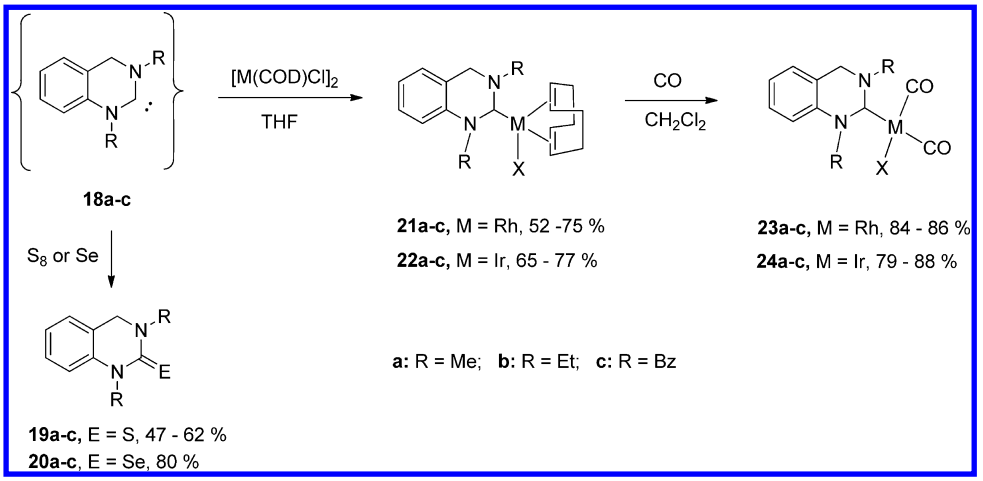
Characteristic downfield resonances for the C2−H fragment were observed in the ^{1}H (8.73−9.87 ppm) and ^{13}C NMR

dx.doi.org/10.1021/om301152n | Organometallics 2013, 32, 854−861

Scheme 3. Preparation of Amidinium Salts 16 and 17



Scheme 4. Reactions of Carbenes 18



spectra (152−153 ppm) of the cations **16a−c**. Anion exchange from halide to PF_6^- did not significantly increase the solubility of the cationic carbene precursors in organic solvents. Both hexafluorophosphates **17** and halide derivatives **16** were used for subsequent reactions.

Treatment of the amidinium salts **16a−c** with NaHMDS in THF at −80 °C led to the formation of the corresponding carbenes **18a−c** (Scheme 4), which were trapped by addition of S_8 or selenium to give the corresponding heteroureas **19** and **20** in good yield after standard workup. In the absence of trapping reagents, formation of the carbenes **18** was evident from the absence of the characteristic downfield signal for the C2H proton of the precursor in the ^{1}H NMR spectra recorded at −80 °C. However, the free carbenes **18** turned out to be extremely moisture sensitive and were hydrolyzed much faster than a ^{13}C NMR spectrum could be recorded. The resulting ring-opened N(*o*-aminobenzyl)formamide was identified by NMR spectra and MALDI mass spectra. No indication of a dimerization product was observed. NHC metal complexes were then obtained as outlined above by reaction of the free carbene—obtained in situ by precursor deprotonation with KOtBu at −80 °C—with $[(COD)MCl]_2$ (M = Rh, Ir) in THF, affording the COD derivatives [(COD)M(**18**)Cl] **21** and **22**, which were subsequently converted to the carbonyl complexes **23** and **24** in good yield (Scheme 4).

All COD complexes were purified by chromatography on silica and completely characterized by NMR and mass spectrometry because halide exchange at the metal center from chloride to iodide or bromide (which were present from the starting materials **16**) prevented correct elemental analyses. The protons of the CH_2 group of the carbene ligand in complexes **21** and **22** appeared to be diastereotopic, giving rise to an AB pattern in the ^{1}H NMR spectra. In the ^{13}C NMR spectra of the Rh complexes **21** the carbene carbon appeared as doublets in the range from 208 to 215 ppm due to a $^1J_{C-Rh}$ coupling of 42−46 Hz, while singlet resonances were obtained in the case of the iridium complexes **22** between 203 and 206 ppm. All complexes were also identified in the ESI mass spectra, where a base peak corresponding to the [M − X] fragment was present.

The CO stretching vibrations recorded for the carbonyl complexes **23** and **24** are listed in Table 1 together with the corresponding TEP values calculated from these data. For the amino−amido NHCs **6**, the TEP values for the Rh (**12**) and Ir (**13**) bound ligands are identical and the influence of the one N substituent (**a**, **b**, **c**) is within a small range of 2 cm^{-1}. A mean TEP value of 2060 cm^{-1} is typical for mixed amino−amido NHCs.[3m,4] For the diamino NHCs **18** an average TEP of 2054 cm^{-1} is calculated, reflecting the increased donor capacity of this NHC type. However, much more scattered individual values are seen: for the same N-substituents, the TEP values derived for Rh (**23**) and Ir (**24**) complexes differ by 3 cm^{-1}, and a difference of 5 cm^{-1} is noted when comparing N-Me and N-Et derivatives **24a** and **24b**, respectively. While it is comprehensible that the variation of substituents at both N atoms of the heterocycle—as is the case for carbenes **18**—has a more pronounced effect on the donor properties of the carbene than the permutation of only one N-substituent as in the case of NHCs **6**, a difference of 5 wavenumbers for the Me and Et NHCs **18a** and **18b**, respectively, is certainly more than one would expect for such a structural variation. Care should thus be taken in order not to overestimate TEP values, especially if they are obtained under nonidentical conditions.[1c] Interestingly, Shi and co-workers reported IR data for complexes of NHCs similar to **18** bearing different substituents on the N atoms (e.g., iPr and Bz), which were recorded as KBr disks.[6] Conversion of their CO stretching vibrations leads to TEP

dx.doi.org/10.1021/om301152n | *Organometallics* 2013, 32, 854−861

values around 2044 cm^{-1}, well apart from our values, which were recorded in dichloromethane solution.

CONCLUSION

Two six-ring NHC systems with benzo anellation are easily accessible from convenient starting materials in high yield. Assessment of the electronic properties of the new ligands by means of IR spectroscopy reveals a higher donor capacity for the diamino carbenes **18** compared to the mixed amino−amido NHCs of type **6**. Further studies concerning the reactivity and potential applications especially of the latter type are currently under way.

EXPERIMENTAL SECTION

General Considerations. All reactions were performed with standard Schlenk techniques in an oxygen-free dry nitrogen atmosphere. Glassware was dried at 120 °C in an oven for at least 12 h. Solvents were dried and distilled under nitrogen by using standard procedures. Diethyl ether and THF were distilled over sodium/benzophenone, dichloromethane over CaH_2, and *n*-hexane over sodium. NMR spectra were recorded on a Bruker Avance DRX 200 and a Bruker Avance DRX 500 spectrometer. ^1H and $^{13}C\{^1H\}$ spectra are referenced to the residual solvent signal. Mass spectra were recorded on a Thermo Finnigan Trace DSQ 7000 (EI), Ion Trap-API mass spectrometer, and Bruker Ultraflex I TOF (MALDI). Elemental analyses were recorded on a Perkin CHN 2400 series II. IR spectra were obtained with a Shimadzu IR Affinity-1 spectrometer. Reagents such as potassium *tert*-butoxide and NaHMDS (2 M in THF) were purchased from Acros Organics and Sigma Aldrich and used as received. $[RhCl(COD)]_2$ and $[IrCl(COD)]_2$ were synthesized according to a literature procedure.[13]

Synthesis of Compound 3. A 50 mL Schlenk flask was charged with anthranilic acid (8.2 g, 60 mmol, 1.0 equiv) and formamide (10.0 mL, 250 mmol, 4.2 equiv). The mixture was stirred for 3 h at 150 °C. After 2 h a white precipitate formed. The solid was filtered off, washed with 20 mL of diethyl ether and 20 mL of *n*-hexane, and subsequently dried in vacuo to yield 5.70 g (65%) of **3** as a white powder. ^1H NMR (200 MHz, DMSO-d_6): δ 10.36 (s, 1H, NH), 8.14 (m, 1H, Ar−CH), 8.08 (s, 1H, NCHN), 7.78 (m, 1H, Ar−CH), 7.67 (m, 1H, Ar−CH), 7.49 (m, 1H, Ar−CH). ^{13}C NMR (126 MHz, DMSO-d_6): δ 161.1 (s, C═O), 149.1 (aromatic C), 145.8 (s, NCHN), 135.0, 128.0, 127.1, 126.2, 123.0 (all aromatic C). MS (EI): m/z 146 $[M]^+$. Anal. Calcd (%) for $C_8H_6N_2O$: C, 65.75; H, 4.14; N, 19.17. Found: C, 65.48; H, 4.38; N, 19.34.

Synthesis of Compound 4a. A suspension of **3** (1.00 g, 6.94 mmol, 1.0 equiv) and KOH (1.17 g, 20.8 mmol, 3 equiv) in 60 mL of acetonitrile was stirred for 15 min at room temperature, and iodomethane (0.48 mL, 7.6 mmol, 1.1 equiv) was added dropwise. The resulting suspension was stirred for 4 h at 65 °C. After removing the solvent in vacuo, the crude product was suspended in 20 mL of H_2O and 20 mL of CH_2Cl_2. The organic phase was washed three times with 20 mL of H_2O and dried over sodium sulfate, the combined organic phases were evaporated in vacuo, and **4a** was obtained as a bright yellow solid (720 mg, 65%). ^1H NMR (200 MHz, $CDCl_3$): δ 8.36−8.31 (m, 1H, Ar−CH), 8.08 (s, 1H, NCHN), 7.83−7.69 (m, 2H, Ar−CH), 7.57−7.49 (m, 1H, Ar−CH), 3.62 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.6 (s, C═O), 147.3 (s, NCHN), 145.8, 133.2, 126. 4, 126.3, 125.5, 121.0 (all aromatic C), 33.1 (s, CH_3). MS (EI): m/z 160 $[M]^+$. Spectral data were consistent with literature values.

Synthesis of Compound 5a. A mixture of **4a** (580 mg, 3.63 mmol, 1.0 equiv) and trimethyloxonium tetrafluoroborate (697 mg, 4.71 mmol, 1.3 equiv) in 30 mL of acetonitrile was stirred at room temperature overnight. The solvent was removed in vacuo, and the yellow crude product was dissolved in 5 mL of acetonitrile and treated with 25 mL of diethyl ether. After a few minutes a white solid precipitated and was filtered off, washed with 20 mL of diethyl ether, and subsequently dried in vacuo to yield 780 mg (82%) of **5a** as a white solid. Single crystals of **5a** were grown by slow evaporation from acetonitrile/*n*-hexane. ^1H NMR (200 MHz, DMSO-d_6): δ 9.84 (s, 1H, NCHN), 8.38−8.34 (m, 1H, Ar−CH), 8.22−8.15 (m, 1H, Ar−CH), 8.06−8.01 (m, 1H, Ar−CH), 7.92−7.85 (m, 1H, Ar−CH), 4.06 (s, 3H, CH_3), 3.65 (s, 3H, CH_3). ^{13}C NMR (126 MHz, DMSO-d_6): δ 158.1 (s, C═O), 154.1 (s, NCHN), 138.0, 136.7, 129.9, 127.7, 119.3, 118.4 (all aromatic C), 40.1 (s, CH_3), 35.8 (s, CH_3). MS (MALDI): m/z 176 $[M - BF_4]^+$. Anal. Calcd (%) for $C_{10}H_{11}BF_4N_2O$: C, 45.84; H, 4.23; N, 10.69. Found: C, 45.81; H, 4.34; N, 10.58.

Synthesis of Compound 5d. A 100 mL Schlenk flask was charged with **4a** (2.19 g, 13.7 mmol, 1.0 equiv) in 30 mL of diethyl ether. After stirring for 15 min at room temperature, methyltriflate (2.0 mL, 17.79 mmol, 1.3 equiv) was added dropwise and the mixture was stirred overnight. A white-yellow solid precipitated and was filtered, washed with small portions of acetonitrile and diethyl ether, and subsequently dried in vacuo to yield 3.63 g (82%) of **5d** as a white solid. ^1H NMR (200 MHz, DMSO-d_6): δ 9.88 (s, 1H, NCHN), 8.40−7.38 (m 4H, Ar−CH), 4.09 (s, 3H CH_3), 3.66 (s, 3H, CH_3). ^{13}C NMR (126 MHz, DMSO-d_6): δ 169.7 (C═O), 160.8 (NCHN), 138.4, 137.2, 129.3, 128.1 (all aromatic C), 122.3 (q, CF_3), 119.8, 118.9 (all aromatic C), 40.1 (s, CH_3), 35.8 (s, CH_3). MS (MALDI): m/z 175 $[M - CF_3SO_3]^+$. Anal. Calcd (%) for $C_{11}H_{11}F_3N_2O_4S{\cdot}H_2O$: C, 39.64; H, 3.63; N, 8.41. Found: C, 39.56; H, 4.00; N, 8.47.

Synthesis of Compound 7a. A suspension of **5a** (150 mg, 0.56 mmol, 1.0 equiv) and S_8 (220 mg, 0.84 mmol, 1.5 equiv) in 20 mL of THF was cooled to −80 °C, and NaHMDS (2 M in THF, 0.23 mL, 1.13 mmol, 2.0 equiv) was added dropwise. The resulting orange solution was stirred for 10 min at −80 °C, the cooling bath was removed, and the solution was allowed to warm to room temperature within 2.5 h. After evaporation of all volatiles, the crude product was dissolved in 20 mL of dichloromethane and filtered through a short pad of Celite. The filtrate was evaporated, and the yellow solid was purified by flash chromatography on aluminum oxide with dichloromethane as mobile phase. All volatiles were evaporated in vacuo, to yield **7a** as a white solid (57.7 mg, 50%). ^1H NMR (200 MHz, $CDCl_3$): δ 8.30−8.25 (m 1H, Ar−CH), 7.78−7.70 (m, 1H, Ar−CH), 7.40−7.32 (m, 2H, Ar−CH), 4.17 (s, 3H CH_3), 3.91 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 178.3 (s, C═S), 159.9 (s, C═O), 141.2, 135.8, 129.4, 125.1, 117.5, 115.4 (all aromatic C), 39.4 (s, CH_3), 36.4 (s, CH_3). MS (EI): m/z 206 $[M]^+$. Spectral data were consistent with literature values.

Synthesis of Compound 8a. A suspension of **5a** (300 mg, 1.15 mmol, 1.0 equiv) and Se (132.2 mg, 1.72 mmol, 1.5 equiv) in 20 mL of THF was cooled to −80 °C, and NaHMDS (2 M in THF, 0.35 mL, 1.72 mmol, 1.5 equiv) was added dropwise. The resulting gray solution was stirred for 10 min at −80 °C, the cooling bath was removed, and the solution was allowed to warm to room temperature within 2.5 h. After evaporation of all volatiles, the crude product was dissolved in 10 mL of CH_2Cl_2 and filtered through a short pad of Celite. The filtrate was treated with 20 mL of *n*-hexane and subsequently dried in vacuo to yield 174.5 mg (65%) of **8a** as a white powder. ^1H NMR (200 MHz, $CDCl_3$): δ 8.34−8.29 (m 1H, Ar−CH), 7.84−7.75 (m, 1H, Ar−CH), 7.50−7.42 (m, 2H, Ar−CH), 4.38 (s, 3H CH_3), 4.09 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 181.2 (s, C═Se), 159.0 (s, C═O), 141.2, 136.0, 129.5, 126.7, 117.8, 115.9 (all aromatic C), 43.5 (s, CH_3), 40.1 (s, CH_3). GC/MS (EI): m/z = 254 $[M]^+$. Anal. Calcd (%) for $C_{10}H_{10}N_2OSe$: C, 47.44; H, 3.98; N, 11.07. Found: C, 48.06; H, 4.36; N, 10.84.

Synthesis of cis/trans-Olefin (9a). To a suspension of **5d** (240 mg, 0.74 mmol, 1.0 equiv) at 25 °C in 20 mL of THF was added NaHMDS (2 M in THF, 0.18 mL, 0.89 mmol, 1.2 equiv) dropwise. After 25 min at 25 °C the clear yellow solution was dried in vacuo and the yellow crude product was washed with 20 mL of *n*-hexane and 20 mL of diethyl ether to give **9** as a colorless solid (183 mg, 71%). cis-Isomer: ^1H NMR (200 MHz, $CDCl_3$): δ 8.02 (m, 2H, Ar−H), 7.52−7.41 (m, 2H, Ar−H), 7.09−6.90 (4H, Ar−H), 3.26 (s, 6H, CH_3), 3.16 (s, 6H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 163.8 (C═O), 147.2, 134.0, 129.4, 127.0, 121.3, 119.7, 115.5, 40.0 (s, CH_3), 34.6. trans-Isomer: ^1H NMR (200 MHz, $CDCl_3$): δ 8.02 (m, 2H, Ar−CH), 7.47 (m, 2H, Ar−CH), 7.09−6.90 (m, 4H, Ar−H), 3.22 (s, 6H, CH_3), 3.14

dx.doi.org/10.1021/om301152n | *Organometallics* 2013, 32, 854−861

(s, 6H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 164.1 (C═O), 147.1, 134.0, 129.2, 127.0, 120.7, 119.21, 114.53, 39.4 (s, CH_3), 34.5 (s, CH_3). MS (MALDI): m/z 348 $[M]^+$. HRMS (ESI): $[M + H^+]^+$ calcd for $C_{20}H_{21}N_4O_2$ 349.41250, found 349.1659.

Synthesis of Complex 10a. A 50 mL Schlenk flask was charged with **5a** (250 mg, 0.95 mmol, 1.0 equiv), KOtBu (117.3 mg, 1.05 mmol, 1.1 equiv), and $[(Rh(COD)Cl)]_2$ (233.7 mg, 0.47 mmol, 0.5 equiv). The solid mixture was cooled to −80 °C. After 10 min at −80 °C 20 mL of THF was added dropwise with vigorous stirring. The mixture was stirred for 15 min at −80 °C, the cooling bath was removed, and the suspension was warmed to room temperature and stirred overnight. The resulting brown solution was evaporated to dryness in vacuo, and the crude product was purified by flash chromatography on silica gel 60 with THF as mobile phase. All volatiles were evaporated in vacuo to yield **10a** as a yellow solid (320 mg, 80%). Single crystals of **10a** were grown by slow evaporation from CH_2Cl_2/diethyl ether. ^1H NMR (200 MHz, $CDCl_3$): δ 8.33−8.29 (m, 1H, Ar−CH), 7.82−7.78 (m, 1H, Ar−CH), 7.55−7.44 (m, 2H Ar−CH), 5.19 (br s, 2H, CH_{COD}), 4.96 (s, 3H, CH_3), 4.65 (s, 3H, CH_3), 3.39 (br s, 2H, CH_{COD}), 2.51 (m, 4H, $CH_{2\ COD}$), 2.05 (m, 4H, $CH_{2\ COD}$). ^{13}C NMR (126 MHz, $CDCl_3$): δ 219.4 (d, $^1J_{RhC}$ = 50.3 Hz, NCN), 158.7 (s, C═O), 140.7, 135.4, 129.0, 126.9, 118.5, 115.3 (all aromatic C), 100.4 (d, J_{RhC} = 6.3 Hz, CH_{COD}), 100.1 (d, J_{RhC} = 6.3 Hz, CH_{COD}), 71.0 (d, J_{RhC} = 13.8 Hz, CH_{COD}), 70.6 (d, J_{RhC} = 13.8 Hz, CH_{COD}), 44.7 (s, CH_3), 40.8 (s, CH_3), 33.2 (s, $CH_{2\ COD}$), 32.6 (s, $CH_{2\ COD}$), 29.3 (s, $CH_{2\ COD}$), 29.0 (s, $CH_{2\ COD}$). MS (MALDI): m/z 420 $[M]^+$. Anal. Calcd (%) for $C_{18}H_{22}ClN_2ORh{\cdot}0.5CH_2Cl_2$: C, 47.97; H, 5.00; N, 6.05. Found: C, 47.48; H, 4.74; N, 6.10.

Synthesis Complex 11a. A 50 mL Schlenk flask was charged with **5a** (154 mg, 0.59 mmol, 1.0 equiv), KOtBu (73 mg, 0.65 mmol, 1.1 equiv), and $[(Ir(COD)Cl)]_2$ (197 mg, 0.29 mmol, 0.5 equiv). The solid mixture was cooled to −80 °C. After 10 min at −80 °C 20 mL of THF was added dropwise with vigorous stirring. The mixture was stirred for 15 min at −80 °C, the cooling bath was removed, and the suspension was warmed to room temperature and stirred overnight. The solvent was removed in vacuo, and the red crude product was purified by flash chromatography on silica gel 60 with diethyl ether/CH_2Cl_2 as mobile phase. All volatiles were evaporated in vacuo to yield **11a** as bright yellow solid (250 mg, 83%). ^1H NMR (200 MHz, $CDCl_3$): δ 8.36−8.31 (m, 1H, Ar−CH), 7.83−7.79 (m, 1H, Ar−CH), 7.56−7.46 (m, 2H Ar−CH), 4.84 (br s, 2H, CH_{COD}), 4.76 (s, 3H, CH_3), 4.44 (s, 3H, CH_3), 3.00 (br s, 2H, CH_{COD}), 2.31 (m, 4H, $CH_{2\ COD}$), 1.87 (m, 4H, $CH_{2\ COD}$). ^{13}C NMR (126 MHz, $CDCl_3$): δ 210.7 (s, NCN), 159.8 (s, C═O), 141.5, 135.5, 129.0, 126.7, 118.4, 115.4 (all aromatic C), 87.2 (s, CH_{COD}), 86.8 (s, CH_{COD}), 54.9 (s, CH_{COD}), 54.5 (s, CH_{COD}), 44.1 (s, CH_3), 40.3 (s, CH_3), 33.8 (s, $CH_{2\ COD}$), 33.2 (s, $CH_{2\ COD}$), 29.8 (s, $CH_{2\ COD}$), 29.5 (s, $CH_{2\ COD}$). MS (MALDI): m/z 510 $[M - Cl]^+$. Anal. Calcd (%) for $C_{18}H_{22}ClIrN_2O$: C, 42.39; H, 4.35; N, 5.49. Found: C, 42.29; H, 4.31; N, 5.28.

General Synthesis of Dicarbonylhalogenido-Rhodium/Iridium Complexes 12a and 13a. CO was bubbled into a stirred solution of complex **10a** or **11a** (100 mg) in CH_2Cl_2 (5 mL) for 5 min at room temerature. All volatiles were removed in vacuo, and the residue was washed with 5 mL of *n*-hexane. **12a** and **13a** were obtained as solids, which were characterized by IR, NMR, and MS spectrometry. The carbonyl complexes were too sensitive to provide correct elemental analyses.

*Complex **12a**.* Yield: bright yellow solid (76.0 mg, 84%). ^1H NMR (500 MHz, $CDCl_3$): δ 8.21−8.19 (m, 1H, Ar−CH), 7.73−7.70 (m, 1H, Ar−CH), 7.48−7.36 (m, 2H Ar−CH), 4.85 (s, 3H, CH_3), 4.54 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 218.0 (d, J_{RhC} = 49.1 Hz, NCN), 184.5 (d, J_{RhC} = 54.4 Hz, CO), 180.8 (d, J_{RhC} = 75.2 Hz, CO), 157.4 (s, NCO), 134.6, 127.7, 127.5, 125.5, 114.8, 113.9 (all aromatic C), 43.3 (s, CH_3), 39.4 (s, CH_3). MS (ESI): m/z 368 $[M - 2CO]^+$. IR (CH_2Cl_2): ν 2089 (CO), 2010 (CO), 1693 (NCON) cm^{-1}.

*Complex **13a**.* Yield: bright yellow solid (80.0 mg, 87%). ^1H NMR (500 MHz, $CDCl_3$): δ 8.40−8.38 (m, 1H, Ar−CH), 7.91−7.89 (m, 1H, Ar−CH), 7.65−7.56 (m, 2H Ar−CH), 4.54 (s, 3H, CH_3), 4.21 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 198.8 (s, NCN), 178.2 (s, CO), 166.3 (s, CO), 157.9 (s, CO), 139.5 134.7, 127.9, 126.9, 117.7, 115.0 (all aromatic C), 44.0 (s, CH_3), 39.8 (s, CH_3). IR (CH_2Cl_2): ν (CH_2Cl_2) 2075 (CO), 1994 (CO), 1701 (NCON) cm^{-1}.

Synthesis of Compound 16a. A 100 mL Schlenk flask was charged with **15** (1.69 g, 12.9 mmol, 1.0 equiv) and KOtBu (1.59 g, 14.2 mmol, 1.1 equiv) in 60 mL of acetonitrile. Iodomethane (1.61 mL, 25.8 mmol, 2.0 equiv) was added dropwise, and the yellow solution was stirred for 4 h at 80 °C. After removing the solvent in vacuo, the crude product was suspended in 5 mL of acetonitrile and treated with 25 mL of diethyl ether. Directly a white solid precipitated and was filtered, washed with 20 mL of diethyl ether, and subsequently dried in vacuo to yield 3.40 g (91%) of **16a** as a white powder. ^1H NMR (200 MHz, DMSO-d_6): δ 8.73 (s, 1H, NCHN), 7.37−7.24 (m, 4H, Ar−CH), 4.83 (s, 2H, Ph−CH_2), 3.46 (s, 3H, CH_3), 3.24 (s, 3H, CH_3). ^{13}C NMR (126 MHz, DMSO-d_6): δ 153.1 (s, NCHN), 132.2, 129.5, 127.8, 127.1, 118.9, 115.6 (all aromatic C), 48.5 (s, Ph−CH_2), 41.9 (s, CH_3), 37.8 (s, CH_3). MS (MALDI): m/z 162 $[M - I]^+$. HRMS (ESI): $[M - I]^+$ calcd for $C_{10}H_{13}N_2$ 161.10732, found 161.10732.

Synthesis of Compound 17a. A solution of **16a** (666.1 mg, 2.31 mmol, 1.0 equiv) in H_2O (20 mL) was cooled to 0 °C. Ammonium hexafluorophosphate (570.1 mg, 3.5 mmol, 1.5 equiv) was added in small portions with vigorous stirring. Immediately a white solid precipitated, and the suspension was stirred for 15 min at 0 °C. The white solid was filtered off, washed with 10 mL of diethyl ether and 10 mL of *n*-hexane, and subsequently dried in vacuo to yield 694.8 mg (98%) of **16a**. ^1H NMR (200 MHz, DMSO-d_6): δ 8.51 (s, 1H, NCHN), 7.46−7.20 (m, 4H, Ar−CH), 4.79 (s, 2H, PH−CH_2), 3.45 (s, 3H, CH_3), 3.22 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR (81 MHz, DMSO-d_6): δ −142.95 (sept, J_{PF} = 711.3 Hz, PF_6^-). ^{13}C NMR (126 MHz, DMSO-d_6): δ 153.2 (s, NCHN), 132.1, 129.5, 127.9, 127.1, 118.8, 115.5 (all aromatic C), 48.3 (s, Ph−CH_2), 41.9 (s, CH_3), 37.7 (s, CH_3). MS (MALDI): m/z 161 $[M - PF_6]^+$. Anal. Calcd (%) for $C_{10}H_{13}F_6N_2P{\cdot}H_2O$: C, 37.05; H, 4.66; N, 8.64. Found: C, 36.68; H, 4.18; N, 8.67.

Synthesis of Compound 19a. A suspension of **16a** (250 mg, 0.86 mmol, 1.0 equiv) and S_8 (41.2 mg, 1.29 mmol, 1.5 equiv) in 20 mL of THF was cooled to −80 °C, and NaHMDS (2 M in THF, 0.35 mL, 1.72 mmol, 2.0 equiv) was added dropwise. The resulting orange solution was stirred for 10 min at −80 °C, the cooling bath was removed, and the solution was allowed to warm to room temperature within 2.5 h. After evaporation of all volatiles, the orange crude product was purified by flash chromatography (Al_2O_3, diethyl ether 100%). All volatiles were evaporated in vacuo and yielded **19a** as a white solid (79.6 mg, 47%). ^1H NMR (200 MHz, $CDCl_3$): δ 7.38−7.32 (m, 1H, Ar−CH), 7.14−7.11 (m, 2H, Ar−CH), 7.02−6.98 (m, 1H, Ar−CH), 4.47 (s, 2H, Ph−CH_2), 3.81 (s, 3H, CH_3), 3.55 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 179.72 (s, C═S), 137.40, 127.59, 124.06, 122.63, 119.77, 112.89 (all aromatic C), 50.36 (s, Ph−CH_2), 42.27 (s, CH_3), 36.95 (s, CH_3). GC/MS (EI): m/z 192 $[M]^+$. Anal. Calcd (%) for $C_{10}H_{12}N_2S$: C, 62.46; H, 6.29; N, 14.57; S, 16.68. Found: C, 62.28; H, 6.22; N, 14.36; S, 16.41.

Synthesis of Compound 20a. A suspension of **16a** (300 mg, 1.04 mmol, 1.0 equiv) and selenium (106.7 mg, 1.35 mmol, 1.3 equiv) in 20 mL of THF was cooled to −80 °C, and NaHMDS (2 M in THF, 0.32 mL, 1.56 mmol, 1.5 equiv) was added dropwise. The resulting gray solution was stirred for 10 min at −80 °C, the cooling bath was removed, and the solution was allowed to warm to room temperature within 2.5 h. After evaporation of all volatiles, the crude product was taken up in 20 mL of dichloromethane and filtered through a short pad of Celite. The filtrate was evaporated, taken up in 5 mL of dichloromethane, precipitated in 10 mL of *n*-hexane, and subsequently dried in vacuo to yield 200 mg (80%) of **6a** as a white powder. ^1H NMR (200 MHz, $CDCl_3$): δ 7.41−7.33 (m, 1H, Ar−CH), 7.21−7.03 (m, 3H, Ar−CH), 4.49 (s, 2H, Ph−CH_2), 3.94 (s, 3H, CH_3), 3.68 (s, 3H,CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 180.1 (s, C═Se), 136.4, 127.8, 124.2, 123.3, 113.0, 50.3 (all aromatic C), 45.6 (s, Ph−CH_2), 40.4 (s, CH_3), 29.9 (s, CH_3). GC/MS (EI): m/z 240 $[M]^+$. Anal. Calcd (%) for $C_{10}H_{12}N_2Se{\cdot}H_2O$: C, 46.60; H, 5.49; N, 10.89. Found: C, 46.49; H, 5.18; N, 9.38.

dx.doi.org/10.1021/om301152n | *Organometallics* 2013, 32, 854−861

Synthesis of Complex 21a. A 50 mL Schlenk flask was charged with **16a** (290 mg, 1.01 mmol, 1.0 equiv), KOtBu (124.5 mg, 1.11 mmol, 1.1 equiv), and $[(Rh(COD)Cl)]_2$ (245 mg, 0.5 mmol, 0.5 equiv). The solid mixture was cooled to −80 °C. After 10 min at −80 °C 20 mL of THF was added dropwise with vigorous stirring. The mixture was stirred for 15 min at −80 °C, the cooling bath was removed, and the suspension was warmed to room temperature and stirred overnight. The resulting brown solution was evaporated to dryness in vacuo, the crude product was taken up in 5 mL of dichloromethane, the reagent was precipitated in 30 mL of *n*-hexane, and the solution was dried in vacuo to yield 264 mg (52%) of **21a** as a green-yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25−6.92 (m, 4H, Ar−CH), 5.15 (br s, 2H, CH_{COD}), 4.36 (d, 1H, J = 15.0 Hz, Ph−CH_2), 4.29 (d, 1H, J = 10.0 Hz, Ph−CH_2), 4.26 (s, 3H, CH_3), 3.92 (s, 3H, CH_3), 3.49 (br s, 2H, CH_{COD}), 2.31 (m, 4H, $CH_{2\ COD}$), 1.85 (m, 4H, $CH_{2\ COD}$). ^{13}C NMR (126 MHz, $CDCl_3$): δ 210.3 (d, $^1J_{RhC}$ = 45.3 Hz, NCN), 134.1, 127.6, 124.7, 123.3, 118.7, 111.6 (all aromatic C), 94.5 (d, J_{RhC} = 7.5 Hz, CH_{COD}), 94.39 (d, J_{RhC} = 7.5 Hz, CH_{COD}), 71.51 (d, J_{RhC} = 13.8 Hz, CH_{COD}), 71.3 (d, J_{RhC} = 15.09 Hz, CH_{COD}), 49.1 (s, Ph−CH_2), 45.1 (s, CH_3), 40.5 (s, CH_3), 31.1 (s, $CH_{2\ COD}$), 30.9 (s, $CH_{2\ COD}$), 28.5 (s, $CH_{2\ COD}$), 28.4 (s, $CH_{2\ COD}$). MS (MALDI): m/z 498 $[M - I]^+$. Halide exchange at the metal center from chloride to iodide prevented correct elemental analyses.

Synthesis of Complex 22a. A 50 mL Schlenk flask was charged with **16a** (250 mg, 0.86 mmol, 1.0 equiv), KOtBu (106 mg, 0.95 mmol, 1.1 equiv), and $[(Ir(COD)Cl)]_2$ (289 mg, 0.43 mmol, 0.5 equiv). The solid mixture was cooled to −80 °C. After 10 min at −80 °C 20 mL of THF was added dropwise with vigorous stirring. The mixture was stirred for 15 min at −80 °C, the cooling bath was removed, and the suspension was warmed to room temperature and stirred overnight. The solvent was removed in vacuo, and the red crude product was purified by flash chromatography on silica gel 60 with *n*-hexane/diethyl ether as mobile phase. All volatiles were evaporated in vacuo and yielded **22a** as a red solid (329 mg, 65%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.88−7.01 (m, 4H, Ar−CH), 4.78 (br s, 2H, CH_{COD}), 4.48 (d, 2H, J = 6.8 Hz, Ph−CH_2), 4.12 (s, 3H, CH_3), 3.80 (s, 3H, CH_3), 3.08 (br s, 2H, CH_{COD}), 2.21 (m, 4H, $CH_{2\ COD}$), 1.83 (m, 4H $CH_{2\ COD}$). ^{13}C NMR (126 MHz, $CDCl_3$): δ 203.2 (s, NCN), 129.3, 128.3, 126.5, 125.8, 123.3, 116.8 (all aromatic C), 79.5 (s, CH_{COD}), 65.4 (s, CH_{COD}), 59.5 (s, Ph−CH_2), 36.1 (s, CH_3), 35.6 (s, CH_3), 31.3 (s, $CH_{2\ COD}$), 30.9 (s, $CH_{2\ COD}$), 29.8 (s, $CH_{2\ COD}$), 28.6 (s, $CH_{2\ COD}$). MS (MALDI): m/z 588 $[M - I]^+$. Halide exchange at the metal center from chloride to iodide prevented correct elemental analyses.

General Synthesis of Dicarbonylhalogenido-Rhodium/Iridium Complexes 23a and 24a. The carbonyl complexes **23a** and **24a** were prepared according to the protocol described above for the synthesis of complexes **12a** and **13a**. Due to slow decomposition, no elemental analyses could be obtained. The complexes were characterized by IR and NMR spectroscopy.

*Complex **23a**.* Yield: red-orange solid (50 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33−7.02 (m, 4H, Ar−CH), 4.52 (q, 2H, J = 14.8 Hz, PH−CH_2), 3.86 (s, 3H, CH_3), 3.56 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 198.2 (d, J_{RhC} = 37.7 Hz, NCN), 186.6 (d, J_{RhC} = 52.8 Hz, CO), 180.3 (d, J_{RhC} = 79.2 Hz, CO), 161.8 (s, CO), 133.7, 128.0, 124.9, 124.4, 118.3, 112.3 (all aromatic C), 49.4 (s, Ph−CH_2), 45.4 (s, CH_3), 40.9 (s, CH_3). IR (CH_2Cl_2): ν 2075 (CO), 2003 cm^{-1} (CO).

*Complex **24a**.* Yield: dark red solid (60 mg, 79%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75−6.97 (m, 4H, Ar−CH), 4.52 (m, 2H, Ph−CH_2), 3.78 (s, 3H, CH_3), 3.49 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 200.8 (s, NCN), 179.7 (s, CO), 179.6 (s, CO), 166.3 (s, NCO), 129.3, 128.3, 126.5, 125.8, 124.9, 116.8 (all aromatic C), 49.9 (s, Ph−CH_2), 45.0 (s, CH_3), 40.5 (s, CH_3). IR (CH_2Cl_2): ν 2062 (CO), 1986 cm^{-1} (CO).

Crystal Structure Determinations. A colorless plate (0.42 mm × 0.39 mm × 0.08 mm) of **5a**-$[BF_4]$, a yellow prism (0.30 mm × 0.30 mm × 0.10 mm) of **10a**, and a yellow prism (0.15 mm × 0.10 mm × 0.07 mm) of **10c** suitable for X-ray study were selected by means of a polarization microscope and investigated at 291 K with a STOE imaging plate diffraction system (**5a**-$[BF_4]$) and an Oxford Diffraction Excalibur diffractometer, respectively, using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). Unit cell parameters were determined by least-squares refinements on the positions of 3066, 17 838, and 9818 reflections, respectively. For **5a**-$[BF_4]$, the monoclinic crystal system and systematic absences are consistent with space group types $P2_1$ and $P2_1/m$. In accordance with E-statistics significantly better results were observed in the centrosymmetric type $P2_1/m$ in the course of structure refinement, taking into account a structural model with a 1:1 disorder of the tetrafluoroborate anion. For **10a**, the monoclinic crystal system and systematic absences are consistent with space group types *Cc* and *C*2/*c*. The latter proved to be the right choice in the course of structure refinement. Corrections for Lorentz and polarization effects and multiscan absorption corrections in the case of **10a** (T_{min} = 0.402, T_{max} = 0.613) and **10c** (T_{min} = 0.768, T_{max} = 1.000) were applied. The structures were solved by direct methods[14] and subsequent ΔF syntheses. Approximate positions of all the hydrogen atoms were found in different stages of converging refinements by full-matrix least-squares calculations[15] on F^2 (max. shift/s.u. = 0.001 in each case). Selected crystallographic data are shown in Table S1. Anisotropic displacement parameters were refined for all atoms heavier than hydrogen. With idealized bonds lengths and angles assumed for all the CH, CH_2, and CH_3 groups, the riding model was applied for the corresponding H atoms and their isotropic displacement parameters were constrained to 120%, 120%, and 150% of the equivalent isotropic displacement parameters of the parent carbon atoms, respectively. In addition, the H atoms of the CH_3 groups were allowed to rotate around the neighboring C−C bonds. The disordered anion of **5a**-$[BF_4]$ was treated as rigid groups with idealized geometry. Appropriate anisotropic displacement restraints had to be applied for its atoms. CCDC-912080 (**5a**-$[BF_4]$), CCDC-912081 (**10a**), and CCDC-912588 (**10c**) contain the supplementary crystallographic data (excluding structure factors) for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures and analytical data for compounds not described in the experimental section. Crystallographic data (Table S1, CIF files) for compounds **5a**-BF_4, **10a**, and **10c**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: christian.ganter@uni-duesseldorf.de.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Dr. Guido Reiß for help with the structure determination of complex **10c** and Maximilian Klopotowski for valuable assistance with the experimental work.

■ REFERENCES

(1) For current comprehensive reviews see for example: (a) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (b) Jahnke, M. C.; Hahn, F. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122. (c) Dröge, T.; Glorius, F. *Angew. Chem.* **2010**, *122*, 7094. (d) Benhamou, L.; Chardon, E.; Lavigne, G.; Bellemin-Laponnaz, S.; César, V. *Chem. Rev.* **2011**, *111*, 2705. (e) Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612. (f) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5606. (g) Schaper, L.-A.; Hock, S. J.; Herrmann, W. A.; Kühn, F. E. *Angew. Chem.* **2013**, *125*, 284. (h) Martin, D.; Soleilhavoup, M.; Bertrand, G.

Chem. Sci. **2011**, *2*, 389. (i) Siemeling, U. *Eur. J. Inorg. Chem.* **2012**, *22*, 3523.

(2) (a) Khramov, D. M.; Lynch, V. M.; Bielawski, C. W. *Organometallics* **2007**, *26*, 6042. (b) Sanderson, M. D.; Kamplain, J. W.; Bielawski, C. W. *J. Am. Chem. Soc.* **2006**, *128*, 16514. (c) Khramov, D. M.; Rosen, E. L.; Er, J. A. V.; Vu, P. D.; Lynch, V. M.; Bielawski, C. W. *Tetrahedron* **2008**, *64*, 6853. (d) Bittermann, A.; Härter, P.; Herdtweck, E.; Hoffmann, S. D.; Hermann, W. A. *J. Organomet. Chem.* **2008**, *693*, 2079. (e) Wolf, S.; Plenio, H. *J. Organomet. Chem.* **2009**, *694*, 1487. (f) Hobbs, M. G.; Knapp, C. J.; Welsh, P. T.; Borau-Garcia, J.; Ziegler, T.; Roesler, R. *Chem.—Eur. J.* **2010**, *16*, 14520.

(3) (a) César, V.; Lugan, N.; Lavigne, G. *J. Am. Chem. Soc.* **2008**, *130*, 11286. (b) César, V.; Lugan, N.; Lavigne, G. *Eur. J. Inorg. Chem.* **2010**, 361. (c) César, V.; Lugan, N.; Lavigne, G. *Chem.—Eur. J.* **2010**, *16*, 11432. (d) Hudnall, T. W.; Bielawski, C. W. *J. Am. Chem. Soc.* **2009**, *131*, 16039. (e) Hudnall, T. W.; Moerdyk, J. P.; Bielawski, C. W. *Chem. Commun.* **2010**, *46*, 4288. (f) Hudnall, T. W.; Moorhead, E. J.; Gusev, D. G.; Bielawski, C. W. *J. Org. Chem.* **2010**, *75*, 2763. (g) Moerdyk, J. P.; Bielawski, C. W. *Organometallics* **2011**, *30*, 2278. (h) For a seven-membered diamido carbene see: Hudnall, T. W.; Tennyson, A. G.; Bielawski, C. W. *Organometallics* **2010**, *29*, 4569. (I) Moerdyk, J. P.; Bielawski, C. W. *J. Am. Chem. Soc.* **2012**, *134*, 6116. (j) Moerdyk, J. P.; Bielawski, C. W. *Nat. Chem.* **2012**, *4*, 275. (k) Wiggins, K. M.; Moerdyk, J. P.; Bielawski, C. W. *Chem. Sci.* **2012**, *3*, 2986. (l) Braun, M.; Reiß, G. J.; Ganter, C. *Organometallics* **2010**, *29*, 4418. (m) Braun, M.; Frank, W.; Ganter, C. *Organometallics* **2012**, *31*, 1927.

(4) (a) Biju, A. T.; Hirano, K.; Fröhlich, R.; Glorius, F. *Chem. Asian J.* **2009**, *4*, 1786. (b) Benhamou, L.; César, V.; Gornitzka, H.; Lugan, N.; Lavigne, G. *Chem. Commun.* **2009**, 4720. (c) Benhamou, L.; Vujkovic, N.; César, V.; Gornitzka, H.; Lugan, N.; Lavigne, G. *Organometallics* **2010**, *29*, 2616. (d) Vujkovic, N.; César, V.; Lugan, N.; Lavigne, G. *Chem.—Eur. J.* **2011**, *17*, 13151. (e) Blake, G. A.; Moerdyk, J. P.; Bielawski, C. W. *Organometallics* **2012**, *31*, 3373. (f) Mushinski, R. M.; Squires, B. M.; Sincerbox, K. A.; Hudnall, T. W. *Organometallics* **2012**, *31*, 4862. (g) Makhloufi, A.; Frank, W.; Ganter, C. *Organometallics* **2012**, *31*, 7272. (h) Makhloufi, A.; Frank, W.; Ganter, C. *Organometallics* **2012**, *31*, 2001.

(5) See refs 3l, m, 4g, h, and (a) Hildebrandt, B.; Frank, W.; Ganter, C. *Organometallics* **2011**, *30*, 3483. (b) Hildebrandt, B.; Raub, S.; Frank, W.; Ganter, C. *Chem.—Eur. J.* **2012**, *18*, 6670. (c) Hildebrandt, B.; Ganter, C. *J. Organomet. Chem.* **2012**, *717*, 83.

(6) Zhang, J.; Qin, X.; Fu, J.; Wang, X.; Su, X.; Hu, F.; Jiao, J.; Shi, M. *Organometallics* **2012**, *31*, 8275.

(7) Endicott, M. M.; Wick, E.; Mercury, M. L.; Sherrill, M. L. *J. Am. Chem. Soc.* **1946**, *68*, 1299.

(8) Dobereiner, G. E.; Chamberlin, C. A.; Schley, N. D.; Crabtree, R. H. *Organometallics* **2010**, *29*, 5728.

(9) Wolf, S.; Plenio, H. *J. Organomet. Chem.* **2009**, *694*, 1487.

(10) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. *Chem.—Eur. J.* **1996**, *2*, 772.

(11) Kelly, R. A., III; Clavier, H.; Giudice, S.; Scott, N. M.; Stevens, E. D.; Bordner, J.; Samardjiev, I.; Hoff, C. D.; Cavallo, L.; Nolan, S. P. *Organometallics* **2008**, *27*, 202.

(12) Lewis, J. C.; Wiedemann, S. H.; Bergman, R. G.; Ellman, J. A. *Org. Lett.* **2004**, *6*, 35.

(13) Giordano, G.; Crabtree, R. H.; Heintz, R. M.; Fortser, D.; Morris, D. E. *Inorg. Synth.* **1990**, *28*, 88.

(14) Sheldrick, G. M. *SHELXS86, Program for the Solution of Crystal Structures*; University of Göttingen: Germany, 1985.

(15) Sheldrick, G. M. *SHELXL97, Program for the Refinement of Crystal Structures*; University of Göttingen: Germany, 1997.