Coupling between 3-Iminoisoindolin-1-ones and Complexed Isonitriles as a Metal-Mediated Route to a Novel Type of Palladium and Platinum Iminocarbene Species

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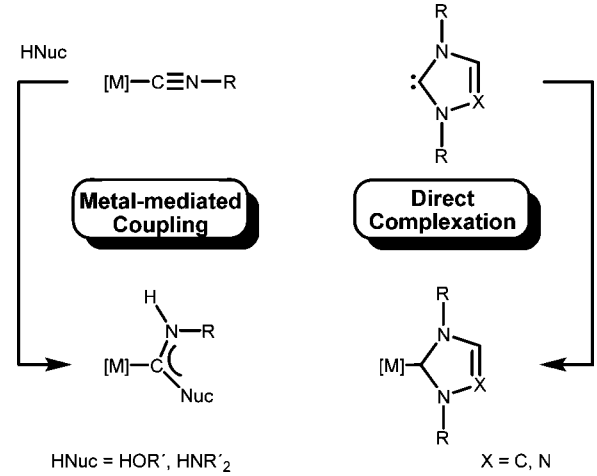
The reaction between isonitrile in *cis*-[$MCl_2(C{\equiv}NR)_2$] [M = Pd, R = Cy **1**, Bu^t **2**, C_6H_3(2,6-Me_2) **3**; M = Pt, R = Cy **4**, Bu^t **5**, C_6H_3(2,6-Me_2) **6**] and various unsubstituted or substituted iminoisoindolin-1-ones HN=$CC_6R^1R^2R^3R^4CONH$ [R_1−R_4 = H **7**; R_1, R_3, R_4 = H, R_2 = Me/R_1, R_2, R_4 = H, R_3 = Me **8** (isomeric mixture); R_1, R_4 = H, R_2, R_3 = Cl **9**] proceeds under reflux conditions in $CHCl_3$ for 2 h. The subsequent workup provides complexes [MCl{C(N=$C(C_6R^1R^2R^3R^4CON)$)=N(H)R}(C≡NR)] (M = Pd, **10**−**18**; M = Pt, **19**−**27**), bearing a novel type of carbene ligands, which were isolated in good (80−85% for the Pd^{II} complexes) to moderate (60−65% for the Pt^{II} species) yields. The addition of the iminoisoindolin-1-one to isonitriles is metal-mediated and has a general character. The reaction of *cis*-[$PtCl_2$(C≡NC_6H_4OMe-4)$_2$] (**28**) with **7** affords a mixture of Pt^{II}-containing species including the monoadduct [PtCl{C(N=$C(C_6H_4CON)$)=N(H)C_6H_4OMe-4}(C≡NC_6H_4OMe-4)] (**29**), the unusual binuclear compound [Pt_2{C(N=$C(C_6H_4CON)$)=N(H)C_6H_4OMe-4}$_2$(C≡NC_6H_4OMe-4)$_2$(μ-HN=CC_6H_4-CON)](Cl) (**30**) with a bridging monodeprotonated 3-iminoisoindolin-1-one, and [Pt(C_6H_4CONC=NH){C(N=$C(C_6H_4CON)$)=N(H)C_6H_4OMe-4}(C≡NC_6H_4OMe-4)] (**31**), the latter resulting from the replacement of the chloro ligand in **29** by the deprotonated iminoisoindolin-1-one. Complexes **10**−**27** were characterized by elemental analyses (C, H, N), ESI^+-MS, IR, and 1D (^{1}H, ^{13}C{^{1}H}) and 2D (^{1}H,^{1}H-COSY, ^{1}H,^{13}C-HMQC/^{1}H,^{13}C-HSQC, ^{1}H,^{13}C-HMBC) NMR spectroscopies, while **29**−**31** by ESI^+-MS, IR, and ^{1}H NMR. In addition, the structures of three carbene complexes (**10**, **27**, and **30**) were elucidated by single-crystal X-ray diffraction analysis.

Introduction

Isonitriles, RN≡C, are versatile reagents in organic and organometallic chemistry, and their transformations allow the synthesis of a wide range of important products.[1] Besides the application of uncomplexed isonitriles for the stereoselective synthesis of bis-amides, heterocycles, and peptides via the so-called multicomponent reactions,[1−3] RN≡C species also attract attention in coordination chemistry due to their ability to form a diversity of types of complexes including aminocarbynes[4,5] and heteroatom-stabilized metallacarbenes[6,7] (Scheme 1).

The heteroatom-stabilized (carbene)[M] species, especially those with N-containing heterocycles, are prominent in organometallic catalysis, e.g. for hydrosylation of alkenes,[7b] and in a wide range of cross-coupling systems (e.g., Heck, Suzuki, Suzuki−Miyaura, Sonogashira, Kosugi−Migita, and Stille

Scheme 1. Generation of Heteroatom-Stabilized Carbene Complexes via Nucleophilic Addition to Metal-Bound Isonitriles and Direct Complexation



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(1) *Isonitrile Chemistry, Organic Chemistry—A Series of Monographs*; Ugi, I., Ed.; Academic Press: New York, 1971.

(2) (a) Ugi, I.; Lohberger, S.; Karl, R. The Passerini and Ugi reactions. In *Comprehensive Organic Synthesis: Selectivity for Synthetic Efficiency*; Trost, B. M., Heathcock, C. H., Eds.; Pergamon: Oxford, 1991; Vol. 2, Chapters 4, 6. (b) Ugi, I., Marquarding, D.; Urban, R. Syntheses of peptides by four-component condensation. In *Chemistry and Biochemistry of Amino Acids. Peptides and Proteins*; Weinstein, B., Ed.; Marcel Dekker: New York, 1982; Vol. 6, pp 245−289.

(3) (a) Dömling, A. *Chem. Rev.* **2006**, *106*, 17–89. (b) Dömling, A.; Ugi, I. *Angew. Chem., Int. Ed.* **2000**, *39*, 3168–3210.

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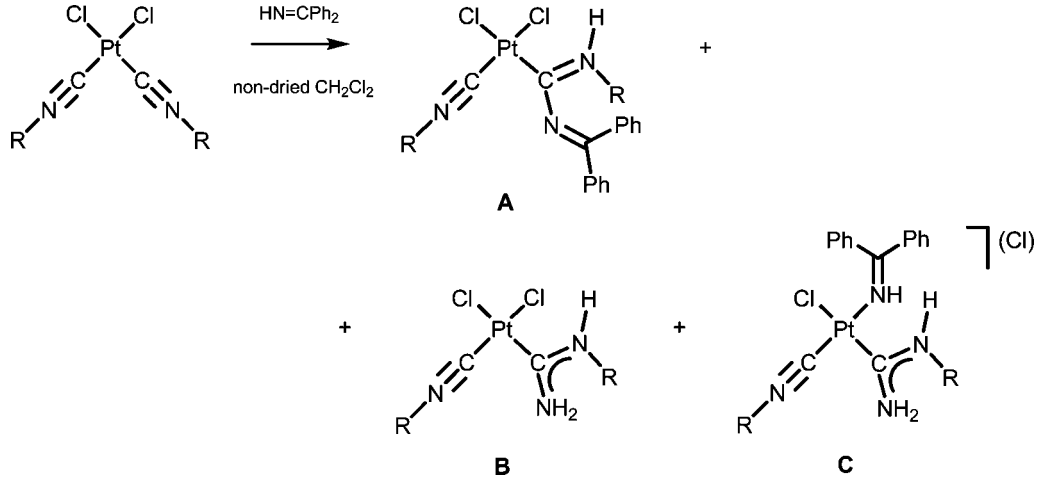
Scheme 2. Interplay between $Ph_2C{=}NH$ and Pt-Bound Isonitrile Species Producing Aminoimino-Carbene and the Detected Decomposition and/or Side Products



reactions).[7a,8] Moreover, some of these carbenes exhibit luminescent properties.[7b]

Two general routes for the preparation of heteroatom-stabilized metallacarbenes are commonly utilized, viz., the coordination of preprepared free carbenes to a metal center, and the transformation of the metal-bound isonitrile upon nucleophilic attack (Scheme 1). The former method is limited mostly to imidazol-2-ylidene, 1,2,4-triazole-3-ylidene, and 1,3-thiazol-2-ylidene derivatives with bulky substituents (some noncyclic species are also known[7]) due to an insufficient stability of the uncomplexed carbenes, while the limitation of the latter route is the relatively low electrophilic activation of the isonitriles. However, the metal-mediated approach appears to be more versatile than the route associated with the direct complexation due to the wide range of available nucleophiles and isonitriles, thus providing a great variety of (carbene)[M] species.

Reactions of complexed isonitriles with nucleophiles have been repeatedly reviewed[6,7] (including a survey by one of us[6]), showing that the vast majority of the reported examples are based on the addition of nucleophiles with sp^3-N or O donor centers, viz. amines and alcohols.[6,7] In this context, additions of sp^3-N nucleophiles, viz. ammonia or primary or secondary amines, to metal-bound RNC molecules are well documented, and this interaction brings about formation of the amino-carbene C(NR≡R″)N(H)R ligands.[6]

In contrast to the additions of nucleophiles with sp^3-N donor centers, the interaction of isonitriles with sp^2-N nucleophiles such as imines is almost unexplored. Thus, only recently, we reported evidence for the integration between a Pt-bound isonitrile and benzophenone imine, affording an aminoimino-carbene complex, which rapidly decomposes in solution prior to isolation.[9] Herein we report on the first unequivocally confirmed examples for the coupling between an imine and complexed isonitriles. Our aims were threefold: (i) to study the coupling between Pd^{II}- and Pt^{II}-bound isonitriles and sp^2-N nucleophiles such as iminoisoindolin-1-ones, (ii) to characterize the complexes formed upon this coupling and bearing iminocarbene ligands of a novel type, and (iii) to compare the reactivity of the iminoisoindolin-1-ones toward isonitriles at these two metal centers. Our results are disclosed in the sections that follow.

Results and Discussions

General Approach. Recently, we reported on the coupling of a Pt-bound isonitrile with an imine, i.e., benzophenone imine, affording an aminoimino-carbene complex **A** depicted in Scheme 2, which derived from a nucleophilic attack of the sp^2-N center on the isonitrile C atom.[9] However, the reaction proceeds nonselectively and the obtained aminoimino-carbene species is unstable even at room temperature. It was characterized spectroscopically in the reaction mixture, while its isolation as a solid failed due to easy hydrolytic conversion to the diaminocarbene *cis*-[$PtCl_2$(C≡NR){C(=NH_2)N(H)R}] (**B**), while formation of the related complex **C** was also observed.

Following our ongoing project on metal-mediated and/or metal-catalyzed activation of small molecules[10] (viz. dinitrogen,[11] alkanes,[12,13] carbon monoxide,[14] cyanides,[15] oximes,[16,17] nitriles,[18−20] and isonitriles[4−6,21]) we have recently discovered that iminoisoindolin-1-ones—which represent a family of stable aromatic imines—exhibit nucleophilic properties toward metal-bound organonitriles RC≡N. It is important that iminoisoin-

(4) Pombeiro, A. J. L.; Guedes da Silva, M. F. C.; Michelin, R. *Coord. Chem. Rev.* **2001**, *218*, 43–74.

(5) (a) Guedes da Silva, M. F. C.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L.; Pellinghelli, M. A.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1996**, 2763–2772. (b) Pombeiro, A. J. L.; Guedes da Silva, M. F. C. *J. Organomet. Chem.* **2001**, *617−618*, 65–69.

(6) Michelin, R.; Pombeiro, A. J. L.; Guedes da Silva, M. F. C. *Coord. Chem. Rev.* **2001**, *218*, 75–112.

(7) (a) Cavell, K. J.; McGuiness, D. S. Palladium complexes with carbonyl, isocyanide and carbene ligands. In *Comprehensive Organometallic Chemistry III*, 1st ed.; Canty, A., Ed.; Elsevier: Oxford, 2007; Vol. 8, Chapter 8.04, pp 197−268. (b) Rourke, J. P. Platinum complexes with carbonyl, isocyanide and carbene ligands. In *Comprehensive Organometallic Chemistry III*, 1st ed.; Canty, A., Ed.; Elsevier: Oxford, 2007; Vol. 8, Chapter 8.07, pp 405−444.

(8) Nolan, S. P.; Navarro, O. C−C bond formation by cross-coupling. In *Comprehensive Organometallic Chemistry III*, 1st ed.; Canty, A., Ed.; Elsevier: Oxford, 2007; Vol. 11, Chapter 11.01, pp 1−38, and references therein.

(9) Luzyanin, K. V.; Guedes da Silva, M. F. C.; Kukushkin, V. Yu.; Pombeiro, A. J. L. *Inorg. Chim. Acta* (Topical Volume Dedicated to B. Lippert), 2008,. in press (doi: 10.1016/j.ica.2008.02.026).

(10) Pombeiro, A. J. L.; Kukushkin, V. Yu. Ligand Reactivity: General Introduction. In *Comprehensive Coordination Chemistry,* 2nd ed.; Lever, A. B. P., Ed.; Elsevier: New York, 2004; Vol. 1, Chapter 1.29, pp 585−594.

(11) (a) Pombeiro, A. J. L.; Costa, M. T. A. R. S.; Wang, Y.; Nixon, J. F. *J. Chem. Soc., Dalton Trans.* **1999**, 3755–3758. (b) Cunha, S. M. P. R. M.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans.* **2002**, 1791–1799. (c) Cunha, S. M. P. R. M.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L. *Inorg. Chem.* **2003**, *42*, 2157–2164. (d) Kirillov, A. M.; Haukka, M.; Guedes da Silva, M. F. C.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *J. Organomet. Chem.* **2006**, *691*, 4153–4158. (e) Smolenski, P.; Pombeiro, A. J. L. *Dalton Trans.* **2008**, 87–91.

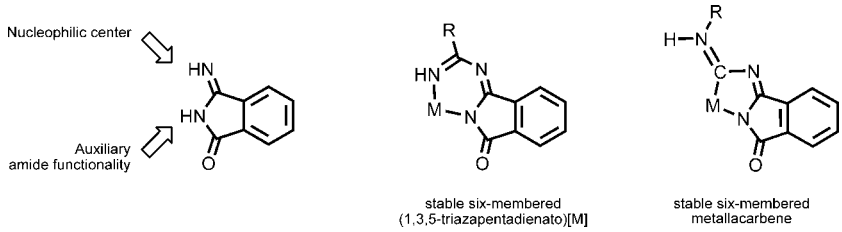


Figure 1. Iminoisoindolin-1-one, (1,3,5-triazapentadienato)[M] chelates, and metallacarbenes.

dolin-1-ones have an endocyclic auxiliary amide functionality, which upon deprotonation might be involved in the complexation forming relatively stable *chelated* metallacycles (Figure 1). Thus, the interplay between iminoisoindolin-1-ones and metal-bound organonitriles leads to the formation of unsymmetrical (1,3,5-triazapentadienato)[M] (M = Ni^{II},[22] Cu^{II} [23]) complexes (Figure 1).

These observations on the stability of the imine (i.e., iminoisoindolin-1-one) and of the products of its addition to nitriles (chelated 1,3,5-triazapentadienato species) prompted us to amplify this type of chemistry to the isomeric isonitriles, and thus we decided to employ iminoisoindolin-1-ones for coupling with palladium(II)- and platinum(II)-bound isonitriles. For this study we addressed, on one hand, the known palladium(II)[24] and platinum(II)[24] isonitrile complexes *cis*-[$MCl_2(C{\equiv}NR)_2$] [M = Pd, R = cyclohexyl (Cy) **1**, Bu^t **2**, $C_6H_3(2,6\text{-}Me_2)$ **3**; M = Pt, R = Cy **4**, Bu^t **5**, $C_6H_3(2,6\text{-}Me_2)$ **6**] and, on the other hand, various unsubstituted (3-iminoisoindolin-1-one **7**) or substituted (isomeric mixture 5-methyl-3-iminoisoindolin-1-one/6-methyl-3-iminoisoindolin-1-one **8** or 5,6-dichloro-3-iminoisoindolin-1-one **9**) iminoisoindolin-1-ones.[25]

Metal-Mediated Addition of Iminoisoindolin-1-ones to Coordinated Isonitriles. The interaction between *cis*-[$MCl_2(C'NR)_2$] (**1**−**6**) and iminoisoindolin-1-ones (**7**−**9**) in $CHCl_3$ (Schemes 3 and 4, Table 1) was studied at different temperatures. Thus, when *cis*-[$MCl_2(C{\equiv}NBu^t)_2$] (M = Pd **2**, Pt **5**) and the *unsubstituted* iminoisoindolin-1-one (**7**) were used as the starting materials, the reaction mixtures rapidly (ca. 5 min, 20−25 °C) changed their color from pale yellow to intense lemon-yellow, following the dissolution of the initial solid of **7**. In the case of Pd^{II}, the system contains a ca. 2:8 mixture (based on TLC and ^{1}H NMR integration data) of the [$PdCl(C_6H_4CO\underline{N}CNH)(C{\equiv}NBu^t)_2$] (**33**) and [$PdCl\{\underline{C}(N{=}C(C_6H_4CO\underline{N})){=}N(H)Bu^t\}(C{\equiv}NBu^t)$] (**13**) complexes (Scheme 3). After 2 h at 20−25 °C, the reaction mixture contained only **13** (ca. 85%) along with some other byproduct, while **33** was no longer detected.

In the case of Pt^{II}, the reaction solution contains comparable amounts of [$PtCl(C_6H_4CO\underline{N}CNH)(C{\equiv}NBu^t)_2$] (**34**) and [$PtCl\{\underline{C}(N{=}C(C_6H_4CO\underline{N})){=}N(H)Bu^t\}(C{\equiv}NBu^t)$] (**22**) along with some yet unidentified species (three spots on TLC apart from those of **34** and **22**). Complex **34** was isolated in ca. 10% yield upon subsequent separation of the components of the mixture based on their different solubilities and characterized by IR, ESI-MS, and ^{1}H NMR (see Experimental Section). When a chloroform solution of **34** was refluxed for ca. 2 h, no formation of **22** was achieved, and only an insignificant thermal degradation of **34** was observed. Reflux of a chloroform solution of a previously isolated and redissolved **22** for ca. 2 h results in its slow thermal degradation, affording a broad mixture of products (four spots on TLC), where minor quantities of **34** were detected. For details of the reactions between the other complexes *cis*-

(12) (a) Reis, P. M.; Silva, J. A. L.; Palavra, A. F.; Fraústo da Silva, J. J. R.; Kitamura, T.; Fujiwara, Y.; Pombeiro, A. J. L. *Angew. Chem., Int. Ed.* **2003**, *42*, 821–823. (b) Kirillov, A. M.; Kopylovich, M. N.; Kirillova, M. V.; Haukka, M.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L. *Angew. Chem., Int. Ed.* **2005**, *44*, 4345–4349. (c) Kirillov, A. M.; Haukka, M.; Kirillova, M. V.; Pombeiro, A. J. L. *Adv. Synth. Catal.* **2005**, *347*, 1435–1446. (d) Reis, P. M.; Silva, J. A. L.; Palavra, A. F.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *J. Catal.* **2005**, *235*, 333–340. (e) Kirillov, A. M.; Kopylovich, M. N.; Kirillova, M. V.; Karabach, E. Yu.; Haukka, M.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L. *Adv. Synth. Catal.* **2006**, *348*, 159–174. (f) Mishra, G. S.; Pombeiro, A. J. L. *J. Appl. Catal. A: Gen.* **2006**, *304*, 185–194.

(13) (a) Mishra, G. S.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *J. Mol. Catal. A: Chem.* **2006**, *265*, 59–69. (b) Kirillova, M. V.; Kirillov, A. M.; Reis, P. M.; Silva, J. A. L.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *J. Catal.* **2007**, *248*, 130–136. (c) Kirllova, M. V.; Kuznetsov, M. L.; Reis, P. M.; Silva, J. A. L.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *J. Am. Chem. Soc.* **2007**, *129*, 10531–10545. (d) Kirillova, M. V.; Da Silva, J. A. L.; Fraústo da Silva, J. J. R.; Palavra, A. F.; Pombeiro, A. J. L. *Adv. Synth. Catal.* **2007**, *349*, 1765–1774. (e) Kirillova, M. V.; Da Silva, J. A. L.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L *Appl. Catal. A: Gen.* **2007**, *332*, 159–165. (f) Kirillova, M. V.; Kuznetsov, M. L.; Silva, J. A. L.; Guedes da Silva, M. F. C.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *Chem.*−*Eur. J.* **2008**, *14*, 1828–1842. (g) Silva, T. F. S.; Alegria, E. C. B. A.; Martins, L. M. D. R. S.; Pombeiro, A. J. L. *Adv. Synth. Catal.* **2008**, *350*, 706–716.

(14) (a) Guedes da Silva, M. F. C.; Ferreira, C. M. P.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans.* **1998**, 4139–4145. (b) Kuznetsov, M. L.; Pombeiro, A. J. L. *Dalton Trans.* **2003**, 738–747. (c) Kirillov, A. M.; Haukka, M.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L. *Eur. J. Inorg. Chem.* **2007**, 1556–1565. (d) Smolenski, P.; Dinoi, C.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L. *J. Organomet. Chem*.,in press.

(15) (a) Carvalho, M. F. N. N.; Duarte, M. T.; Galvão, A. M.; Pombeiro, A. J. L. *J. Organomet. Chem.* **1996**, *511*, 163–169. (b) Guedes da Silva, M. F. C.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L.; Pellinghelli, M. A.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1996**, 2763–2772. (c) Carvalho, M. F. N. N.; Duarte, M. T.; Galvão, A. M.; Pombeiro, A. J. L.; Henderson, R.; Fuess, H.; Svoboda, I. *J. Organomet. Chem.* **1999**, *583*, 56–62. (d) Carvalho, M. F. N. N.; Galvão, A. M.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans.* **2000**, 3393–3400.

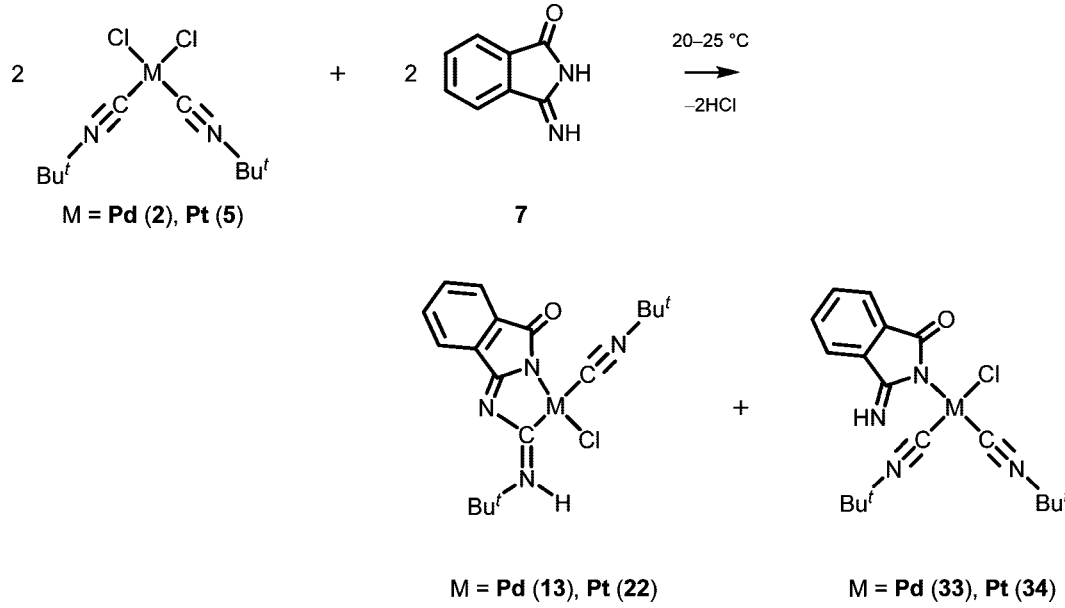
(16) (a) Kukushkin, V. Yu.; Pombeiro, A. J. L. *Coord. Chem. Rev.* **1999**, *181*, 147–175. (b) Kukushkin, V. Yu.; Tudela, D.; Pombeiro, A. J. L. *Coord. Chem. Rev.* **1996**, *156*, 333–362. (c) Pombeiro, A. J. L.; Kukushkin, V. Yu. Reactions of coordinated oximes. In *Comprehensive Coordination Chemistry*, 2nd ed.; Elsevier: New York, 2004; Vol. 1, Chapter 1.33, pp 631−637.

(17) (a) Kukushkin, V. Yu.; Belsky, V. K.; Aleksandrova, E. A.; Konovalov, V. E.; Kirakosyan, G. A. *Inorg. Chem.* **1992**, *31*, 3836–3840. (b) Kukushkin, V. Yu.; Tudela, D.; Izotova, Y. A.; Belsky, V. K.; Stash, A. I. *Inorg. Chem.* **1996**, *35*, 4926–4931.

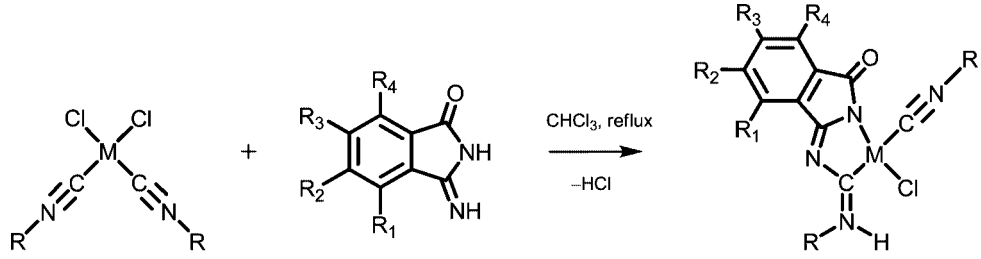
(18) (a) Kukushkin, V. Yu.; Pombeiro, A. J. L *Chem. Rev.* **2002**, *102*, 1771. (b) Pombeiro, A. J. L.; Kukushkin, V. Yu. Reactions of Coordinated Nitriles. In *Comprehensive Coordination Chemistry*, 2nd ed.; Lever, A. B. P., Ed.; Elsevier: New York, 2004; Vol. 1, Chapter 1.34, pp 639−660.

(19) (a) Luzyanin, K. V.; Kukushkin, V. Yu.; Kuznetsov, M. L.; Garnovskii, D. A.; Haukka, M.; Pombeiro, A. J. L. *Inorg. Chem.* **2002**, *41*, 2981–2986. (b) Guedes da Silva, M. F. C.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *Inorg. Chem.* **2002**, *41*, 219–228. (c) Kopylovich, M. N.; Pombeiro, A. J. L.; Fischer, A.; Kloo, L.; Kukushkin, V. Yu. *Inorg. Chem.* **2003**, *42*, 7239–7248. (d) Kopylovich, M. N.; Kukushkin, V. Yu.; Haukka, M.; Luzyanin, K. V.; Pombeiro, A. J. L. *J. Am. Chem. Soc.* **2004**, *126*, 15040–15041. (e) Luzyanin, K. V.; Kukushkin, V. Yu.; Ryabov, A. D.; Haukka, M.; Pombeiro, A. J. L. *Inorg. Chem.* **2005**, *44*, 2944–2953. (f) Luzyanin, K. V.; Kukushkin, V. Yu.; Kuznetsov, M. L.; Ryabov, A. D.; Galanski, M.; Haukka, M.; Tretyakov, E. V.; Ovcharenko, V. I.; Kopylovich, M. N.; Pombeiro, A. J. L. *Inorg. Chem.* **2006**, *45*, 2296–2306.

Scheme 3. Interplay between *cis*-[$MCl_2(C{\equiv}NBu^t)_2$] (M = Pd, Pt) and 7 at 20−25 °C



Scheme 4. Reaction of Iminoisoindolin-1-ones with an Isonitrile in *cis*-[$MCl_2(C{\equiv}NR)_2$]



M = **Pd**
R = Cy **1**, Bu^t **2**, $Me_2C_6H_3$ **3**

M = **Pt**
R = Cy **4**, Bu^t **5**, $Me_2C_6H_3$ **6**

R^1–R^4 = H **7**
R^1, R^3, R^4 = H; R^2 = Me **8**
R^1, R^4 = H; R^2, R^3 = Cl **9**

10–**27**

Table 1

M(CNR) species	iminoisoindolin-1-one	product	M(CNR) species	iminoisoindolin-1-one	product
1	**7**	**10**	**4**	**7**	**19**
	8	**11**		**8**	**20**
	9	**12**		**9**	**21**
2	**7**	**13**	**5**	**7**	**22**
	8	**14**		**8**	**23**
	9	**15**		**9**	**24**
3	**7**	**16**	**6**	**7**	**25**
	8	**17**		**8**	**26**
	9	**18**		**9**	**27**

[$MCl_2(C{\equiv}NR)_2$] (**1**, **3**, **4**, and **6**) and iminoisoindolin-1-ones (**7**−**9**) see Appendix 1, Supporting Information.

In order to increase the reactivity of the isonitrile ligands and/or the solubility of the iminoisoindolin-1-ones, the reactions were performed in $CHCl_3$ under reflux conditions to achieve higher yields of **10**−**27**. Thus, the reaction between a metal-bound isonitrile in *cis*-[$MCl_2(C'NR)_2$] (**1**−**6**) and the iminoisoindolin-1-ones (**7**−**9**) proceeds in $CHCl_3$ under reflux for 2 h (Scheme 4), and the subsequent workup provides the carbene species [MCl{C(N=C($C_6R^1R^2R^3R^4$CON))=N(H)R}(C≡NR)] (M = Pd, **10**−**18**; M = Pt, **19**−**27**; Table 1) in good (80−85% for the Pd^{II} complexes) to moderate (60−65% for the Pt^{II} species) isolated yields.

For the reaction under reflux conditions, the influences of the ratio of the reagents and reaction time on the yields and purity of the coupling products were studied (see Appendix 2, Supporting Information, for the detailed studies). Thus, for the reaction of palladium(II) complex **1** with **7**, the best results were obtained for the 1:1 molar ratio; the change to 1:2 or 1:4 ratios did not significantly affect the reaction, but the coupling product **10** was strongly contaminated with **7** (ESI^+-MS, *m*/*z* 146) and **7**·HCl (ESI^+-MS, *m*/*z* 182). In the case of 1:2 or 1:4 molar ratios, the increase of the reaction time from 4 to 24 h provides a mixture of **10** with unreacted **7**, **7**·hydrochloride, phthalimide (which originates from the hydrolytic decomposition of **7** (ESI^+-MS, *m*/*z* 147; ^{1}H NMR in $CDCl_3$, δ 7.84 (s, 4H), 11.35 (s, 1H); lit.[26] 7.85 (s, 4H), 11.38 (s, 1H)), and some other yet unidentified byproducts.

For the reaction of Pt^{II}-bound isonitriles in **6** with **7**, the best results were obtained with a 1:2 ratio. Similarly to the palladium(II) complex, the change of the molar ratio of the reagents to 1:4 does not significantly affect the reaction, but affords **27** contaminated with **7** and some decomposition species.

For 1:2 or 1:4 molar ratios, the increase of the reaction time to 24 h results in the slow thermal decomposition of **27** and, consequently, in a decrease of its isolated yield from 60% to 45%.

In general, the addition of the iminoisoindolin-1-ones along the C≡N triple bond of isonitrile proceeds at a higher degree of selectivity in the case of the palladium(II) species as compared to the corresponding platinum(II) complexes. In the latter case, some byproducts were identified by ^{1}H NMR and ESI-MS, viz. phthalimide, derived from the hydrolysis of the starting 3-iminoisoindolin-1-one, and previously unknown platinum iminoisoindolin-1-one complexes (**34**), among other unidentified species.

One should mention that the coupling reaction proceeds in a rather efficient way with the isonitriles bearing either alkyl or aryl R groups and also with nonsubstituted (**7**) and substituted (**8** and **9**) iminoisoindolin-1-ones. Furthermore, the addition of the iminoisoindolin-1-one has a metal-mediated character. Indeed, in a blank experiment conducted in $CDCl_3$ at 50 °C, no reaction between the metal-free isonitriles and 3-iminoisoindolin-1-one was observed for 1 day.

The comparison of the integration between iminoisoindolin-1-ones (**7**−**9**) and metal-bound organonitriles RC≡N (see refs 22 and 23) versus **7**−**9** and coordinated isonitriles RN≡C (this work) points out that, in both cases, the interplay leads to chelated species due to the complexation of the auxiliary amide functionality of the iminoisoindolin-1-ones to yield six- and five-membered metallacycles, respectively (Figure 1). However, the isonitrile-based system affords solely monoiminocarbene complexes, while the second RN≡C ligand remains intact probably due to the deactivation of the second isonitrile species in *cis*-$[MCl_2(C{\equiv}NR)_2]$ after the nucleophilic addition to the first isonitrile ligand. Unlikely, the coupling between iminoisoindolin-1-ones and metal-bound organonitriles RCN produces (1,3,5-triazapentadienato)[M] complexes (M = Ni^{II},[22] Cu^{II},[23] Pd^{II} [27]) with two equivalent 1,3,5-triazapentadienato ligands formally derived from the coupling with two nitriles.[22,23,27]

Characterization of the Palladium and Platinum Carbene Complexes 10−27. Complexes **10**−**27** were characterized by elemental analyses (C, H, N), ESI^+-MS, IR, and 1D (^{1}H, ^{13}C{^{1}H}) and 2D (^{1}H,^{1}H-COSY, ^{1}H,^{13}C-HMQC/^{1}H,^{13}C-HSQC, ^{1}H,^{13}C-HMBC) NMR spectroscopies. In addition, the structures of complexes **10** and **27** were elucidated by single-crystal X-ray diffraction studies.

Complexes **10**−**27** gave satisfactory C, H, and N elemental analyses, which are consistent with the proposed formulations of the mixed (isonitrile/carbene)Pd^{II} or (isonitrile/carbene)Pt^{II} complexes [MCl{C(N=C($C_6R^1R^2R^3R^4$CON))=N(H)R}(C≡NR)], obtained via nucleophilic addition of the iminoisoindolinone to one isonitrile ligand and chelation of the newly formed species. The ESI^+-MS mass spectra of **10**−**27** display molecular ion peaks and/or a fragmentation corresponding to the loss of Cl's from the molecular ion, viz. $[M - nCl]^+$.

The IR spectra of **10**−**27** exhibit one strong ν(C≡N) stretching vibration in the range between 2220 and 2198 cm^{-1}, while the starting *cis*-$[MCl_2(C{\equiv}NR)_2]$ (M = Pd, Pt) complexes usually display two overlapped stretches in the interval 2250−2150 cm^{-1}.[28] This suggests the presence of only one isonitrile ligand in the product of the reaction between *cis*-$[MCl_2(C{\equiv}NR)_2]$ and an iminoisoindolin-1-one. In the newly formed C=N(H)R carbene moiety, ν(N−H) bands emerge in the range 3256−3210 cm^{-1}, while the corresponding very strong bands due to ν(C=N) appear between 1561 and 1521 cm^{-1}. In the IR spectra of **10**−**27**, two (for **13**, **14**, **18**−**20**, and **27**), three (for **10**−**12**, **15**, **17**, and **20**−**25**), or four (for **16**) bands between 1738 and 1607 cm^{-1} belong to the overlapped ν(C=O) and ν(*C*=N) vibrations from the iminoisoindolin-1-one moiety. The medium intensity/weak bands in the range 3032−2989 cm^{-1} are characteristic of ν_s(C−H) and ν_{as}(C−H) vibrations.

The ^{1}H NMR spectra of the carbene complexes **10**−**27** display a broad peak in the range δ 8.90−10.70 assigned to the M−$C_{carbene}$=N(*H*)R proton. This value is typical for a NH proton involved into an intramolecular hydrogen bonding, which was also found in the solid state upon examination of the X-ray structure of **10** (see below). In each of **10**−**12** and **19**−**21**, obtained from *cis*-$[MCl_2(C{\equiv}NCy)_2]$, the characteristic signals of the proton and carbon of the tertiary HC from the cyclohexyl ring of the C≡NR ligand resonates at ca. 4.50 and 54.5 ppm, correspondingly, while in the carbene species the relevant signals appear at a higher field (ca. 4.00 and 53.5 ppm, respectively). Addition of the iminoisoindolin-1-one to the coordinated isonitrile is accompanied by a pronounced δ ^{13}C shift to lower field of the quaternary C atom of one isonitrile to the carbene (C≡N to C=N). Thus, in **10**−**27**, the $C_{carbene}$=NH ^{13}C signals were found to resonate at ca. 200 ppm, i.e., approximately 80 ppm to lower field in comparison with the starting (isonitrile)M^{II} complexes (e.g., 115 ppm for C≡N in *cis*-$[PdCl_2(C{\equiv}NC_6H_{11})_2]$). In the ^{13}C{^{1}H} spectra of **13**−**15** obtained from *cis*-$[PdCl_2(C{\equiv}NBu^t)_2]$, a peak at ca. 115 ppm was assigned to C≡N from the unreacted isonitrile moiety, while in the other

(20) (a) Wagner, G.; Pombeiro, A. J. L.; Kukushkin, V.Yu. *J. Am. Chem. Soc.* **2000**, *122*, 3106–3111. (b) Wagner, G.; Haukka, M.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L.; Kukushkin, V. Yu. *Inorg. Chem.* **2001**, *40*, 264–271. (c) Belluco, U.; Benetollo, F.; Bertani, R.; Bombieri, G.; Michelin, R. A.; Mozzon, M.; Tonon, O.; Pombeiro, A. J. L.; Guedes da Silva, M. F. C. *Inorg. Chim. Acta* **2002**, *334*, 437–447. (d) Bokach, N. A.; Khripoun, A. V.; Kukushkin, V. Yu.; Haukka, M.; Pombeiro, A. J. L. *Inorg. Chem.* **2003**, *42*, 896–903. (e) Kuznetsov, M. L.; Nazarov, A. A.; Pombeiro, A. J. L. *J. Phys. Chem. A* **2005**, *109*, 8187–8198. (f) Makarycheva-Mikhailova, A. V.; Golenetskaya, J. A.; Bokach, N. A.; Balova, I. A.; Haukka, M.; Kukushkin, V. Yu. *Inorg. Chem.* **2007**, *46*, 8323–8331. (g) Lasri, J.; Charmier, M. A. J.; Haukka, M.; Pombeiro, A. J. L. *J. Org. Chem.* **2007**, *72*, 750–755.

(21) (a) Guedes da Silva, M. F. C.; Hitchcock, P. B.; Hughes, D. L.; Marjani, K.; Pombeiro, A. J. L.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1997**, 3725–3731. (b) Tong, Y.-Y.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L.; Wagner, G.; Herrmann, R. *J. Organomet. Chem.* **1998**, *552*, 17–21. (c) Costa, M. T. A. R. S.; Dilworth, J. R.; Duarte, M. T.; Fraústo da Silva, J. J. R.; Galvão, A. M.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans.* **1998**, 2405–2410. (d) Almeida, S. S. P. R.; Guedes da Silva, M. F. C.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans.* **1999**, 467–472. (e) Zhang, L.; Gamasa, M. P.; Gimeno, J.; Carbajo, R. J.; López-Ortiz, F.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L. *Eur. J. Inorg. Chem.* **2000**, 341–350. (f) Guedes da Silva, M. F. C.; Lemos, M. A. N. D. A.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L.; Pellinghelli, M. A.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **2000**, 373–380.

(22) (a) Gushchin, P. V.; Luzyanin, K. V.; Kopylovich, M. N.; Haukka, M.; Pombeiro, A. J. L.; Kukushkin, V. Yu. *Inorg. Chem.* **2008**, *47*, 3088–3094. (b) Kopylovich, M. N.; Haukka, M.; Kirillov, A. M.; Kukushkin, V. Yu.; Pombeiro, A. J. L. *Chem.−Eur. J.* **2007**, *13*, 786–791.

(23) Kopylovich, M. N.; Luzyanin, K. V.; Haukka, M.; Pombeiro, A. J. L.; Kukushkin, V. Yu., *Dalton Trans.* **2008**, in press (doi: 10.1039/b805243c).

(24) (a) Michelin, R. A.; Zanotto, L.; Braga, D.; Sabatino, P.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 85–92. (b) Michelin, R. A.; Zanotto, L.; Braga, D.; Sabatino, P.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 93–99. (c) Bertani, R.; Mozzon, M.; Michelin, R. A. *Inorg. Chem.* **1988**, *27*, 2809. (d) Bertani, R.; Mozzon, M.; Michelin, R. A.; Benetollo, F.; Bombieri, G.; Castilho, T. J.; Pombeiro, A. J. L. *Inorg. Chim. Acta* **1991**, *189*, 175–187.

(25) (a) Luzyanin, K. V.; Kukushkin, V. Yu.; Kopylovich, M. N.; Nazarov, A. A.; Galanski, M.; Pombeiro, A. J. L. *Adv. Synth. Catal.* **2008**, *350*, 135–142. (b) Pombeiro, A. J. L.; Luzyanin, K. V.; KukushkinV. Yu.; KopylovichM. N. Patent PT-103718, Apr. 13, 2007.

(26) Pouchert, C. J. *Aldrich Library of ^{13}C and ^{1}H FT-NMR Spectra*; Wiley: New York, 2008.

(27) Carvalho, R.; Gushchin, P. V.; Luzyanin, K. V.; Kopylovich, M. N.; Haukka, M.; Pombeiro, A. J. L.; Kukushkin, V. Yu., unpublished results.

(28) Bonati, F.; Minghetti, G. *J. Organomet. Chem.* **1970**, *24*, 251–256.

Table 2. Crystal Data for 10, 27, and 30

	10	27	30
empirical formula	$C_{22}H_{27}ClN_4OPd$	$C_{26}H_{21}Cl_3N_4OPt$	$C_{56}H_{44}ClN_{10}O_8Pt_2$
fw	505.33	706.91	1410.64
temp (K)	120(2)	120(2)	120(2)
λ (Å)	0.71073	0.71073	0.71073
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
a (Å)	8.9322(3)	8.3009(3)	21.9505(5)
b (Å)	11.5556(5)	12.4324(6)	17.3228(5)
c (Å)	11.6712(5)	12.7236(7)	15.5420(4)
α (deg)	109.128(2)	74.722(3)	90
β (deg)	107.747(2)	77.042(3)	113.9340(10)
γ (deg)	93.895(3)	85.816(3)	90
V (Å^3)	1064.97(7)	1234.28(10)	5401.6(2)
Z	2	2	4
ρ_{calc} (Mg/m^3)	1.576	1.902	1.735
μ(Mo Kα) (mm^{-1})	1.018	6.037	5.288
reflns collected	19 446	16 007	39 169
unique reflns	4493	5610	6152
$R_{int.}$	0.0530	0.0621	0.0458
R1[a] ($I \geq 2\sigma$)	0.0318	0.0391	0.0384
wR2[b] ($I \geq 2\sigma$)	0.0631	0.0649	0.0838

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

complexes the corresponding peak was not observed due to its low intensity.

The ^{1}H and ^{13}C signal assignments were performed by interpretation of gradient-enhanced two-dimensional ^{1}H,^{13}C-HMQC/^{1}H,^{13}C-HSQC and ^{1}H,^{13}C-HMBC NMR spectra. Especially the long-range shift correlation experiments via $^2J_{H,C}$ and $^3J_{H,C}$ coupling were found to be of high value because they distinguished the signals of the newly formed carbene species from C═O and C═N of the iminoisoindolin-1-one moiety. Thus, in the low-field region (150−200 ppm) of the ^{1}H,^{13}C-HMBC NMR spectrum of **12** (Supporting Information, Figure S1), the ^{13}C signals of the imine and carbonyl carbons from the iminoisoindolin-1-one moiety were detected at 171.4 and 184.0 ppm, correspondingly, and assigned through the shift correlation peaks with the corresponding protons from the phenyl ring. A signal resonating at 197.9 ppm displays no cross-coupling with the phenyl protons, thus being assigned to the carbene carbon atom ($C_{carbene}$).

The crystallographic data and processing parameters for **10** and **27** are summarized in Table 2, while the corresponding plots can be found in Figure 2, and bond lengths and angles are given in Table 3.

The crystal structure of either **10** or **27** consists of discrete molecules and metal centers adopt a distorted square-planar geometry. The unreacted isonitrile is in the *trans* position to the carbene carbon atom of {C(N═C($C_6R^1R^2R^3R^4$CON))═N(H)R}, which acts as a bidentate ligand, forming the five-membered chelate ring. In the metallacycle, the angles N(1)−Pd(1)−C(9) and N(1)−Pt(1)−C(9) are 77.55(18)° and 78.09(10)°, being slightly smaller than that previously observed in the related palladium and platinum five-membered chelates [Pd(phen){C(═O)NPhC(═O)NPh}](80.14 Å),[29] [PdI{C≡NC_6H_3(2,6-Me_2)}{C(C_6H_4(2-NH_2))═NC_6H_3(2,6-Me_2)}] (82.89 Å),[30] *cis*-[PtCl(NH_3)(NH_2CH_2COO)] (81.56 Å),[31] or [PtCl(PPh_3)(NMe_2-$CH_2NMe_2CH_2$)](Cl) (82.30 Å).[32] The carbene ligands in both **10** and **27** are in the *E*-configuration, and the Pd−$C_{carbene}$ [Pd(1)−C(9) 2.001(3) Å] distance in **10** is slightly longer, while the Pt−$C_{carbene}$ [Pt(1)−C(9) 2.002(5) Å] in **27** is equal within 3σ to those reported for the related palladium and platinum carbene complexes *cis*-[$PdCl_2${C(OMe)═N(H)Me}$_2$] (1.953−1.972 Å),[33] *cis*-[$PdCl_2${C(═NHCy)NHNHC(═NHCy)}$_2$] (1.958−1.964 Å),[34] [Pt{η^2-(*S*,*S*′)-S_2C═C(C(O)Me)}(CNBu^t){C(NEt_2)(NHBu^t)}] [2.053(2) Å],[35] and *cis*-[$PtCl_2${CNC_6H_3(2,6-Me_2)}{C(NH_2)N(H)C_6H_3(2,6-Me_2)}] [1.983(7) Å].[9] In both complexes, the $C_{carbene}$═N(H)R moiety of the carbene ligand is roughly planar, and the $C_{carbene}$−N moiety [C(9)−N(3) in **10**: 1.308(3) Å, in **27**: 1.329(7) Å] has a double-bond character, with the bond length in accord with those found in the related carbene complexes above (1.29−1.33 Å).[9,33−35]

The C(18)−N(4) triple bond of the unreacted isonitrile ligand [**10**: 1.140(3), **27**: 1.163(6) Å] has a normal value for the triple CN bond and is consistent with that observed in related isonitrile palladium and platinum complexes, e.g., *cis*-[$PdCl_2$(C≡$NR)_2$], R = Cy (1.128−1.142 Å),[36] Bu^t (1.108−1.149 Å),[37] C_6H_3(2,6-Me_2)(1.145−1.156Å),[38] [PtCl{CNC_6H_3(2,6-Me_2)}{C(NH_2)N(H)C_6H_3-(2,6-Me_2)}(Ph_2C═NH)](Cl) [1.151(9) Å],[9] and [Pt{η^2-(*S*,*S*′)-S_2C═C{C(O)Me}$_2$}{CNC_6H_3(2,6-Me_2)}$_2$] [1.152(3) Å].[35] An intramolecular hydrogen bond between the proton (H3) from the carbene $C_{carbene}$═N(H)R moiety and the chloride ligand [**10**: d(N−H) 0.83(3), d(N···Cl) 3.119(2), d(H···Cl) 2.52 Å, ∠(NHCl) 130(3)°; **27**: d(N−H) 0.96(7), d(N···Cl) 3.122(4), d(H···Cl) 2.329 Å, ∠(NHCl) 139(6)°] can be recognized.

All other bond lengths in **10** and **27** have normal values and they agree with those reported[9,33−35] for related platinum(II) and palladium(II) carbene and isonitrile complexes.

Coupling of an Isonitrile in *cis*-[$PtCl_2$(C≡NC_6H_4OMe-4)$_2$] and 3-Iminoisoindolin-1-one. We also attempted to employ for our studies the platinum(II) complex bearing the aromatic isonitrile C≡NC_6H_4OMe-4, viz. *cis*-[$PtCl_2$(C≡NC_6H_4OMe-4)$_2$] (**28**), but in this particular case the interaction proceeds with a very low selectivity. Thus, refluxing for ca. 4 h a mixture of **28** and **7** in $CHCl_3$ in a 1:2 molar ratio of the reactants leads to a broad mixture of Pt^{II}-containing species, which are difficult to separate even by TLC, where more than five spots were detected. However, among the products we succeeded in identifying the expected monoadduct **29** (yield is ca. 25%, based on the ^{1}H NMR integration), the unusual type binuclear complex **30**, containing the deprotonated 3-iminoisoindolin-1-one, which bridges two platinum centers, and complex **31** (ESI$^+$-MS, m/z 751 [M]$^+$; IR, cm^{-1} 2196 ν(C≡N)). Complex **31** at least formally results from the replacement of the chloride ligand in **29** by the deprotonated iminoisoindolin-1-one (Scheme 5).

When the reaction of **28** and **7** in $CHCl_3$ was performed at 20−25 °C for 4 h, monitoring of the reaction mixture by TLC shows that it contains at least three products, which are different from **29**−**31**. ESI-MS monitoring indicated the presence of [PtCl(C_6H_4CONCNH)(C≡NC_6H_4OMe-4)$_2$] (**32**) (m/z 641 [M]), derived from the substitution of a chloride in **28** for a monodeprotonated **7**, while the absence of the characteristic

(29) Paul, F.; Fischer, J.; Ochsenbein, P.; Osborn, J. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1638–1640.
(30) Vicente, J.; Abad, J.-A.; Frankland, A. D.; Lopez-Serrano, J.; De Arellano, M. C. R.; Jones, P. G. *Organometallics* **2002**, *21*, 272–282.
(31) Baidina, I. A.; Podberezskaya, N. V.; Krylova, L. F.; Borisov, S. V.; Bakakin, V. V. *Zh. Strukt. Khim. (Russ. J. Struct. Chem.)* **1980**, *21*, 106–110.
(32) Barefield, E. K.; Carrier, A. M.; Sepelak, D. J.; Van Derveer, D. G. *Organometallics* **1982**, *1*, 103–110.
(33) Domiano, P.; Musatti, A.; Nardelli, M.; Predieri, G. *J. Chem. Soc., Dalton Trans.* **1975**, 2165–2168.
(34) Moncada, A. I.; Khan, M. A.; Slaughter, L. M. *Tetrahedron Lett.* **2005**, *46*, 1399–1403.
(35) Vicente, J.; Chicote, M. T.; Huertas, S. *Inorg. Chem.* **2003**, *42*, 4268–4274.
(36) Kitano, Y.; Hori, T. *Acta Crystallogr. B* **1981**, *37*, 1919–1921.
(37) Perreaul, D.; Drouin, M.; Michel, A.; Harvey, P. D. *Inorg. Chem.* **1993**, *32*, 1903–1912.
(38) Drouin, M.; Perreaul, D.; Harvey, P. D.; Michel, A. *Acta Crystallogr. C* **1991**, *47*, 752–754.

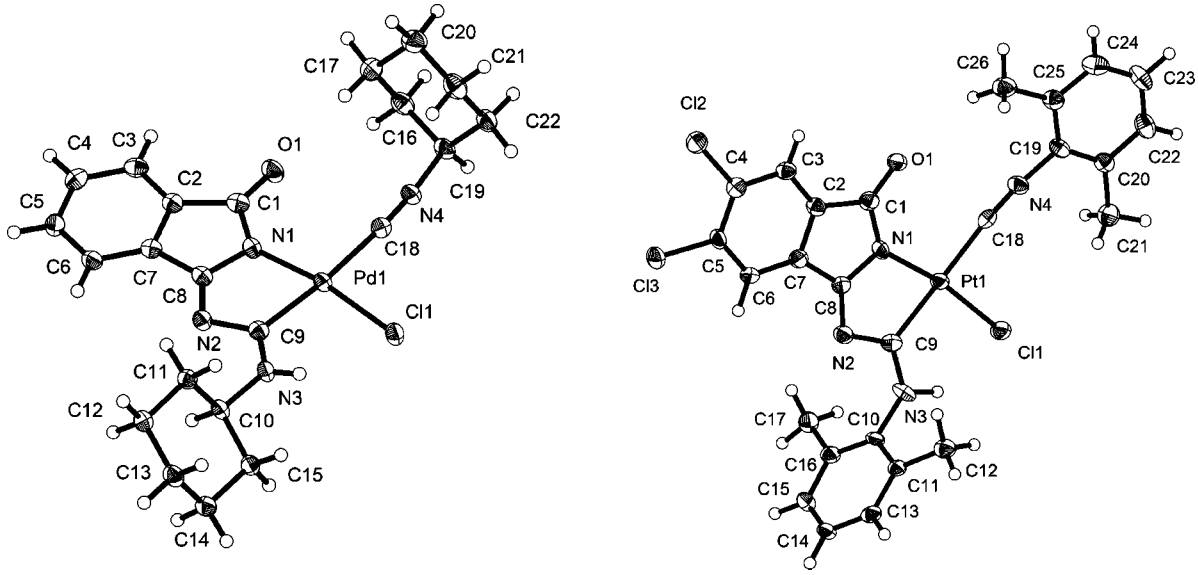


Figure 2. View of **10** (left) and **27** (right) with atomic numbering schemes. Thermal ellipsoids are drawn with 50% probability.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for 10 and 27

	10	**27**
Pd(1)−N(1)	2.000(2)	
Pt(1)−N(1)		1.994(4)
Pd(1)−C(9)	2.001(3)	
Pt(1)−C(9)		2.002(5)
Pd(1)−C(18)	2.044(3)	
Pt(1)−C(18)		1.983(5)
Pd(1)−Cl(1)	2.3256(7)	
Pt(1)−Cl(1)		2.3157(14)
O(1)−C(1)	1.217(3)	1.216(6)
N(1)−C(8)	1.370(3)	1.363(6)
N(1)−C(1)	1.394(3)	1.381(7)
N(2)−C(8)	1.313(3)	1.310(6)
N(2)−C(9)	1.381(3)	1.392(6)
N(3)−C(9)	1.308(3)	1.329(7)
N(3)−C(10)	1.484(3)	1.453(6)
N(4)−C(18)	1.140(3)	1.163(6)
N(4)−C(19)	1.461(3)	1.402(6)
N(1)−Pd(1)−C(9)	78.09(10)	
N(1)−Pt(1)−C(9)		77.55(18)
C(18)−Pd(1)−Cl(1)	93.74(8)	
C(18)−Pt(1)−Cl(1)		90.01(15)
C(8)−N(2)−C(9)	109.5(2)	108.8(4)
C(18)−N(4)−C(19)	174.6(3)	173.9(5)
N(3)−C(9)−N(2)	117.2(2)	118.2(4)
C(9)−N(3)−C(10)	126.9(2)	124.4(4)

signals (viz. the carbene NH and the C═N group in the ^{1}H and ^{13}C{^{1}H} NMR spectra, correspondingly) clearly demonstrated that no addition of **7** to **28** giving **29** occurred. Our attempts to promote the selectivity of the process by decreasing the reaction temperature to −20 °C were not successful because even at this low temperature the interplay still gave a mixture having a composition similar to that obtained at 20−25 °C.

The identification of **29**−**32** was based on ESI$^+$-MS (1357 [M_{30} − Cl]; 751 [M_{31}]; 641 [M_{29}]) and NMR spectra [^{1}H NMR ($CDCl_3$, δ) for **31**: 10.02 (s, br, 1H, NH), 7.80−7.68 (m, 4H) (aryls from the isoindolin-1-one moiety), 7.25−7.14 (m, 6H, aryls), 3.85 (s, 3H), and 3.83 (s, 3H, OMe)]. In addition, slow evaporation of the reaction mixture resulted in the release of crystals of **30**·H_2O suitable for an X-ray diffraction study (Figure 3); our attempts to isolate pure **29** and **31** from the reaction mixture were not successful insofar as they are strongly contaminated with other products.

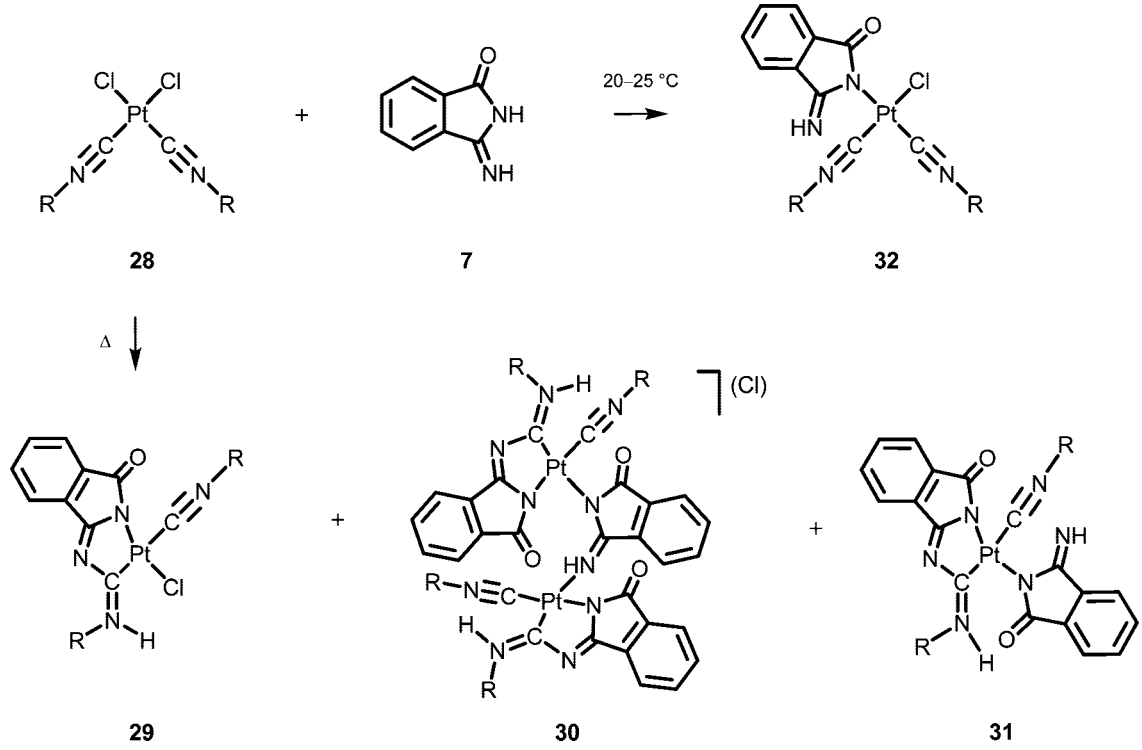
In the crystal structure of **30**·H_2O, both Pt^{II} centers exhibit a slightly distorted square-planar geometry. They have the same coordination environment, viz. one C(N═C(C_6H_4CON))═N(H)-(C_6H_4OMe-4) ligand coordinated by both the carbene C atom and the N(2) atom from the deprotonated iminoisoindolin-1-one moiety, and one isonitrile ligand. The fourth coordination site at each Pt^{II} center is occupied by one of the two nitrogens from the deprotonated 3-iminoisoindolin-1-one, which bridges the two platinum centers. The Pt···Pt separation is ca. 3.1485(4) Å, suggesting that in **30**·H_2O there is no real Pt−Pt bond. One should mention that the structure of **30**·H_2O represents the first crystallographic evidence for metal complexes bearing any coordinated iminoisoindolin-1-one.

In **30**·H_2O, the unreacted isonitrile ligand is located in the *trans* position to N(2) from the iminoisoindolin-1-one functionality of the carbene. The latter ligand forms a five-membered metallacycle, with the N(1)−Pt(1)−C(9) angle [78.2(2)°] slightly smaller than in previously characterized relevant platinum five-membered chelates, e.g. [$PtCl_2$(2,2′-bpy)] (79.06−80.80 Å),[39] *cis*-[PtCl(NH_3)(NH_2CH_2CON)] (81.56 Å),[31] or [PtCl(NMe_2-CH_2NMe_2CH_2)(PPh_3)](Cl) (82.30 Å).[32] The carbene ligand is in the *Z*-configuration, and both Pt−$C_{carbene}$ [Pt(1)−C(9) 1.999(6) Å] and $C_{carbene}$−N [C(9)−N(3) 1.322(7) Å] distances are in good agreement with those previously observed in the related platinum carbene complexes [PtCl{CNC_6H_3(2,6-Me_2)}{C(NH_2)N(H)C_6H_3-(2,6-Me_2)}(Ph_2C═NH)](Cl) [1.995(6) and 1.330(8) Å][9] and [$PtCl_2${CNC_6H_3(2,6-Me_2)}{C(NH_2)N(H)C_6H_3(2,6-Me_2)}][1.983(7) and 1.295(8) Å].[9] The C(17)−N(4) multiple bond length of the isonitrile [1.149(7) Å] has a normal value for the triple CN bond and is consistent with those reported for related isonitrile platinum complexes, e.g., [PtCl{CNC_6H_3(2,6-Me_2)}{C(NH_2)N(H)-C_6H_3(2,6-Me_2)}(Ph_2C═NH)]Cl [1.151(9) Å][9] and [Pt{η^2-(*S*,*S*′)-S_2C═C{C(O)Me}$_2$}{CNC_6H_3(2,6-Me_2)}$_2$] [1.152(3) Å].[35]

The identification of **30** and **31** allows the understanding of the lower selectivity for the Pt^{II}-mediated addition of 3-iminoisoindolin-1-one to isonitrile as compared to the Pd^{II} system. Thus, in the case of platinum, the integration of **7** and the ligated

(39) (a) Osborn, R. S.; Rogers, D. *J. Chem. Soc., Dalton Trans.* **1974**, 1002–1004. (b) Textor, M.; Oswald, H. R. *Z. Anorg. Allg. Chem.* **1974**, *407*, 244–256. (c) Canty, A. J.; Skelton, B. W.; Traill, P. R.; White, A. H. *Aust. J. Chem.* **1992**, *45*, 417–422. (d) Connick, W. B.; Henling, L. M.; Marsh, R. E.; Gray, H. B. *Inorg. Chem.* **1996**, *35*, 6261–6265. (e) Falvello, L. R.; Garde, R.; Miqueleiz, E. M.; Tomas, M.; Urriolabeitia, E. P. *Inorg. Chim. Acta* **1997**, *264*, 297–303. (f) Grzesiak, A. L.; Matzger, A. J. *Inorg. Chem.* **2007**, *46*, 453–457.

Scheme 5. Reaction of the 3-Iminoisoindolin-1-one with *cis*-[PtCl$_2$(C≡NR)$_2$] (R = C$_6$H$_4$OMe-*p*)



C≡NR to furnish the carbene species occurs concurrently with the replacement of the chlorides from the starting material, forming rather inert substitution products, which are thus removed from further coupling.

Final Remarks

This paper reports on the first unequivocally confirmed example of a metal-mediated integration between an *imine* and an *isonitrile* affording chelate-stabilized iminocarbene species. Thus, we have demonstrated that the reaction between one isonitrile in *cis*-[MCl$_2$(C≡NR)] (M = Pd^{II}, Pt^{II}) and an iminoisoindolin-1-one opens up a route to palladium and platinum complexes containing iminocarbene ligands of a novel type (see Scheme 3) derived from a metal-mediated nucleophilic attack by the sp^2-N nucleophilic center of the iminoisoindolin-1-one on the CN moiety of the coordinated RN≡C. The coupling proceeds with a higher selectivity in the case of the Pd^{II} species as compared to the corresponding Pt^{II} complexes,

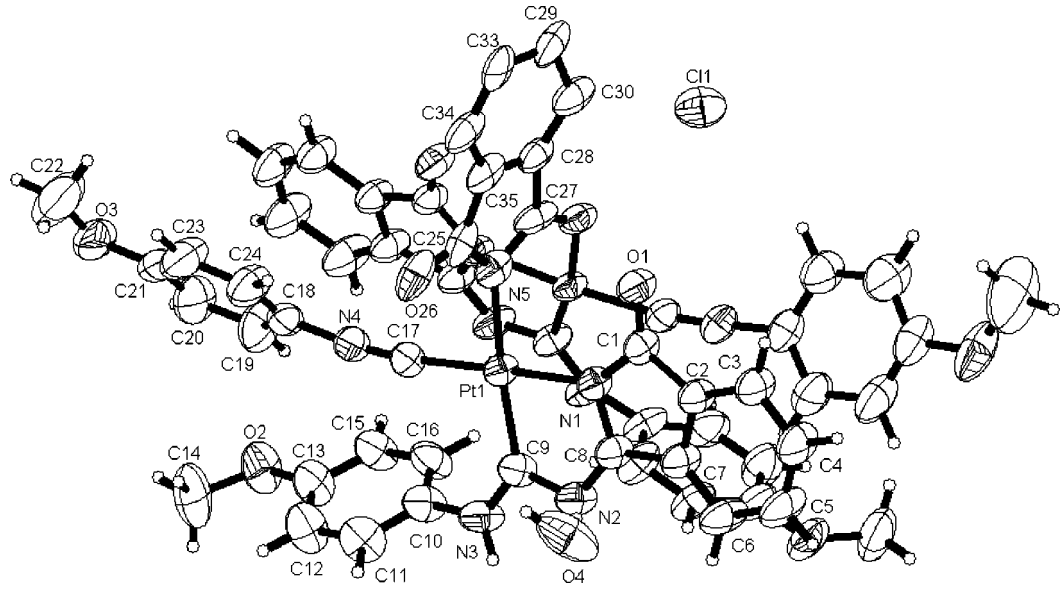


Figure 3. Thermal ellipsoid view of **30** with atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability. The bridging ligand is highly disordered, and the similar coordination environment for the second platinum atom is not shown. Selected bond lengths [Å] and angles [deg] for **30**: Pt(1)−C(17) 1.923(6), Pt(1)−C(9) 1.999(6), Pt(1)−N(1) 2.020(4), Pt(1)−N(5) 2.076(5), Pt(1)−Pt(1)#1 3.1485(4), N(2)−C(9) 1.385(7), N(3)−C(9) 1.322(7), N(3)−C(10) 1.417(7), N(4)−C(17) 1.149(7), N(4)−C(18) 1.403(8), C(17)−Pt(1)−C(9) 101.3(2), C(9)−Pt(1)−N(1) 78.2(2), C(17)−Pt(1)−N(5) 86.9(2), N(1)−Pt(1)−N(5) 93.14(18), C(9)−N(3)−C(10) 126.6(5), C(17)−N(4)−C(18) 174.7(6), N(3)−C(9)−N(2) 111.7(5), N(4)−C(17)−Pt(1) 169.7(5).

presumably due to (i) a stronger activation of the isocyanide by a Pd^{II} center as compared to the Pt^{II} center on account of the higher charge density on the former metal center (see ref 18 for examples), and (ii) a different balance between kinetic lability and thermodynamic stability for the Pd^{II} and Pt^{II} species.

Further studies directed to widening the family of metal heteroatom-stabilized carbenes derived from the addition of various imine nucleophiles to metal-bound isonitriles are currently under way in our group with particular emphasis on the aliphatic AlkN≡C species, which are substantially less activated toward the coupling than the aromatic isonitriles ArN≡C.

Experimental Section

Materials and Instrumentation. Solvents, $PdCl_2$, $K_2[PtCl_4]$, and all isonitriles were obtained from commercial sources and used as received apart from chloroform, which was purified by conventional distillation over calcium chloride. The complexes *cis*-$[PdCl_2(RNC)_2]$ (R = Cy **1**, Bu^t **2**, $C_6H_3(2,6\text{-}Me_2)$ **3**),[24] *cis*-$[PtCl_2(RNC)_2]$ (R = Cy **4**, Bu^t **5**, $C_6H_3(2,6\text{-}Me_2)$ **6**, $C_6H_4OMe\text{-}4$ **28**),[24,28] 3-iminoisoidolin-1-one **7**,[25] and its substituted derivatives (R_1, R_3, R_4 = H, R_2 = Me/R_1, R_2, R_4 = H, R_3 = Me **8** (isomeric mixture); R_1, R_4 = H, R_2, R_3 = Cl **9**)[25] were prepared as previously reported. C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. ESI^+ mass spectra were obtained on a Varian 500-MS LC ion trap mass spectrometer. Infrared spectra (4000−400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. 1D (^1H, $^{13}C\{^1H\}$) and 2D (^1H,^1H-COSY, ^1H,^{13}C-HMQC, ^1H,^{13}C-HSQC, and ^1H,^{13}C-HMBC) NMR spectra were recorded on Bruker Avance II+ 300 and 400 MHz (UltraShield Magnet) and Bruker Avance II+ 500 MHz (UltraShield Plus Magnet) spectrometers at ambient temperature.

X-ray Structure Determinations. Crystals were immersed in CryoOil, mounted in a nylon loop, and measured at a temperature of 120 K. The single-crystal X-ray diffraction data were collected by means of a Nonius KappaCCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). The DENZO/SCALEPACK[40] program package was used for cell refinement and data reduction. The structures were solved by direct methods using the SHELXS-97[41] or SIR97[42] programs with WinGX[43] graphical user interface. A multiscan absorption correction based on equivalent reflections (SADABS[44] or SORTAV[45]) was applied to all the data. Structural refinements were carried out using SHELXL-97.[46] In **30**·H_2O, the bridging ligand and the counterion Cl^- were disordered over two positions with equal occupancies of 0.5. The bond lengths between C33 and C34 as well as between C33 and C29#1 (#1 = 1−x, +y, 1.5−z) in the disordered moiety were fixed to 1.390(1) Å. Also, the aromatic hydrogen atoms in the disordered unit were omitted. In **30**·H_2O, the H_2O hydrogen atoms were located from the difference Fourier map but constrained to ride on their parent atom, with U_{iso} = 1.5U_{eq}(parent atom). In **10** and **27**, the NH hydrogen atoms were located from the difference Fourier map and refined isotropically. Other hydrogen atoms were positioned geometrically and were constrained to ride on their parent atoms, with N−H = 0.88 Å, U_{iso} = 1.2U_{eq}(parent atom), C···H = 0.95−1.00 Å, and U_{iso} = (1.2−1.5)U_{eq}(parent atom). The crystallographic data are summarized in Table 2, and selected bond lengths and angles in Table 3.

Synthetic Work. Reaction of *cis*-$[MCl_2(C{\equiv}NR)_2]$ (M = Pt, Pd; R = Cy, Bu^t, $C_6H_3(2,6\text{-}Me_2)$) and 3-Iminoisoindolin-1-one [or 5-methyl-3-iminoisoindolin-1-one, or 5,6-dichloro-3-iminoisoindolin-1-one]. A suspension of the corresponding iminoisoindolin-1-one (**7**−**9**) (0.2 mmol) in $CHCl_3$ (2 mL) was added to a solution of *cis*-$[MCl_2(RNC)_2]$ (M = Pd, 0.2 mmol; M = Pt, 0.1 mmol) in $CHCl_3$ (5 mL). The reaction mixture was then refluxed for 2 h. During the reaction time, the color of the mixture turned from yellow to bright yellow-green (in the case of **1**−**3**) or to yellow-orange (in the case of **4**−**6**). After 2 h, the reaction mixture was evaporated at 20−25 °C to dryness under a stream of nitrogen, and the solid residue was extracted with two 5 mL portions of $CHCl_3$ (five 5 mL portions for the reactions with **9**). The bright yellow solution was filtered off to remove some insoluble material, and the filtrate was evaporated to dryness under a stream of nitrogen at room temperature, washed with five 5 mL portions of Pr^i_2O, 1 mL portion of cold (5 °C) Et_2O, and again with five 5 mL portions of Pr^i_2O, and dried *in vacuo* at 20−25 °C. Yields range from 80% to 85% for **10**−**18** and 60−65% for **19**−**27**.

[PdCl{C0(N=C(C_6H_4CON))=N(H)Cy}(C≡NCy)] (10). Anal. Calcd for $C_{22}H_{27}N_4ClOPd$: C, 52.29; H, 5.39; N, 11.09. Found: C, 51.29; H, 5.61; N, 10.66. ESI^+-MS, *m/z*: 469 [M − Cl − H]$^+$. IR (KBr, selected bands, cm^{-1}): 3256 m ν(N−H); 2934 m, 2856 mw ν(C−H); 2216 s ν(C≡N); 1722 s, 1685 m, 1622 s ν(C=O) + ν(C=N); 1541 vs ν($C_{carbene}$=N); 712 s δ(C−H from aryls). ^1H NMR ($CDCl_3$, δ): 8.90 (s, br, 1H, NH), 7.85−7.52 (m, 4H, aryls), 4.52 (m, br, 1H, *H*CCy), 3.91 (m, br, 1H, *H*CCy), 1.99−1.64 and 1.44−1.40 (m, 20H, Cy). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 198.4 ($C_{carbene}$=N), 186.2 (C=O), 173.7 (C=N), 136.1, 133.9, 133.3, 132.2, 124.0, 123.2 (aryls), 54.5 (H*C*Cy), 53.5 (H*C*Cy), 32.5, 32.1, 25.3, 24.9, 24.4, 23.0 (Cy). Crystals of **10** suitable for single-crystal X-ray diffraction study were obtained upon slow evaporation of 10:1 (v/v) acetone−toluene solutions of **10** in air at ca. 20−25 °C.

[PdCl{C(N=C(C_6H_3(Me)CON))=N(H)Cy}(C≡NCy)] (11). Anal. Calcd for $C_{23}H_{29}N_4ClOPd$: C, 53.19; H, 5.63; N, 10.79. Found: C, 53.51; H, 5.61; N, 11.29. ESI^+-MS, *m/z*: 521 [M]$^+$. IR (KBr, selected bands, cm^{-1}): 3248 m ν(N−H); 2936 m, 2852 mw ν(C−H); 2215 s ν(C≡N); 1728 s, 1678 m, 1616 s ν(C=O) + ν(C=N); 1538 vs ν($C_{carbene}$=N); 723 s δ(C−H from aryls). ^1H NMR ($CDCl_3$, δ): 8.97 (s, br, 1H, NH), 7.65−7.51 (m, 4H, aryls), 4.57 (m, br, 1H, *H*CCy), 4.02 (m, br, 1H, *H*CCy), 2.45 (s, 3H, Me), 1.97−1.62 and 1.55−1.41 (m, 20H, Cy). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 199.4 ($C_{carbene}$=N), 184.3 (C=O), 172.1 (C=N), 136.2, 135.1, 134.0, 133.9, 124.2, 123.1 (aryls), 54.4 (H*C*Cy), 53.5 (H*C*Cy), 32.1, 32.0, 25.35, 24.8, 24.2, 23.1 (Cy), 21.1 (Me).

[PdCl{C(N=C($C_6H_2(Cl_2)$CON))=N(H)Cy}(C≡NCy)] (12). Anal. Calcd for $C_{22}H_{25}N_4Cl_3OPd$: C, 46.01; H, 4.39; N, 9.76. Found: C, 46.08; H, 4.20; N, 9.80. ESI^+-MS, *m/z*: 540 [M − Cl]$^+$. IR (KBr, selected bands, cm^{-1}): 3256 m ν(N−H); 2934 m, 2856 mw ν(C−H); 2216 s ν(C≡N); 1722 s, 1685 m, 1622 s ν(C=O) + ν(C=N); 1541 vs ν($C_{carbene}$=N); 712 s δ(C−H from aryls). ^1H NMR ($CDCl_3$, δ): 8.99 (s, br, 1H, NH), 7.94 (s, 1H) and 7.82 (s, 1H) (aryls), 4.51 (m, br, 1H, *H*CCy), 3.93 (m, br, 1H, *H*CCy), 1.97−1.81 and 1.49−1.25 (m, 20H, Cy). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 197.5 ($C_{carbene}$=N), 184.0 (C=O), 171.4 (C=N), 137.8, 136.5, 135.4, 133.1, 125.6, 125.1 (aryls), 54.4 (H*C*Cy), 53.6 (H*C*Cy), 32.4, 31.9, 31.7, 24.2, 24.3, 22.7 (Cy).

[PdCl{C(N=C(C_6H_4CON))=N(H)Bu^t}(C≡NBu^t)] (13). Anal. Calcd for $C_{18}H_{23}N_4ClOPd$: C, 47.70; H, 5.11; N, 12.36. Found: C, 46.98; H, 5.11; N, 12.45. ESI^+-MS, *m/z*: 455 [M]$^+$. IR (KBr, selected bands, cm^{-1}): 3245 mw ν(N−H); 2981 m, 2934 mw ν(C−H); 2212 s ν(C≡N); 1688 vs, 1627 m ν(C=O) + ν(C=N);

(40) Otwinowski, Z.; Minor, W. Processing of X-ray Diffraction Data Collected in Oscillation Mode. In *Methods in Enzymology, Macromolecular Crystallography, Part A*; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997; Vol. 276, pp 307−326.

(41) Sheldrick, G. M. *SHELXS-97*, Program for Crystal Structure Determination; University of Göttingen: Göttingen, Germany, 1997.

(42) Altomare, A.; Burla, M. C.; Camalli, M. C.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

(43) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

(44) Sheldrick, G. M. *SADABS*, Bruker Nonius scaling and absorption correction, v 2.10; Bruker AXS, Inc.: Madison, WI, 2003.

(45) Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *A51*, 33–38.

(46) Sheldrick, G. M. *SHELXL-97*, Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, 1997.

1549 vs ν($C_{carbene}$=N); 723 m δ(C−H from Ar). ^{1}H NMR ($CDCl_3$, δ): 9.00 (s, br, 1H, NH), 7.84−7.76 (m, 4H, aryls), 1.57 (s, 9H) and 1.53 (s, 9H, Bu^t). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 200.1 ($C_{carbene}$=N), 174.0 (C=O), 165.1 (C=N), 133.7, 133.5, 133.4, 133.1, 132.5, 132.1, 124.0, 123.6, 123.0, 122.9, 121.9 (aryls), 60.1 and 57.7 (*C*Me$_3$), 30.0 and 29.3 (C*Me*$_3$).

[PdCl{C(N=C(C$_6$H$_3$(Me)CON))=N(H)Bu^t}(C≡NBu^t)] (14). Anal. Calcd for $C_{19}H_{25}N_4ClOPd$: C, 48.83; H, 5.39; N, 11.99. Found: C, 48.80; H, 5.37; N, 11.75. ESI$^+$-MS, *m/z*: 491 [M + Na − H]$^+$. IR (KBr, selected bands, cm^{-1}): 3240 mw ν(N−H); 2982 m, 2935 mw ν(C−H); 2214 s ν(C≡N); 1682 vs, 1617 m ν(C=O) + ν(C=N); 1546 vs ν($C_{carbene}$=N); 732 m δ(C−H from Ar). ^{1}H NMR ($CDCl_3$, δ): 9.12 (s, br, 1H, NH), 7.94−7.58 (m, 4H, aryls), 2.44 (s) and 2.38 (s, 3H, Me from the isoindolinone moiety), 1.56 (s, 9H) and 1.55 (s, 9H, Bu^t). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 199.8 ($C_{carbene}$=N), 175.5 (C=O), 167.2 (C=N), 134.5, 132.4, 132.1, 132.0, 129.1, 124.6, 122.0, 121.7, 121.6 (aryls), 60.3 and 56.7 (*C*Me$_3$), 21.2 and 21.0 (Me).

[PdCl{C(N=C(C$_6$H$_2$(Cl$_2$)CON))=N(H)Bu^t}(C≡NBu^t)] (15). Anal. Calcd for $C_{18}H_{21}N_4Cl_3OPd$: C, 41.40; H, 4.05; N, 10.73. Found: C, 41.45; H, 4.28; N, 10.83. ESI$^+$-MS, *m/z*: 546 [M + Na]$^+$. IR (KBr, selected bands, cm^{-1}): 3229 mw ν(N−H); 2981 mw, 2935 mw, 2877 w ν(C−H); 2217 m ν(C≡N); 1717 m, 1675 mw, 1611 w ν(C=O) + ν(C=N); 1561 vs ν($C_{carbene}$=N); 731 s δ(C−H). ^{1}H NMR ($CDCl_3$, δ): 9.04 (s, br, 1H, NH), 7.84 (s, 1H) and 7.79 (s, 1H) (aryls), 1.55 (s, 9H) and 1.52 (s, 9H, Bu^t). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 199.6 ($C_{carbene}$=N), 183.3 (C=O), 171.7 (C=N), 137.9, 136.6, 135.5, 133.4, 125.5, 125.2 (aryls), 115.1 (C≡N), 60.3 and 58.2 (*C*Me$_3$), 30.0 and 29.4 (C*Me*$_3$).

[PdCl{C(N=C(C$_6$H$_4$CON))=N(H)C$_6$H$_3$(2,6-Me$_2$)}{C≡NC$_6$H$_3$-(2,6-Me$_2$)}] (16). Anal. Calcd for $C_{26}H_{23}N_4ClOPd$: C, 56.84; H, 4.22; N, 10.20. Found: C, 57.21; H, 4.28; N, 10.11. ESI$^+$-MS, *m/z*: 551 [M]$^+$. IR (KBr, selected bands, cm^{-1}): 3217 mw ν(N−H); 2961 mw, 2951 mw ν(C−H); 2199 s ν(C≡N); 1727 vs, 1687 s, 1629 w, 1607 w ν(C=N) + ν(C=O); 1521 vs ν($C_{carbene}$=N); 713 s δ(C−H from Ar). ^{1}H NMR ($CDCl_3$, δ): 10.24 (s, br, 1H, NH), 7.75−7.70 (m, 4H) (aryls from isoindolinone moiety), 7.27−7.14 (m, 6H, aryls), 2.61 (s, 6H) and 2.31 (s, 6H, Me). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 201.3 ($C_{carbene}$=N), 188.0 (C=O), 173.4 (*C*=N), 136.4, 135.7, 135.6, 134.0, 133.9, 133.4, 132.3, 130.0, 128.4, 128.3, 128.2, 128.0, 124.3, 123.2 (aryls), 18.9 and 18.8 (Me).

[PdCl{C(N=C(C$_6$H$_3$(Me)CON))=N(H)C$_6$H$_3$(2,6-Me$_2$)}{C≡NC$_6$-H$_3$(2,6-Me$_2$)}] (17). Anal. Calcd for $C_{27}H_{25}N_4ClOPd$: C, 57.56; H, 4.47; N, 9.94. Found: C, 57.46; H, 4.36; N, 8.55. ESI$^+$-MS, *m/z*: 528 [M − Cl]$^+$. IR (KBr, selected bands, cm^{-1}): 3214 mw ν(N−H); 3032 mw, 2959 w, 2920 mw ν(C−H); 2198 s ν(C≡N); 1725 s, 1681 s, 1616 m ν(C=O) + ν(C=N); 1522 vs ν($C_{carbene}$=N); 778 + 723 s δ(C−H from Ar). ^{1}H NMR ($CDCl_3$, δ): 10.24 (s, br, 1H, NH), 7.75−7.70 (m, 4H) (aryls from the isoindolinone moiety), 7.27−7.14 (m, 6H, aryls), 2.60 (s, 6H) and 2.31 (s, 6H, Me), 2.47 (s, 3H, Me from the isoindolinone moiety). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 199.9 ($C_{carbene}$=N), 187.2 (C=O), 168.9 (C=N), 136.6, 136.5, 136.4, 134.0, 131.1, 130.7, 128.4, 128.3, 128.2, 128.0 (aryls), 21.2 (Me from the isoindolinone moiety), 18.9 and 18.6 (Me).

[PdCl{C(N=C(C$_6$H$_2$(Cl$_2$)CON))=N(H)C$_6$H$_3$(2,6-Me$_2$)}{C≡NC$_6$-H$_3$(2,6-Me$_2$)}] (18). Anal. Calcd for $C_{26}H_{21}N_4Cl_3OPd$: C, 50.51; H, 3.42; N, 9.06. Found: C, 50.79; H, 3.42; N, 8.58. ESI$^+$-MS, *m/z*: 549 [M − 2Cl]$^+$. IR (KBr, selected bands, cm^{-1}): 3210 m ν(N−H); 3037 mw, 2971 mw, 2921 w, 2855 mw ν(C−H); 2197 s ν(C≡N); 1728 vs, 1677 m ν(C=O) + ν(C=N); 1536 vs ν($C_{carbene}$=N); 770 s δ(C−H from Ar). ^{1}H NMR ($CDCl_3$, δ): 10.31 (s, br, 1H, NH), 7.84 and 7.80 (m, 2H) (aryls from the isoindolinone moiety), 7.27−7.17 (m, 6H, aryls), 2.60 (s, 3H), 2.51 (s, 3H) and 2.30 (s, 6H, Me). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 201.1 ($C_{carbene}$=N), 186.1 (C=O), 171.2 (C=N), 136.5, 136.4, 133.9, 131.0, 130.1, 128.4, 128.2, 128.1, 128.0, 125.9, 125.6, 125.3 (aryls), 18.7 and 18.5 (Me).

[PtCl{C(N=C(C$_6$H$_4$CON))=N(H)Cy}(C≡NCy)] (19). Anal. Calcd for $C_{22}H_{27}N_4ClOPt$: C, 44.48; H, 4.58; N, 9.43. Found: C, 44.38; H, 4.61; N, 9.62. ESI$^+$-MS, *m/z*: 595 [M]$^+$. IR (KBr, selected bands, cm^{-1}): 3201 m ν(N−H); 2932 m, 2856 mw ν(C−H); 2223 s ν(C≡N); 1726 s, 1610 s ν(C=O) + ν(C=N); 1546 vs ν($C_{carbene}$=N); 717 s δ(C−H from aryls). ^{1}H NMR ($CDCl_3$, δ): 8.97 (s, br, 1H, NH), 7.85−7.60 (m, 4H, aryls), 4.57 (m, br, 1H, *H*CCy), 4.15 (m, br, 1H, *H*CCy), 2.02−1.62 and 1.47−1.42 (m, 20H, Cy). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 192.7 ($C_{carbene}$=N), 186.2 (C=O), 169.7 (C=N), 136.0, 134.4, 133.6, 132.8, 124.5, 123.6 (aryls), 58.0 (H*C*Cy), 55.6 (H*C*Cy), 32.6, 32.2, 25.4, 25.1, 24.9, 24.7, 24.5, 23.0, 22.8 (Cy).

[PtCl{C(N=C(C$_6$H$_3$(Me)CON))=N(H)Cy}(C≡NCy)] (20). Anal. Calcd for $C_{23}H_{29}N_4ClOPt$: C, 45.43; H, 4.81; N, 9.21. Found: C, 45.82; H, 4.92; N, 9.18. ESI$^+$-MS, *m/z*: 573 [M − Cl]$^+$. IR (KBr, selected bands, cm^{-1}): 3215 m ν(N−H); 2931 m ν(C−H); 2229 s ν(C≡N); 1748 s, 1667 m, 1616 s ν(C=O) + ν(C=N); 1545 vs ν($C_{carbene}$=N); 738 s δ(C−H from aryls). ^{1}H NMR ($CDCl_3$, δ): 9.06 (s, br, 1H, NH), 7.80−7.41 (m, 4H, aryls), 4.77 (m, br, 1H, *H*CCy), 4.20 (m, br, 1H, *H*CCy), 2.51 and 2.46 (s, 3H, Me), 2.15−1.80 and 1.44−1.13 (m, 20H, Cy). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 194.4 ($C_{carbene}$=N), 184.2 (C=O), 167.3 (C=N), 145.9, 135.0, 134.5, 133.6, 130.1, 126.7, 126.1, 124.4, 124.1, 123.5 (aryls), 56.4 (H*C*Cy), 55.5 (H*C*Cy), 31.9, 29.6, 25.3, 24.6, 22.1, 13.0 (Cy), 22.9 (Me).

[PtCl{C(N=C(C$_6$H$_2$(Cl$_2$)CON))=N(H)Cy}(C≡NCy)] (21). Anal. Calcd for $C_{22}H_{25}N_4Cl_3OPt$: C, 39.86; H, 3.80; N, 8.45. Found: C, 39.92; H, 3.79; N, 8.32. ESI$^+$-MS, *m/z*: 651 [M − Cl + Na]$^+$. IR (KBr, selected bands, cm^{-1}): 3246 m ν(N−H); 2932 m, 2852 mw ν(C−H); 2228 s ν(C≡N); 1732 s, 1681 m, 1618 s ν(C=O) + ν(C=N); 1542 vs ν($C_{carbene}$=N); 722 s δ(C−H from aryls). ^{1}H NMR ($CDCl_3$, δ): 8.97 (s, br, 1H, NH), 7.92 (s, 1H) and 7.80 (s, 1H) (aryls), 4.41 (m, br, 1H, *H*CCy), 4.12 (m, br, 1H, *H*CCy), 2.02−1.79 and 1.42−1.12 (m, 20H, Cy). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 194.2 ($C_{carbene}$=N), 184.0 (C=O), 170.1 (C=N), 137.8, 133.2, 133.0, 126.4, 125.5, 125.2, 125.1 (aryls), 54.5 (H*C*Cy), 53.2 (H*C*Cy), 32.3, 31.8, 31.7, 31.5, 24.2, 24.3, 22.7 (Cy).

[PtCl{C(N=C(C$_6$H$_4$CON))=N(H)Bu^t}(C≡NBu^t)] (22). Anal. Calcd for $C_{18}H_{23}N_4ClOPt$: C, 39.89; H, 4.28; N, 10.34. Found: C, 39.98; H, 4.11; N, 10.45. ESI$^+$-MS, *m/z*: 543 [M]$^+$. IR (KBr, selected bands, cm^{-1}): 3240 mw ν(N−H); 2982 m ν(C−H); 2229 s ν(C≡N); 1718 mw, 1674 vs, 1609 m ν(C=O) + ν(C=N); 1543 vs ν($C_{carbene}$=N); 707 m δ(C−H from Ar). ^{1}H NMR ($CDCl_3$, δ): 8.56 (s, br, 1H, NH), 7.83−7.41 (m, 4H, aryls), 1.61 (s, 9H) and 1.49 (s, 9H, Bu^t). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 198.7 ($C_{carbene}$=N), 173.8 (C=O), 168.6 (C=N), 134.2, 133.6, 132.4, 124.0, 123.9, 123.5, 123.2 (aryls), 58.2 and 53.0 (*C*Me$_3$), 30.0, 29.8 and 27.8 (C*Me*$_3$).

[PtCl{C(N=C(C$_6$H$_3$(Me)CON))=N(H)Bu^t}(C≡NBu^t)] (23). Anal. Calcd for $C_{19}H_{25}N_4ClOPt$: C, 41.05; H, 4.53; N, 10.08. Found: C, 41.01; H, 4.52; N, 10.45. ESI$^+$-MS, *m/z*: 580 [M + Na]$^+$. IR (KBr, selected bands, cm^{-1}): 3252 mw ν(N−H); 2976 m, 2945 mw, 2935 mw ν(C−H); 2214 s ν(C≡N); 1734m, 1679 vs, 1616 m ν(C=O) + ν(C=N); 1542 vs ν($C_{carbene}$=N); 744 m δ(C−H from Ar). ^{1}H NMR ($CDCl_3$, δ): 10.67 (s, br, 1H, NH), 7.98−7.26 (m, 4H, aryls), 2.50 (s) and 2.48 (s, 3H, Me), 1.64 (s, 9H) and 1.54 (s, 9H, Bu^t). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 199.9 ($C_{carbene}$=N), 172.0 (C=O), 166.4 (C=N), 145.6, 144.7, 144.5, 134.8, 134.3, 132.8, 124.1, 124.0, 123.4, 123.0 (aryls), 53.0 (*C*Me$_3$), 29.9 and 27.9 (C*Me*$_3$), 22.0 and 21.9 (Me).

[PtCl{C(N=C(C$_6$H$_2$(Cl$_2$)CON))=N(H)Bu^t}(C≡NBu^t)] (24). Anal. Calcd for $C_{18}H_{21}N_4Cl_3OPt$: C, 35.39; H, 3.47; N, 9.17. Found: C, 36.01; H, 3.48; N, 9.23. ESI$^+$-MS, *m/z*: 634 [M + Na]$^+$. IR (KBr, selected bands, cm^{-1}): 3234 mw ν(N−H); 2980 mw and 2872 w ν(C−H); 2230 m ν(C≡N); 1728 m, 1673 mw, 1618 w ν(C=O) + ν(C=N); 1545 vs ν($C_{carbene}$=N); 723 s δ(C−H). ^{1}H NMR ($CDCl_3$, δ): 10.56 (s, br, 1H, NH), 7.84 (s, 1H) and 7.73 (s,

1H) (aryls), 1.63 (s, 9H) and 1.54 (s, 9H, Bu^t). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 199.8 ($C_{carbene}$=N), 174.3 (C=O), 169.7 (C=N), 137.8, 136.6, 133.4, 125.5, 125.2 (aryls), 115.1 (C≡N), 60.2 and 58.1 (*C*Me$_3$), 23.2 and 22.0 (C*Me*$_3$).

[PtCl{C(N=C(C$_6$H$_4$CON))=N(H)C$_6$H$_3$(2,6-Me$_2$)}{C≡NC$_6$H$_3$-(2,6-Me$_2$)}] (25). Anal. Calcd for $C_{26}H_{23}N_4ClOPt$: C, 48.95; H, 3.63; N, 8.78. Found: C, 48.90; H, 3.78; N, 8.58. ESI$^+$-MS, *m*/*z*: 603 [M − Cl]$^+$. IR (KBr, selected bands, cm^{-1}): 3227 mw ν(N−H); 2961 mw, 2951 w, 2941 mw ν(C−H); 2192 s ν(C≡N); 1717 vs, 1677 s, 1619 w ν(C=N) + ν(C=O); 1522 vs ν($C_{carbene}$=N); 723 s δ(C−H from Ar). ^1H NMR ($CDCl_3$, δ): 10.19 (s, br, 1H, NH), 7.82−7.69 (m, 4H) (aryls from isoindolinone moiety), 7.27−7.15 (m, 6H, aryls), 2.59 (s, 6H) and 2.30 (s, 6H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 197.6 ($C_{carbene}$=N), 182.0 (C=O), 174.2 (C=N), 136.6, 135.5, 134.2, 133.8, 132.1, 129.1, 128.4, 128.2, 127.9, 124.3, 123.1 (aryls), 19.2 and 18.9 (Me).

[PtCl{C(N=C(C$_6$H$_3$(Me)CON))=N(H)C$_6$H$_3$(2,6-Me$_2$)}{C≡NC$_6$-H$_3$(2,6-Me$_2$)}] (26). Anal. Calcd for $C_{27}H_{25}N_4ClOPt$: C, 49.73; H, 3.86; N, 8.59. Found: C, 49.67; H, 3.78; N, 8.68. ESI$^+$-MS, *m*/*z*: 654 [M + H]$^+$. IR (KBr, selected bands, cm^{-1}): 3241 mw ν(N−H); 3030 mw, 2961 w, 2920 mw ν(C−H); 2195 s ν(C≡N); 1712 s, 1674 s ν(C=O) + ν(C=N); 1532 vs ν($C_{carbene}$=N); 723 s δ(C−H from Ar). ^1H NMR ($CDCl_3$, δ): 10.21 (s, br, 1H, NH), 7.75−7.70 (m, 4H) (aryls from the isoindolinone moiety), 7.27−7.14 (m, 6H, aryls), 2.51 (s, 6H) and 2.22 (s, 6H, Me), 2.44 (s, 3H, Me from the isoindolinone moiety). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 196.9 ($C_{carbene}$=N), 186.2 (C=O), 167.9 (C=N), 136.7, 136.6, 136.2, 134.0, 131.0, 130.4, 128.5, 128.2, 128.1 (aryls), 21.2 (Me from the isoindolinone moiety), 21.7 and 18.4 (Me).

[PtCl{C(N=C(C$_6$H$_2$(Cl$_2$)CON))=N(H)C$_6$H$_3$(2,6-Me$_2$)}{C≡NC$_6$-H$_3$(2,6-Me$_2$)}] (27). Anal. Calcd for $C_{26}H_{21}N_4Cl_3OPt$: C, 44.18; H, 2.99; N, 7.93. Found: C, 44.19; H, 2.80; N, 8.12. ESI$^+$-MS, *m*/*z*: 672 [M − Cl]$^+$. IR (KBr, selected bands, cm^{-1}): 3242 m ν(N−H); 3035 mw, 2964 mw, 2921 w, 2855 mw ν(C−H); 2195 s ν(C≡N); 1736 vs, 1686 m ν(C=O) + ν(C=N); 1520 vs ν($C_{carbene}$=N); 779 s δ(C−H from Ar). ^1H NMR ($CDCl_3$, δ): 10.21 (s, br, 1H, NH), 7.84 (s, 1H) and 7.82 (s, 1H) (aryls from the isoindolinone moiety), 7.34−7.28 and 7.26−7.17 (m, 6H, aryls), 2.62 (s, 6H) and 2.30 (s, 6H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 202.1 ($C_{carbene}$=N), 186.2 (C=O), 171.0 (C=N), 136.1, 132.7, 130.6, 130.4, 128.4, 128.3, 128.1, 128.0, 125.9, 125.6, 125.3 (aryls), 20.7 and 18.6 (Me). Crystals of **27** suitable for single-crystal X-ray diffraction study were obtained upon slow evaporation of 10:1 (v/v) acetone−toluene solutions of **27** in air at ca. 20−25 °C.

Attempted Reaction between 5 and 7. A suspension of **7** (0.2 mmol) in $CHCl_3$ (2 mL) was added to a solution of **6** (0.2 mmol) in $CHCl_3$ (5 mL). The reaction mixture was then left to stand for 2 h at 20−25 °C, and during this period the color of the mixture turned from yellowish-brown to bright lemon-orange. After 2 h, the reaction mixture was evaporated at 20−25 °C to dryness under a stream of N_2, and the solid residue was extracted with two 5 mL portions of cold (10 °C) $CHCl_3$. The bright yellow-orange solution was filtered off to remove some insoluble material, and the filtrate was evaporated to dryness under a stream of N_2 at room temperature, washed with two 5 mL portions of Pr$^i_2$O and five 10 mL portion of cold (5 °C) Et_2O, and dried *in vacuo* at 20−25 °C. **[PtCl(C$_6$H$_4$CONCNH)(C≡NBu^t)$_2$] (34)**. ESI$^+$-MS, *m*/*z*: 543 [M]$^+$. IR (KBr, selected bands, cm^{-1}): 3242 m ν(N−H); 2896 w, 2855 mw ν(C−H); 2253 and 2239 s ν(C≡N); 1770 vs, 1673 m ν(C=O) + ν(C=N); 782 m δ(C−H from Ar). ^1H NMR ($CDCl_3$, δ): 9.56 (s, br, 1H, NH), 7.83−7.41 (m, 4H, aryls), 1.60 (s) and 1.57 (s, 18H, Bu^t).

Attempted Reaction between 28 and 7. A suspension of **7** (0.2 mmol) in $CHCl_3$ (2 mL) was added to a solution of **28** (0.2 mmol) in $CHCl_3$ (5 mL). The reaction mixture was then refluxed for 2 h, and the color of the mixture turned from yellowish-brown to bright lemon-orange. After 2 h, the reaction mixture was evaporated at 20−25 °C to dryness under a stream of N_2, and the solid residue was extracted with two 5 mL portions of $CHCl_3$. The bright yellow-orange solution was filtered off to remove some insoluble material, and the filtrate was evaporated to dryness under a stream of N_2 at room temperature, washed with five 5 mL portions of Pr$^i_2$O, 1 mL portion of cold (5 °C) Et_2O, and again with five 5 mL portions of Pr$^i_2$O, and dried *in vacuo* at 20−25 °C. The obtained dark yellow-orange solid residue was monitored by TLC, ESI-MS, and ^1H and $^{13}C\{^1H\}$ NMR. The slow evaporation of an acetone solution of this solid residue in air at 20−25 °C resulted in precipitation of crystals of **30** suitable for X-ray study.

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Supporting Information Available: Crystallographic data in CIF format for complexes **10**, **27**, and **30**. This material is available free of charge via the Internet at http://pubs.acs.org.

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