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Phthalazin-2-ylidenes As Cyclic Amino Aryl Carbene Ligands in Rhodium(I) and Iridium(I) Complexes

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The direct metalation of phthalazinium halides with $[Rh(^tBuO)(COD)]_2$ or $[Ir(^tBuO)(COD)]_2$ led to the isolation of stable [MCl(phthalazin-2-ylidene)X(COD)] (M = Rh, Ir) as a new family of cyclic amino aryl carbene transition metal complexes. The X-ray diffraction analysis of several representatives systematically revealed a relatively short C(aryl)−C(carbene) bond distance of 1.44−1.46 Å, shorter than the typical $C(sp^2)-C(sp^2)$ single bond, indicating some electron density delocalization from the π system of the aryl ring over the vacant carbene orbital.

Introduction

N-Heterocyclic carbenes (NHCs) have emerged during the past decade as one of the most useful families of ancillary ligands for transition-metal-catalyzed reactions.[1] In addition to the classic NHCs stabilized by two adjacent heteroatoms, a growing number of related carbenes stabilized by a single nitrogen atom are emerging as interesting alternatives that exhibit even higher σ-donor abilities. Imidazolium-derived ligands with the carbenic carbon at C4 or C5 as well as the pyridinylidene family of NHCs constitute representative examples.[2] In a fundamental contribution to this field, Bertrand and co-workers first demonstrated that a single nitrogen atom effects the required stabilization that makes possible the isolation of stable singlet carbenes, as highlighted with the isolation of acyclic amino aryl carbenes **A**[3] and both acyclic and cyclic amino alkyl carbenes (CAACs) **B**[4] and **D**[5] (Figure 1). Despite efforts directed to their synthesis, free cyclic amino aryl carbenes **C** remain as an unknown family of compounds.

Concerning the formation of transition metal complexes and their application in catalysis, CAAC (aliphatic) derivatives are emerging as an interesting alternative for specific applications.[6] On the other hand, the aromatic analogues (cyclic amino aryl carbenes, CAArCs) **C** are particularly attractive for the opportunities that substitution at the aromatic ring offers for a fine-tuning of the steric and electronic properties. Though the isolation of free carbenes **C** remains, as mentioned above, elusive, indirect routes to a few transition metal complexes have been reported (**C1**−**C4**, Chart 1).[7] In this context, we recently demonstrated that isoquinoline-derived Rh(I) amino aryl carbenes **C5** can be readily synthesized from the corresponding isoquinolinium salts by treatment with strong bases and subsequent reaction with $[RhCl(COD)]_2$, in a reaction that proceeds via isoquinolinium-base adducts that exhibited carbene reactivity.[8] We speculated that the presence of an additional nitrogen

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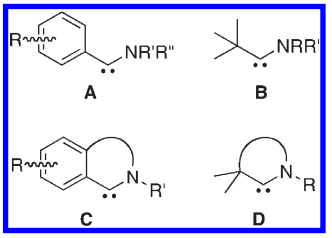
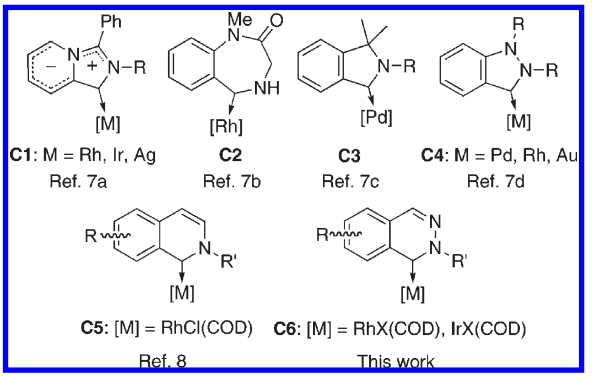


Figure 1. Cyclic and acyclic monoaminocarbenes.

Chart 1. Transition Metal Complexes of Cyclic Amino Aryl Carbenes

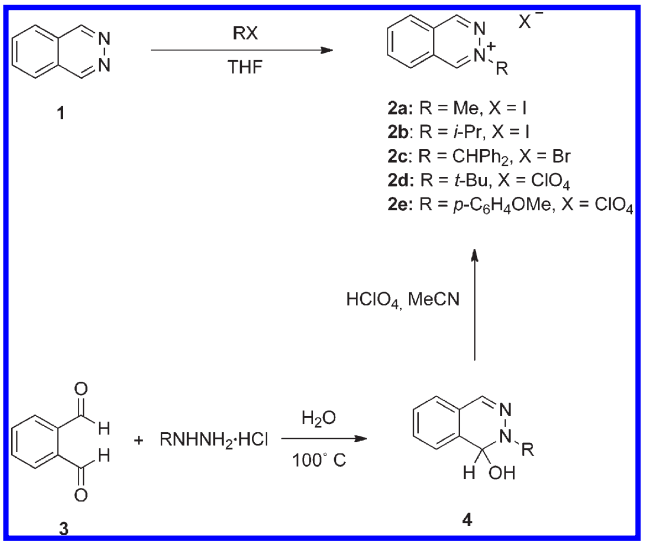


at position 3 in these structures should reduce the basicity of the carbene ligand, therefore making it easier to deprotonate the parent, more acidic azolium salts. In agreement with this hypothesis, literature data corroborate that phthalazinium salts are much more acidic than isoquinolinium analogues.[9] In spite of this apparent experimental advantage, a survey of the literature data reveals that phthalazin-1-ylidene monoamino carbenes have never been described. There are only reports on the dimerization of l-hydroxy-2-aryl-1,2-dihydrophthalazines yielding 1,1′-bis(2-aryl-l,2-dihydrophthalazinylidenes),[10] a process supposed to take place via transient free carbenes. This lack of precedents applies also to the monocyclic series: though a growing number of studies on pyridin-2-ylidenes transition metal complexes have been reported in recent years,[2a] the pyridazin-2-ylidene analogues remain unexplored. We now report on the synthesis and structural characterization of phthalazin-1-ylidene Rh(I) and Ir(I) complexes **C6**.

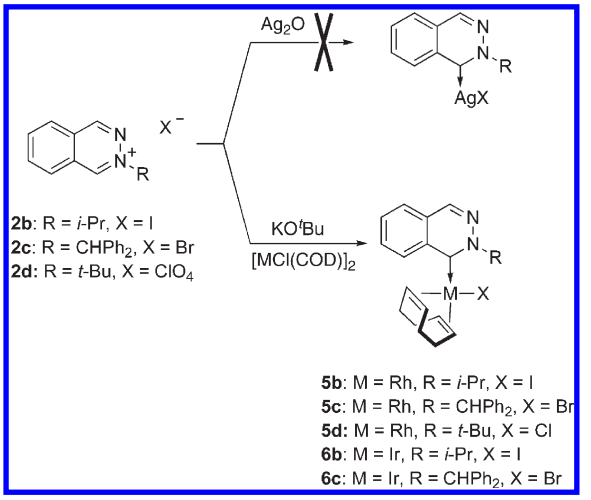
Results and Discussion

A series of phthalazinium salts **2**, required as starting materials, were synthesized following two different methods: (a) alkylation of phthalazine **1** itself; this procedure was used for the introduction of primary (methyl, **2a**) and secondary alkyl groups with moderate to high steric demand [isopropyl (**2b**) and benzhydryl (**2c**)] (Scheme 1); and (b) condensation of phthalaldehyde with monosubstituted hydrazines and subsequent reaction of the resulting pseudobases with perchloric acid[10c] for the introduction of tertiary [*tert*-butyl (**2d**)] or aromatic [*p*-anisyl (**2e**)] groups.

Scheme 1. Synthesis of Phthalazinium Salts 2a−e



Scheme 2. Synthesis of Rh(I) and Ir(I) Phthalazin-1-ylidene Complexes 5 and 6



Attempts to isolate or detect the free carbenes by deprotonation of the phthalazinium salts **2** by strong bases (KO^{t}Bu, LiN^{i}Pr$_2$) failed under a variety of conditions. Disappointingly, the relatively high acidity of these salts did not enable direct metalation reaction with Ag_2O according to the popular method developed by Lin and co-workers.[11] Nevertheless, the reaction of azolium salts **2b−d** with [Rh(O^{t}Bu)(COD)]$_2$, generated *in situ* from KO^{t}Bu and [RhCl(COD)]$_2$,[12] afforded the expected [RhX(CAArC)(COD)] complexes **5b−d** in low to moderate yields (Scheme 2). As exceptions, no product was isolated from the N-Me and the N-anisyl derivatives **2a** and **2e**. Complexes **5b−d** exhibited a considerable stability, which enabled even purification by chromatography on silica gel. The ^{13}C NMR spectra showed characteristic C(carbene) resonances at 221−228 ppm, slightly shifted upfield with respect to isoquinolin-1-ylidene analogues, but still much downfield with respect to the typical resonances in diamino carbene [RhCl(NHC)(COD)]

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Table 1. Selected Spectroscopic and Crystallographic Data for Complexes 5, 6, and 7

	5b	5c	5d	6b	6c	7
M	Rh	Rh	Rh	Ir	Ir	Rh
δ ^{13}C C(1) (ppm)	221.8	227.2	223.7	213.3	217.0	228.0
δ C(8)H (ppm)	9.62	9.85	10.51	9.46	9.52	9.83
δ C$\underline{H}$Me$_2$ (ppm)	6.90			6.57		7.16
δ C$\underline{H}$Ph$_2$ (ppm		9.38			9.06	
δ ^{t}B$\underline{u}$ (ppm)			2.29			
d C(1)−M (Å)	2.016(2)	2.0130(18)	2.0358(18)	2.013(4)	2.025(3)	2.0242(16)
d C(1)−Ar (Å)	1.447(3)	1.450(2)	1.461(3)	1.455(5)	1.453(4)	1.449(2)
mean Rh−C_{COD} (*trans*)	2.224	2.224	2.217	2.186	2.195	2.221
mean Rh−C_{COD} (*cis*)	2.130	2.129	2.121	2.121	2.116	2.132
Δ mean Rh−C_{COD} (*trans*−*cis*)	0.094	0.095	0.096	0.065	0.079	0.089
C(Ar)H−Rh (Å)	2.826	2.770	2.688	2.835	2.783	2.768
C(sp^3)H−Rh (Å)	2.615	2.594	2.365	2.626	2.618	2.555

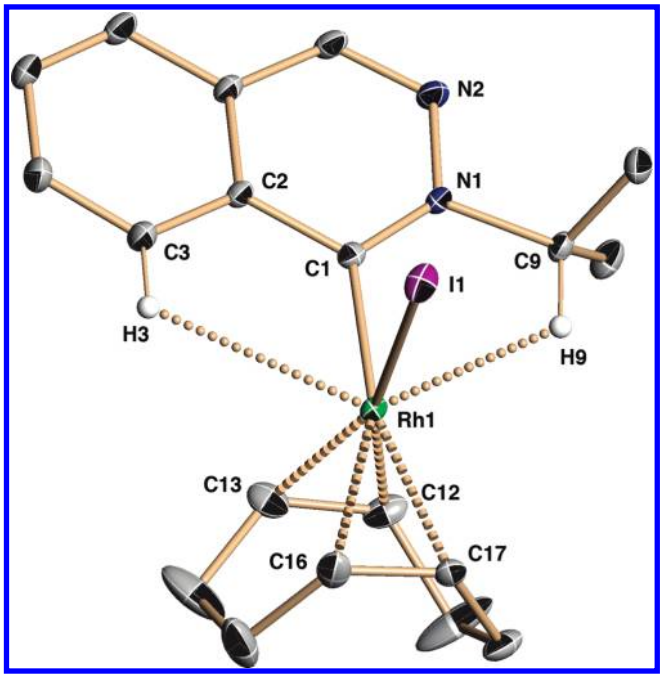

Figure 2. ORTEP drawing of complex **5b**. Thermal ellipsoids are shown at the 30% probability level. Most hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Rh(1)−C(1) 2.016(2), C(1)−C(2) 1.447(3), N(1)−C(1) 1.342(3), Rh(1)−I(1) 2.6699(2), Rh(1)−H(3) 2.826, Rh(1)−H(9) 2.615, Rh(1)−C(12) 2.135(2), Rh(1)−C(13) 2.126(3), Rh(1)−C(16) 2.223(3), Rh(1)−C(17) 2.224(2), C(1)−Rh(1)−I(1) 87.56(6), C(3)−H(3)−Rh(1) 111.70, C(9)−H(9)−Rh(1) 121.62.

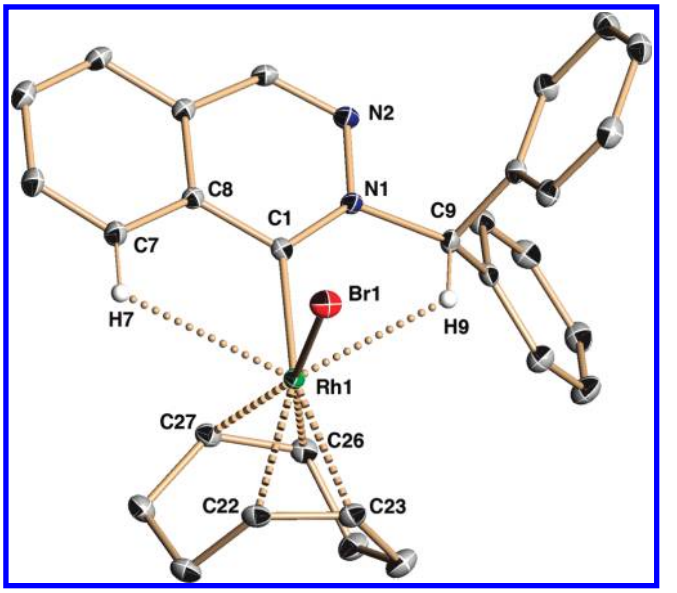

Figure 3. ORTEP drawing of complex **5c**. Thermal ellipsoids are shown at the 30% probability level. Most hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Rh(1)−C(1) 2.0130(18), C(1)−C(8) 1.450(2), N-(1)−C(1) 1.343(2), Rh(1)−Br(1) 2.4973(2), Rh(1)−H(7) 2.770, Rh(1)−H(9) 2.594, Rh(1)−C(22) 2.2289(18), Rh(1)−C(23) 2.2183(18), Rh(1)−C(26) 2.1316(18), Rh(1)−C(27) 2.1164(18), C(1)−Rh(1)−Br(1) 90.26(5), C(7)−H(7)−Rh(1) 112.46, C(9)−H(9)−Rh(1) 124.60.

complexes (180−210 ppm)[13] (Table 1). The coupling constants $J_{C(1),Rh}$ of 41−44 Hz confirmed the formation of the carbene complexes **5**. On the other hand, their ^{1}H NMR spectra revealed a very strong downfield shift for the C(8)-H protons of the phthalazin-2-ylidene ligand, tentatively attributed to CH−Rh preagostic interactions. The spectra of complexes **5b** and **5d** exhibited also a drastic deshielding for the C$\underline{H}$Me$_2$ (δ = 6.90 ppm) and C$\underline{H}$Ph$_2$ (δ = 9.38 ppm) protons, which could also be attributed to significant preagostic CH−Rh interactions. Additionally, the singlet assigned to the *N*-^{t}Bu group in **5c** appears also clearly shifted downfield (from δ 1.80 ppm in the azolium salt to δ 2.29 ppm in the complex), suggesting also in this case the presence of a ^{t}Bu−metal interaction.

Suitable crystals for X-ray diffraction studies could be obtained for complexes **5b**−**d**. The structure of complex **5b** reveals the expected square-planar coordination geometry about Rh, with a C(carbene)−Rh distance of 2.016(2) Å, similar to those observed in related acyclic (type **A**)[3b] and cyclic **C1**, **C2**, **C4**, and **C5** systems.[7,8] Interestingly, the C(aryl)−C(carbene) bond distance of 1.447(3) Å is shorter than the typical distance of a C(sp^2)−C(sp^2) single bond, indicating some electron density delocalization from the π system of the aryl ring over the vacant carbene orbital.[14] The much longer C(aryl)−C(carbene) bond distance of 1.502(3) Å reported for an acyclic derivative (type **B**), where such a delocalization is not possible for geometrical reasons, provides an adequate reference for comparison.[3b] Finally, the Rh(I) (amino)(aryl)carbene complex **E2** obtained by Ellmann, Bergman, et al.[7b] by tautomerization

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(14) Accordingly, it has been demonstrated in the isoquinolin-1-ylidene series (ref 8) that the substitution pattern in the aromatic ring strongly influences the catalytic activity of the complex.

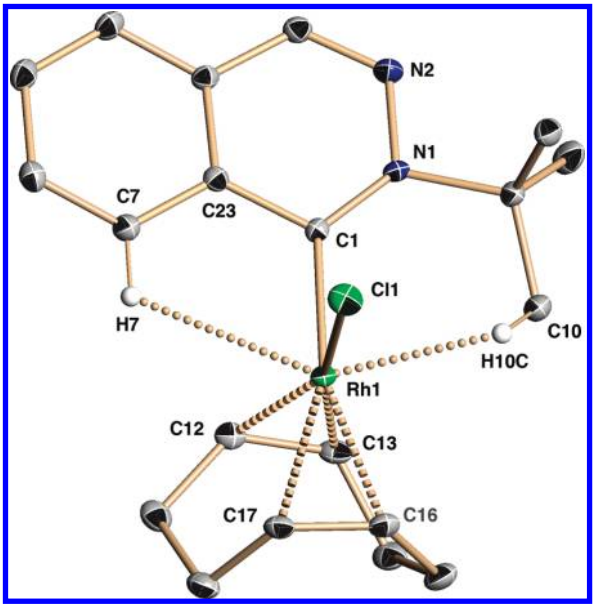

Figure 4. ORTEP drawing of complex **5d**. Thermal ellipsoids are shown at the 30% probability level. Most hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Rh(1)−C(1) 2.0358(18), C(1)−C(23) 1.461(3), N(1)−C(1) 1.340(2), Rh(1)−Cl(1) 2.4005(5), Rh(1)−H(7) 2.688, Rh(1)-H(10C) 2.365, Rh(1)−C(12) 2.111(2), Rh(1)−C(13) 2.1310(19), Rh(1)−C(16) 2.198(2), Rh(1)−C(17) 2.236(2), C(1)−Rh(1)−Cl(1) 87.80(5), C(7)−H(7)−Rh(1) 114.00, C(10)−H(10C)−Rh(1) 122.93.

of a 1,4-benzodiazepine complex exhibits also a longer C(aryl)−C(carbene) bond distance of 1.506(4) Å, consistent again with the absence of delocalization.[7b] Being a bicyclic structure, the absence of delocalization in this case can be explained by the lack of coplanarity imposed by the preferred conformation of the seven-membered ring in the benzodiazepinylidene ligand.[15] The structure of **5b** shows C(8)H−Rh and C$\underline{H}$Me$_2$−Rh bond distances of 2.826 and 2.615 Å, with C−H−Rh angles of 111.7° and 121.6°, respectively. These structural data are characteristic for preagostic Rh−H interactions,[16] as was anticipated from the ^{1}H NMR data. A high σ-donor ability of the phthalazin-1-ylidene ligand can be deduced from the molecular structure: the mean C(COD)−Rh bond distances are 2.130 Å (*trans* to iodine) and 2.224 Å (*trans* to the carbene ligand), the difference of ca. 0.1 Å reflecting the much higher *trans* influence of the monoamino carbene ligand. A direct comparison with the isoquinolin-1-ylidene analogue [RhI(IQUI-^{i}Pr)(COD)] **7**[8] (IQUI = 2-isopropylisoquinolin-1-ylidene) reveals very similar structures for these isoelectronic species, which, interestingly, differ in slightly stronger CH−Rh interactions for **7**, while the *trans* influence is unexpectedly similar in both cases. The crystal structure of **5c** presents almost identical features with those discussed for **5b** (Figure 4), exhibiting also similar preagostic C(8)H−Rh and C$\underline{H}$Ph$_2$−Rh interactions (see data in Table 1). In the case of **5d**, the intramolecular C(sp^3)H−Rh preagostic interaction involves one of the H atoms of the ^{t}Bu

(15) The complex shows a torsion C(ortho)−C-(ipso)−C(carbene)−Rh angle of 35.0(4)°.

(16) (a) Yao, W.; Eisenstein, O.; Crabtree, R. H. *Inorg. Chim. Acta* **1997**, *254*, 105–111. (b) Lewis, J. C.; Wu, J.; Bergman, R. G.; Ellman, J. A. *Organometallics* **2005**, *24*, 5737–5746. (c) Zhang, Y.; Lewis, J. C.; Bergman, R. G.; Ellman, J. A.; Oldfield, E. *Organometallics* **2006**, *25*, 3515–3519.

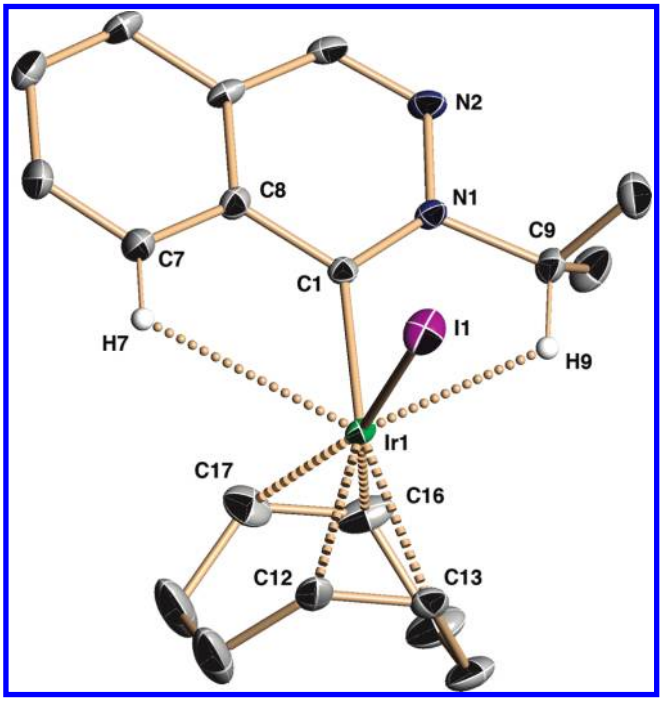

Figure 5. ORTEP drawing of complex **6b**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms not involved in preagostic interactions are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Ir(1)−C(1) 2.013(4), C(1)−C(8) 1.455(5), N(1)−C(1) 1.355(5), Ir(1)−I(1) 2.6610(4), Ir(1)−H(7) 2.835, Ir(1)−H(9) 2.626, Ir(1)−C(12) 2.177(5), Ir-(1)−C(13) 2.194(4), Ir(1)−C(16) 2.103(5), Ir(1)−C(17) 2.117(5), C(1)−Ir(1)−I(1) 89.02(12), C(7)−H(7)−Ir(1) 111.94, C(9)−H(9)−Ir(1) 121.83.

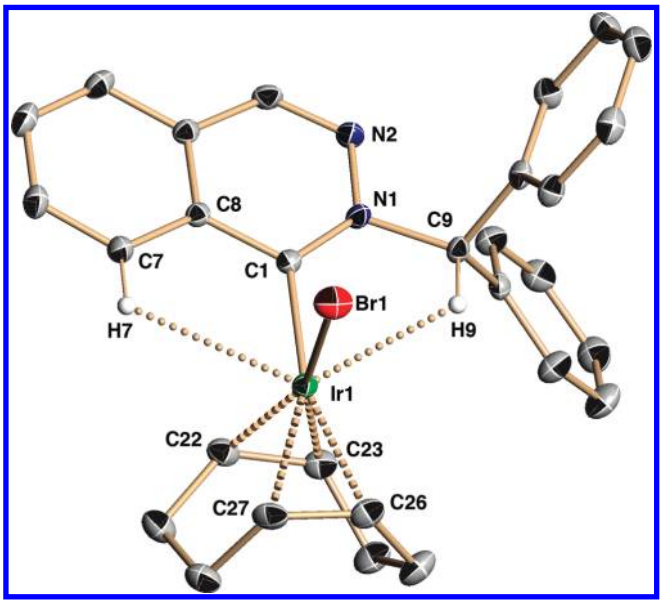

Figure 6. ORTEP drawing of complex **6c**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms not involved in preagostic interactions are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Ir(1)−C(1) 2.025(3), C(1)−C(8) 1.453(4), N(1)−C(1) 1.349(4), Ir(1)−Br(1) 2.4823(4), Ir(1)−H(7) 2.783, Ir(1)−H(9) 2.618, Ir(1)−C(22) 2.110(4), Ir(1)−C(23) 2.122(4), Ir(1)−C(26) 2.191(4), Ir(1)−C(27) 2.199(3), Ir(1)−H(7) 2.783, Ir(1)−H(9) 2.618, C(1)−Ir(1)−Br(1) 90.92(9), C(7)−H(7)−Ir(1) 112.44, C(9)−H(9)−Ir(1) 124.69.

group, resulting in a much shorter Rh−H bond distance of 2.365 Å (Figure 5), with a C−H−Rh angle of 122.9°.[17]

In a similar manner, reaction of phthalazinium salts **2b**,**c** with $[IrCl(COD)]_2$ under the same reaction conditions afforded iridium analogues **6b** and **6c**, although in lower yields. The ^1H NMR data for these complexes showed also a strong downfield shift for the C(8)H protons of the phthalazin-1-ylidene ligand [δ 9.46 and 9.52 ppm for **6b** and **6c**, respectively] and for the proton in the CHR_2 at N(2) [δ 6.57 for **6b** (R = Me); δ 9.06 for **6c** (R = Ph)], slightly weaker than for the Rh analogues. The C(aryl)−C(carbene) bond distances of 1.455(5) and 1.453(4) Å, respectively, indicate also in these cases a significant aryl/carbene electron delocalization.

In addition to the collected structural data, the synthesis of the $[RhCl(CAArC)(CO)_2]$ derivatives was considered of interest in order to obtain an additional index of the σ-donor ability of these ligands according to the "Rh scale".[18] However, no COD to CO ligand exchange was observed after bubbling CO through a solution of **5b** in CH_2Cl_2 for several hours. This unexpected behavior, also observed in acyclic monoamino aryl carbenes,[3b] is in sharp contrast with that exhibited by isoquinolin-2-ylidene analogues, which undergo complete ligand exchange in a few minutes at room temperature.

In summary, the synthesis of phthalazin-1-ylidene Rh(I) and Ir(I) complexes has been accomplished and their structures have been analyzed by X-ray diffraction studies. This new family of cyclic amino aryl carbenes exhibits structural features that suggest an electronic aryl−carbene delocalization that should allow the tuning of the ligand electronic properties. The lack of reactivity of [RhCl(CAArC)(COD)] with CO, however, reveals a different behavior compared to isoquinoline analogues. These examples expand the structural variability available for cyclic amino aryl carbenes.

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Supporting Information Available: Crystallographic data for compounds **5b**−**d**, **6b**, and **6c** (CIF), experimental procedures, and ^1H and ^{13}C NMR spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

(17) As only one peak for the nine protons is observed in the ^1H NMR spectrum (see Supporting Information), a relatively fast H−Rh bond exchange is assumed to occur in solution.

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