Inorganic Chemistry

Article

Organometallic Fragments Coordinated to a Multiisocyanide Ligand and Their Physical Properties

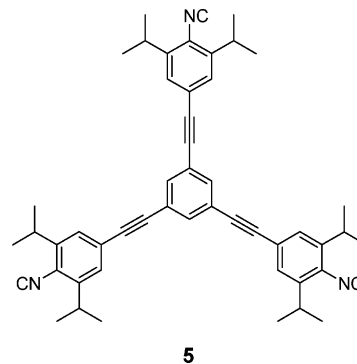**Jong Hyub Paek, Kyu Ho Song, Il Jung, Sang Ook Kang,* and Jaejung Ko***

Department of Chemistry, Korea University, Jochiwon, Chungnam 339-700

Preparation of a triisocyanide ligand, 1,3,5-tris[(4-isocyano-3,5-diisoproyl-phenyl)ethynyl]benzene (**5**), is presented. Ligand **5** is obtained in three steps in 76% overall yield. Reaction of **5** with (η^5-Cp*)Rh(Cab^{s,s})(Cab$^{s,s'}$= 1,2-$S_2C_2B_{10}H_{10}$-S,S′) produced the rhodadithiolene adduct [{(η^5-Cp*)Rh(Cab^{s,s})(CNC$_6$H$_2^i$Pr$_2$-2,6-C≡C-3)}$_3$C$_6$H$_3$-1,3,5] (**6**). Ligand **5** reacts with Cr(CO)$_5$(THF) to give the triisocyanide complex [{Cr(CO)$_5$(CNC$_6$H$_2^i$Pr$_2$-2,6-C≡C-3)}$_3$C$_6$H$_3$-1,3,5] (**8**) and with [AuCl(SMe$_2$)] to give the triisocyanide complex [{AuCl(CNC$_6$H$_2^i$Pr$_2$-2,6-C≡C-3)}$_3$C$_6$H$_3$-1,3,5] (**9**). As revealed by a single-crystal X-ray diffraction study, the C(9)–N(3)–C(61) angle of 5.9° of trichromium complex **8** occurs in the plane of the bridge and the gold center has a slightly bent linear configuration with a Cl(1)–Au(1)–C(21) angle of 175.4(4)°. The rhenation and platination of **5** employing [Re(bpy)(CO)$_3$(AN)]PF$_6$ (AN= acetonitrile) and [(C^N^N)PtCl] ((HC^N^N)= 6-phenyl-2,2′-bipyridine) yielded the luminescent Re(I) and Pt(II) complexes. Full characterization includes structural study of complexes **2**, **8**, and **9**.

Introduction

Transition-metal complexes of organic isocyanides are of long-standing importance in organic and organometallic syntheses, catalysis, materials science, diagnostic medicine,[1] building blocks for molecular self-assembly,[2] and organometallic polymers.[3] They are also of great current interest in photochemistry[4] and surface chemistry,[5] where their bonding on transition metals has been addressed using multidentate isocyanides. Isocyanide ligands are unique in their ability to coordinate to transition metals encompassing

Figure 1. Triisocyanide ligand **5**.

the various oxidation states.[6] Isocyanides stabilize not only low-valent complexes by participating as π-acceptor ligands, but also coordinate to high-valent transition metals as strong σ donors. The most important electronic element of metal isocyanides is the presence of metal–carbon multiple bonds

---

* To whom correspondence should be addressed. E-mail: jko@korea.ac.kr (J.K.).

(1) (a) Weber, L. *Angew. Chem., Int. Ed.* **1998**, *37*, 1515. (b) Carnahan, E. M.; Protasiewicz, J. D.; Lippard, S. J. *Acc. Chem. Res.* **1993**, *26*, 90. (c) Sharma, V.; Piwnica-Worms, D. *Chem. Rev.* **1999**, *99*, 2545. (d) Robinson, R. E.; Holovics, T. C.; Deplazes, S. F.; Lushington, G. H.; Powell, D. R.; Barybin, M. V. *J. Am. Chem. Soc.* **2003**, *125*, 4432.

(2) (a) Mayr, A.; Guo, J. *Inorg. Chem.* **1999**, *38*, 921. (b) Philp, D.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **1996**, *35*, 1154. (c) Burrows, A. D.; Chan, C.-W.; Chowdhry, M. M.; McGrady, J. E.; Mingos, D. M. *Chem. Soc. Rev.* **1995**, 329.

(3) (a) Turcotte, M.; Harvey, P. D. *Inorg. Chem.* **2002**, *41*, 2971. (b) Fortin, D.; Drouin, M.; Harvey, P. D. *Inorg. Chem.* **2000**, *39*, 2758. (c) Guitard, A.; Mari, A.; Beauchamp, A. L.; Dartiguenave, Y.; Dartiguenave, M. *Inorg. Chem.* **1983**, *22*, 1603. (d) Fortin, D.; Drouin, M.; Turcotte, M.; Harvey, P. D. *J. Am. Chem. Soc.* **1997**, *119*, 531.

(4) (a) Villegas, J. M.; Stoyanov, S. R.; Huang, W.; Lockyear, L. L.; Reibenspies, J. H.; Rillema, D. P. *Inorg. Chem.* **2004**, *43*, 6383. (b) Coppens, P.; Gerlits, O.; Vorontsov, I. I.; Kovalersky, A. Y.; Chen, Y.-S.; Graber, T.; Gembicky, M.; Novozhilova, I. V. *Chem. Commun.* **2004**, 2144.

(5) (a) Siemeling, U.; Rother, D.; Bruhn, C.; Fink, H.; Weidner, T.; Träger, F.; Rothenberger, A.; Fenske, D.; Priebe, A.; Maurer, J.; Winter, R. *J. Am. Chem. Soc.* **2005**, *127*, 1102. (b) Murphy, K. L.; Tysoe, W. T.; Bennett, D. W. *Langmuir* **2004**, *20*, 1732. (c) McCreery, R. L. *Chem. Mater.* **2004**, *16*, 4477. (d) Seminario, J. M.; Zacarias, A. G.; Tour, J. M. *J. Am. Chem. Soc.* **1999**, *121*, 411.

(6) (a) Barybin, M. V.; Young, V. G., Jr.; Ellis, J. E. *J. Am. Chem. Soc.* **1998**, *120*, 429. (b) Barybin, M. V.; Young, V. G., Jr.; Ellis, J. E. *J. Am. Chem. Soc.* **1999**, *121*, 9237. (c) Szalda, D. J.; Dewan, J. C.; Lippard, S. J. *Inorg. Chem.* **1981**, *20*, 3851. (d) Nielson, R. M.; Wherland, S. *Inorg. Chem.* **1985**, *24*, 1803.
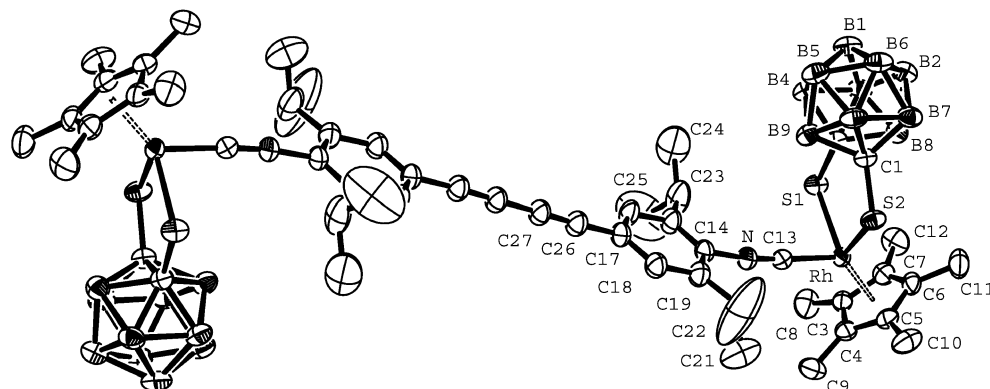
Figure 2. Molecular structure of complex **2** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh−C(13) = 1.927(3), N−C(13) = 1.150(3), N−C(14) = 1.408(3), C(17)−C(26) = 1.429(3), C(26)−C(27) = 1.195-(4), N−C(13)−Rh = 175.1(2), C(13)−N−C(14) = 173.8(3), C(17)−C(26)−C(27) = 177.6(3).

Table 1. Selected Crystallographic Data of Complexes **2**, **8**, and **9**

compound	2	8	9
empirical formula	$C_{54}H_{82}B_{20}N_2S_4Rh_2$	$C_{66}H_{51}N_3O_{15}Cr_3$	$C_{51}H_{51}Cl_3N_3Au_3$
fw	1309.48	1282.10	1403.20
cryst syst	orthorhombic	triclinic	monoclinic
space group	P_{bca}	P-1	$C2/c$
a (Å)	17.2591(7)	14.9119(11)	22.5803(13)
b (Å)	20.7769(9)	14.9973(11)	18.6604(12)
c (Å)	20.9540(9)	18.7576(14)	30.452(2)
α (deg)	90	73.2550(10)	90
β (deg)	90	69.3830(2)	105.370(2)
γ (deg)	90	69.6590(2)	90
vol. (Å³)	7513.9(6)	3615.2(5)	12372.3(13)
Z	4	2	8
D_{calcd}, (g/cm³)	1.158	1.178	1.507
$F(000)$	2696	1320	5328
cryst size, mm	0.24 × 0.16 × 0.12	0.28 × 0.23 × 0.17	0.39 × 0.27 × 0.23
θ range	1.94−28.31	1.18−28.37	1.39−28.34
no. of rflns collected	74 860	49 400	40 930
no. of indep rflns	9333	17 854	15 417
refinement method ($I > 2\sigma(I)$)	R1 = 0.0408	R1 = 0.0584	R1 = 0.0606
	wR2 = 0.1207	wR2 = 0.1557	wR2 = 0.1473
goodness of fit on F^2	1.144	0.884	0.713

via back-bonding.[7] Such metal−carbon π interactions provide the stability of metal−isocyanides and electronic interactions between the metal center and isocyanide ligands.[7b] Therefore, by introducing suitably functionalized isocyanides, such isocyanide metal complexes can be induced to undergo self-assembly with the geometric and electronic information stored in them, together with dimers and oligomers with photophysical properties.

Mayr and co-workers[2a,8] recently prepared various metal complexes of isocyanides with nitrogen donor groups and hydrogen-bonding groups, which can be utilized as building blocks for self-assembly. They also found the functionalized derivatives of 2,6-diisopropylphenylisocyanide to be useful due to the relatively good solubility. Puddephatt and co-workers reported that the gold and platinum complexes reacted with diisocyanide ligands to form covalently linked network polymers.[9]

During the course of our studies concerning the multi-functional isocyanides, we found that the triisocyanide ligand

of type **5** (Figure 1) has not been previously known, and the ligand is suitable to coordinate to a variety of metal complexes with novel properties, although the directional diisocyanides have been well documented to afford organometallic dimers and oligomers.[10] Of particular importance is isocyanide ligation to the luminescent metal complexes. There has been interest in multinuclear metal complexes with chromophoric units. The Lees[11] and Che groups[12] reported the photophysics of luminescent trinuclear metal complexes containing (diimine)Re(CO)$_3$ and [(C^N^N)Pt]$^+$ chromophores bridged by tribranched ligands. We envisioned that the tritopic ligand **5** would be able to coordinate to luminescent metal complexes and have photophysical properties. Here we describe the novel synthesis of 1,3,5-tris[(4-isocyano-3,5-diisopropylphenyl)ethynyl]benzene **5**. The isolation and physical properties of the Rh(I), Cr(I), Au(I), Re(I), and Pt(II) metal complexes containing **5** are described.

(7) (a) Johnston, R. F. *J. Coord. Chem.* **1994**, *31*, 57. (b) Grubisha, D. S.; Rommel, J. S.; Lane, T. M.; Tysoe, W. T.; Bennett, D. W. *Inorg. Chem.* **1992**, *31*, 5022.

(8) (a) Lu, Z.-L.; Mayr, A.; Cheung, K.-K. *Inorg. Chim. Acta.* **1999**, *284*, 205. (b) Lau, K. Y.; Mayr, A.; Cheung, K.-K. *Inorg. Chim. Acta.* **1999**, *285*, 223.

(9) (a) Irwin, M. J.; Manojlović-Muir, L.; Muir, K. W.; Puddephatt, R. J.; Yufit, D. S. *Chem. Commun.* **1997**, 219. (b) Irwin, M. J.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 3541.
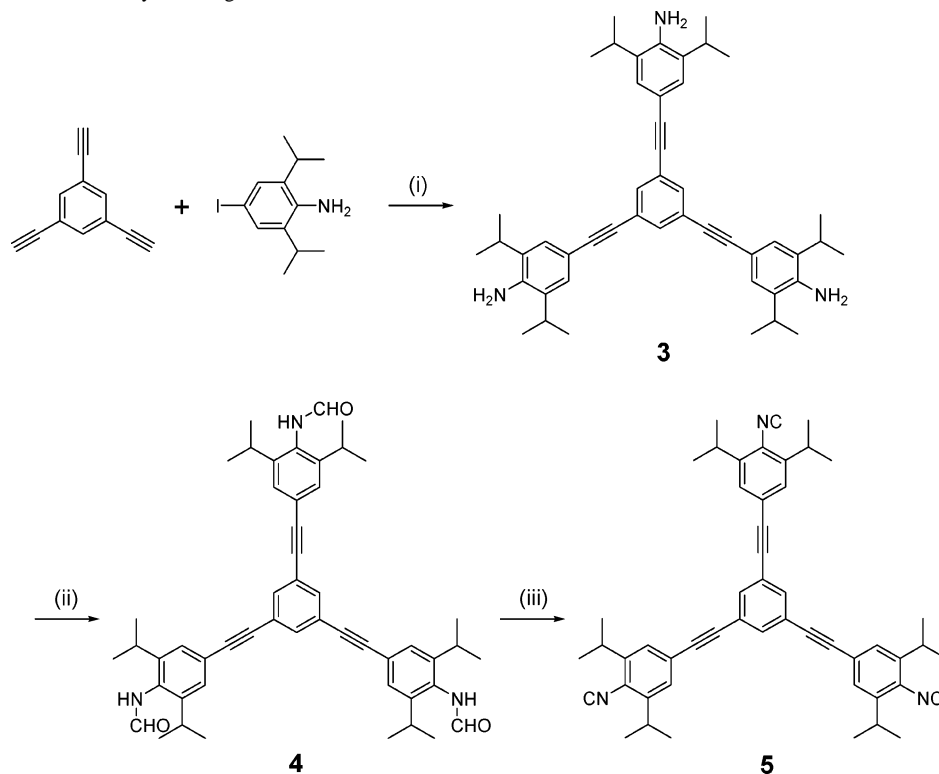
(10) Fournier, E.; Sicard, S.; Decken, A.; Harvey, P. D. *Inorg. Chem.* **2004**, *43*, 1491.

(11) (a) Sun, S.-S.; Robson, E.; Dunwoody, N.; Silva, A. S.; Brinn, I. M.; Lees, A. J. *Chem. Commun.* **2000**, 201. (b) Sun, S.-S.; Lees, A. J. *Organometallics* **2002**, *21*, 39.

(12) Lu, W.; Zhu, N.; Che, C.-M. *Chem. Commun.* **2002**, 900.

Scheme 1. Preparation of Complex **2**[a]
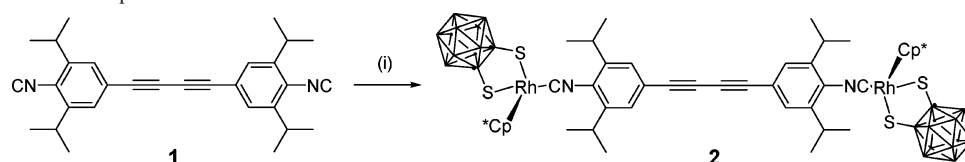
a (i) (η^5-Cp*)Rh(Cab$^{s,s'}$), toluene.

Scheme 2. Synthesis of the Triisocyanide Ligand **5**[a]

a (i) Pd(PPh$_3$)$_4$, CuI, THF/NEt$_3$ (1:1); (ii) HCHO, acetic anhydride; (iii) triphosgene, THF.

Results and Discussion

Synthesis of Dimetallic Rhodium(I) Complexes. The diisocyanide ligand **1** can be prepared by the oxidative homocoupling reaction of 4-isocyanophenylacetylene. The coupling reaction of acetylene was readily accomplished with high yield in the presence of cupric chloride and sodium acetate. Ligand **1** is a crystalline solid that is stable in air. The ^{1}H and ^{13}C NMR spectra support the proposed structure. Ligand **1** was found to be a good model to use as a building block for discrete multicluster assembly. Stirring a mixture of (η^5-Cp*)Rh(Cab$^{s,s'}$)[13] and **1** in toluene at room temperature for 2 h produced an orange solution of **2** in a yield of 92%, which has been characterized by single-crystal crystallography, NMR, IR, and elemental analysis (Scheme 1). As previously reported by us, the 16-electron cobalt complex (η^5-Cp)Co(Cab$^{s,s'}$) acts as a Lewis acid and forms 1:1 adducts with *tert*-butyl isocyanide.[13] Formation of **2** is confirmed by the appearance of the ^{1}H NMR signals at 7.39, 3.51, 1.81, and 1.32 ppm, which are ascribed to the aromatic, isopropyl, and Cp* ligand, respectively. ^{13}C NMR spectroscopy and mass spectrometry also support the proposed

formula. The solid-state structure of **2** is consistent with its assigned solution structure (Figure 2). The crystallographic data and processing parameters are given in Table 1. All of the rhodium centers adopt a three-legged piano-stool conformation. The molecule of **2** possesses a crystallographic inversion (symmetry code: $2 - x$, $1 - y$, $1 - z$) that the middle of the diyne unit goes through. The Rh−C(13) bond length is 1.927(3) Å, which is within the ranges established for the respective types of isocyanide metal complex. The bond angles Rh−C(13)−N and C(17)−C(26)−C(27) are 175.1(2)° and 177.6(3)°, respectively. Although all are close to linear, the distortion from the ideal angel of 180° is greater than those for other transition-metal complexes.[14]

Synthesis of the Triisocyanide Ligand. The triisocyanide ligand **5** can be prepared in three steps, as shown in Scheme 2. In each step the reaction proceeds smoothly and the product can be obtained in high yield. In the first step, substitution of the iodide in 4-iodo-2,6-diisopropylaniline by the ethynyl group to afford **3** is achieved by Sonogashira cross-coupling reaction in the presence of catalytic

(13) Won, J.-H.; Kim, D.-H.; Kim, B. Y.; Kim, S.-J.; Lee, C.; Cho, S.; Ko, J.; Kang, S. O. *Organometallics* **2002**, *21*, 1443.

(14) (a) Hahn, F. E.; Lügger, T. *J. Organomet. Chem.* **1994**, *481*, 189. (b) Bailey, N. A.; Walker, N. W.; Williams, J. A. W. *J. Organomet. Chem.* **1972**, *37*, C49. (c) Che, C.-M.; Herbstein, F. H.; Schaefer, W. P.; Marsh, R. E.; Gray, H. B. *Inorg. Chem.* **1984**, *23*, 2572.

Scheme 3. Preparation of Complexes 6 and 7[a]
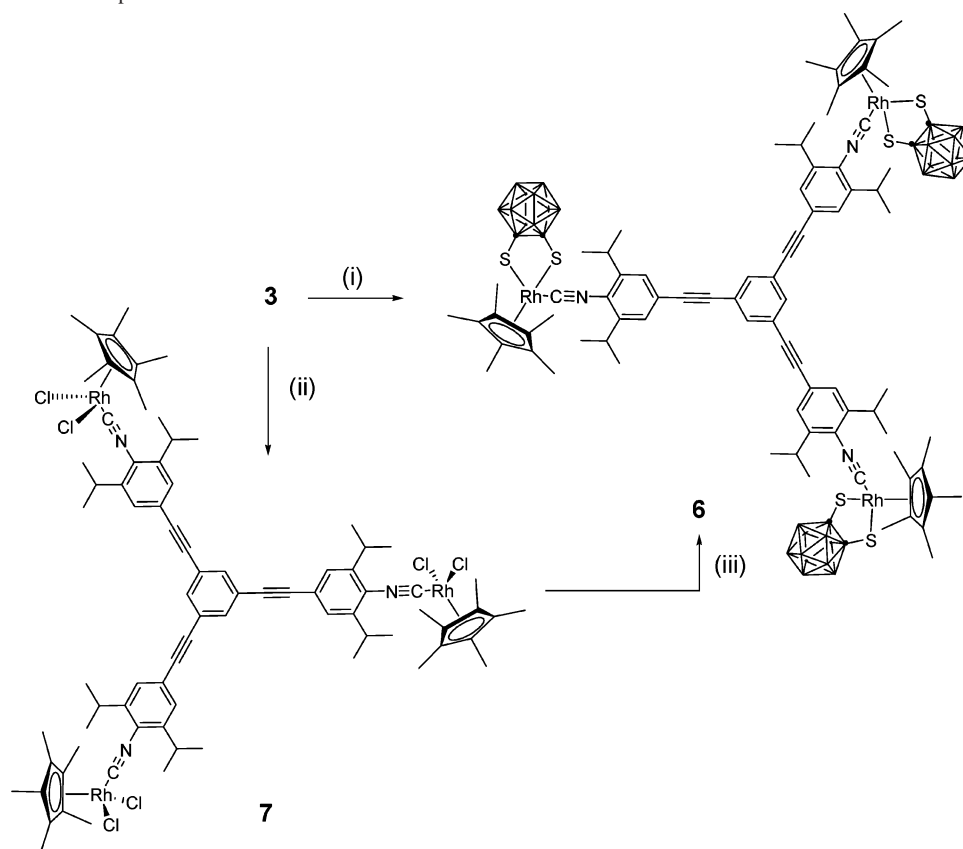
[a] (i) (η^5-Cp*)Rh(Cab$^{s,s'}$), toluene; (ii) [(η^5-Cp*)RhCl$_2$]$_2$, CH$_2$Cl$_2$; (iii) LiS$_2$C$_2$B$_{10}$H$_{10}$.

Scheme 4. Preparation of Complex 8
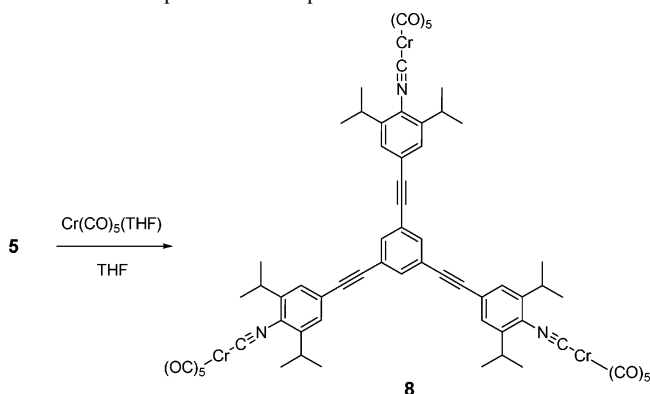
amounts of Pd(PPh$_3$)$_4$ and copper iodide. Formylation of **3** with formic acid and acetic anhydride affords the formamide **4**. Triisocyanide ligand **5** was prepared by the dehydration reaction of **4** with triphosgene/triethylamine.[15] A similar preparation of functionalized derivatives of 2,6-diisopropylphenylisocyanide has been reported by the Mayr group.[8] Ligand **5** is a crystalline white solid that is stable and soluble in toluene, THF, and CH$_2$Cl$_2$. Spectroscopic data for **5** are completely consistent with its proposed structure (Scheme 2).

A parent ion in the mass spectrum of **5** was observed at m/z 705. The ^{1}H NMR spectrum of **5** contained a methine resonance (3.36 ppm) and a methyl resonance (1.31 ppm).

Two singlets (7.71 and 7.32 ppm) in the ^{1}H NMR spectrum and six singlets (145.5−116.8 ppm) in the ^{13}C NMR spectrum could be assigned to the aromatic groups. The ^{13}C NMR resonances of isocyanide groups are generally of low intensity.[16] For **5**, this resonance occurs at δ 170.3. The alkynyl group in **5** gives rise to characteristic ^{13}C NMR resonances at 90.3 and 89.2 ppm. These values are comparable to those observed for the arylisocyanides.[17] The isocyanide **5** exhibits a strong IR absorption band at 2109 cm^{-1} for the C≡N triple bond.

Synthesis of Trimetallic Rhodium(I) Complexes. Triisocyanide **5** was found to be a good scaffold to incorporate triorganometallic fragments because metal complexes of **5** possess higher solubility than other metal complexes of isocyanides without alkyl substituents and have three isocyanide groups. For example, the new rhodium complex **6** was readily prepared from the reaction between the monomeric rhodium complex, (η^5-Cp*)Rh(Cab$^{s,s'}$), and the triisocyanide ligand **5** (Scheme 3). In addition, the coordinatively unsaturated 16-electron iridadithiolene complex (η^5-Cp*)Ir-(Cab$^{s,s'}$) readily reacted with alkynes to afford the new class of addition products.[18] The structure of **6** was determined on the basis of NMR spectroscopy, IR, and mass spectroscopy, as well as elemental analysis. The initial indication of

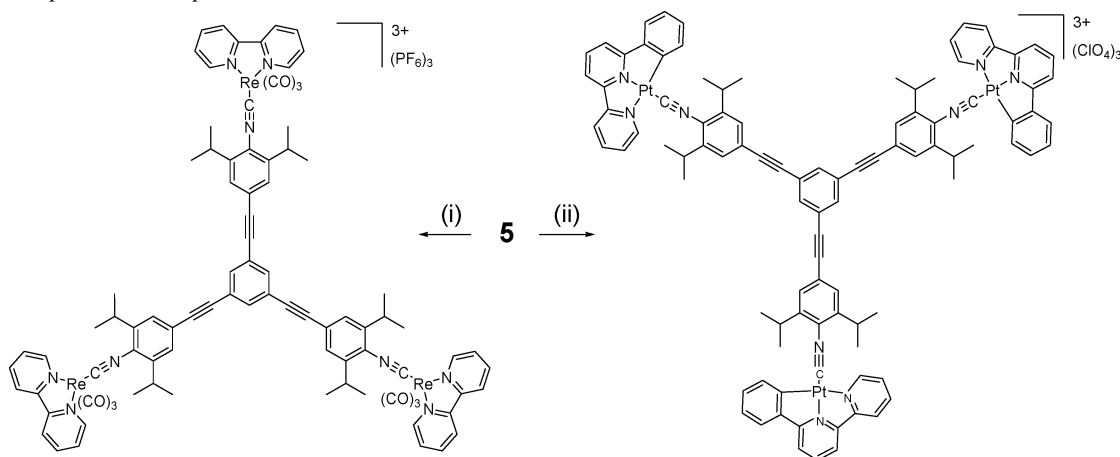(15) Eckert, H.; Forster, B. *Angew. Chem., Int. Ed.* **1987**, *26*, 894.

(16) Lentz, D. *Angew. Chem., Int. Ed.* **1994**, *33*, 1315.
(17) Yang, L.; Cheung, K.-K.; Mayr, A. *J. Organomet. Chem.* **1999**, *585*, 26.
(18) Bae, J.-Y.; Lee, Y.-J.; Kim, S.-J.; Ko, J.; Cho, S.; Kang, S. O. *Organometallics* **2000**, *19*, 1514.

Scheme 5. Preparation of Complexes **9** and **10**[a]
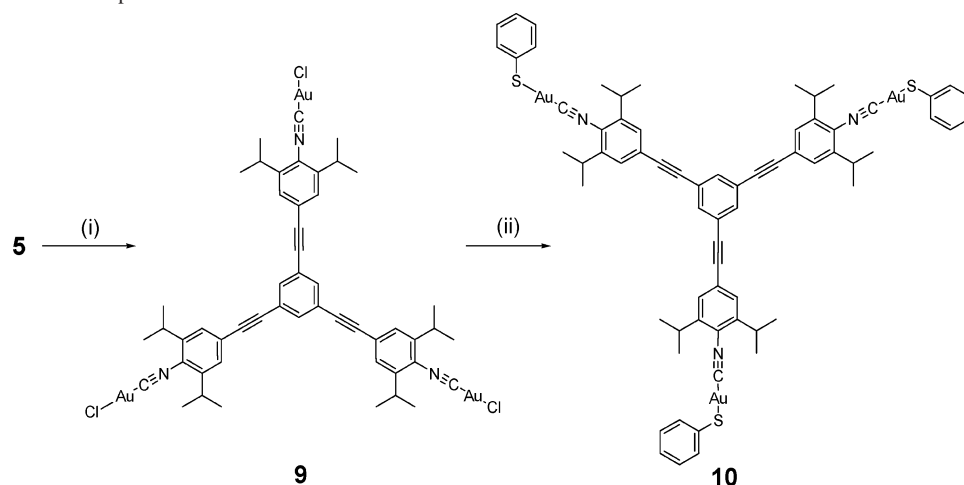
[a] (i) Au(SMe$_2$)Cl, CH$_2$Cl$_2$; (ii)NaSC$_6$H$_5$, THF.

Scheme 6. Preparation of Complexes **11** and **12**[a]

[a] (i) [Re(bpy)(CO)$_3$(CH$_3$CN)]PF$_6$, THF; (ii) (C^N^N)PtCl, LiClO$_4$.

the trinuclear rhodium complex stemmed from the observation of a parent ion in the mass spectrum at *m/z* 2044. Complex **6** exhibited a strong C≡N triple-bond stretching absorption at 2154 cm^{-1} in the IR spectrum, and this wavelength is normal for a terminal Rh−CNR ligand. The ^{13}C NMR spectrum of **6** indicated a signal at δ 173.2 due to an isocyanide group and two signals at δ 91.2 and δ 89.9 due to an alkynyl group. The ^{11}B NMR spectrum consists of three sets of broad resonances at −6.4, −10.2, and −16.2 ppm. All resonances are split into a B−H coupled doublet. The trirhodium complex **6** can be prepared by an alternative procedure in two steps. In the first step, the rhodium dimer [Cp*RhCl$_2$]$_2$ is easily cleavaged by ligand **5** to afford the trirhodium dichloride complex **7**. Such cleavage reaction has been observed for the reaction between the rhodium dimer [Cp*RhCl$_2$]$_2$ and bidentate diisocyanide.[19] The reaction of **7** with the dilithium salt Li$_2$Cab[s,s20] afforded a 62% yield of **6** (Scheme 3). Analytical and spectroscopic data support the formulation of **6**.

Synthesis of Trimetallic Chromium Complex. Treatment of 3 equiv of in-situ-generated Cr(CO)$_5$(THF)[21] to **5** gave its trichromium adduct **8** in 70% yield (Scheme 4). The ^{1}H NMR and ^{13}C NMR spectra of **8** indicated formation of highly symmetrical structure and displayed spectroscopic differences from its monomeric subunit. Complex **8** exhibits a strong IR absorption at 2121 cm^{-1} for the C≡N triple bond. The C≡N stretching frequency in **8** undergoes about 10 cm^{-1} shifts to higher frequency upon bonding to the Cr(CO)$_5$ fragment due to the NC(σ) → M interaction.

The structure of **8** was unambiguously established by single-crystal X-ray analysis and is shown in Figure 3. The average isocyanide carbon−chromium bond length is 1.96 Å. The Cr−C distances are longer than the corresponding bonds of [Cr(CO)$_5$]$_2$(μ-CN azulene NC)[22] and [Cr(CO)$_5$]$_2$-(μ-CNfcNC).[5a] The Cr−C back-bondings in **8** are weaker than those in [Cr(CO)$_5$]$_2$(μ-CNfcNC). The C(9)−N(3)−C(61)

(19) Suzuki, H.; Tajima, N.; Tatsumi, K.; Yamamoto, Y. *Chem. Commun.* **2000**, 1801.
(20) Smith, H. D., Jr.; Obenland, C. O.; Papetti, S. *Inorg. Chem.* **1966**, *5*, 1013.

(21) Herrmann, W. A.; Zybill, C. *In Synthetic Methods of Organometallic and Inorganic Chemistry (Herrmann/Brauer)*; Herrmann, W. A., Salzer, A., Eds.; Thieme: Stuttgart, 1996; Vol. 1, p117.
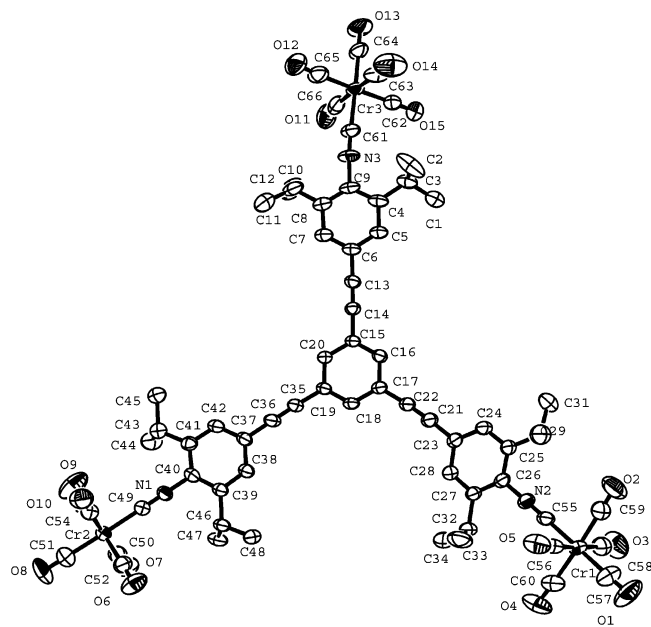
Figure 3. ORTEP drawing of complex **8** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): C(9)−N(3) = 1.408(3), N(3)−C(61) = 1.151(3), C(61)−Cr(3) = 1.968(3), Cr(3)−C(65) = 1.895-(4), C(65)−O(12) = 1.139(4), Cr(3)−C(64) = 1.882(3), C(64)−(O13) = 1.136(4), C(9)−N(3)−C(61) = 174.1(3), N(3)−C(61)−Cr(3) = 173.1(3), C(61)−Cr(3)−C(65) = 93.79(13).
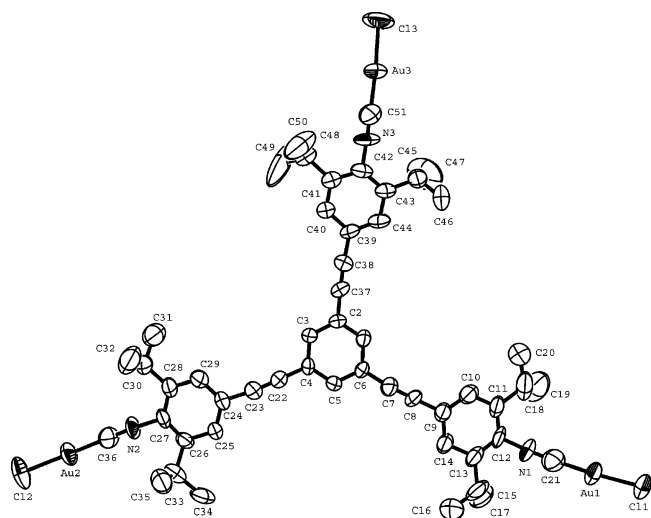

Figure 4. ORTEP drawing of complex **9** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Au(1)−C(21) = 1.846(15), Au(1)−Cl(1) = 2.239(3), C(7)−C(8) = 1.187(12), N(1)−C(21) = 1.218(15), C(21)−Au(1)−Cl(1) = 175.4(4), Au(1)−C(21)−N(1) = 175.1(12).

angle of 5.9° occurs in the plane of the bridge and was attributed a slight M(dπ) → CNR back-bonding.

Synthesis of Trimetallic Gold(I) Complexes. As the monomeric gold(I) complexes of isocyanides have been prepared by reaction of (dimethylsulfide)gold(I) chloride with the corresponding isocyanides,[23] we attempted a similar reaction in anticipation of synthesizing the trinuclear gold

Table 2. Absorption and Emission Data at 298 K[a]

compds	absorption			λ_{em}, nm	Φ_{em}[b]	τ, ns
	λ_{max}, nm (ϵ, $10^4 M^{-1} cm^{-1}$)					
5[c]	225 (3.44)	305 (3.84)	326 (5.24)	430	0.024	<1
10	282 (4.26)	302 (4.63)	318 (6.26)	612		
	342 (1.52)			604[d]	0.0008	124
11	225 (7.48)	288 (9.63)	312 (9.06)	475		
	352 (1.84)			568	0.051	78
12	230 (7.64)	292 (9.63)	325 (10.12)	542	0.052	278
	363 (3.32)					

[a] The excitation wavelength is 350 nm in CH$_2$Cl$_2$/DMF. [b] The emission quantum yields were determined using [Ru(bpy)$_3$](PF$_6$)$_2$ (Φ = 0.029).[32] [c] The excitation wavelength is 330 nm. [d] The solid-state emission data taken at 77 K.

complex. Treatment of **5** with the gold complex (Me$_2$S)-AuCl involves formation of a trinuclear gold complex **9** (Scheme 5). The reaction is quantitative and rapid at room temperature. In the IR spectrum a strong band for υ(C≡N) stretching was observed at 2202 cm^{-1}. The peak appears at higher frequency compared with that of the ligand (2109 cm^{-1}). The increase of ca. 100 cm^{-1} in the CN stretching frequency of gold isocyanide is well documented and probably attributable to σ donation of the carbon lone pair to Au.[24] The ^{13}C NMR spectrum displays distinct resonances for the isocyanide group at 170.8 ppm and the alkynyl group at 90.4 and 89.9 ppm. ^{1}H NMR spectrum and mass spectrum also support the proposed formula. The solid-state structure of **9** is consistent with its assigned solution structure.

An X-ray diffraction study on **9** confirmed that the complex has the expected linear geometry. The molecular structure of **9** is shown in Figure 4. The Au−Cl distance in LAuCl complexes is quite sensitive to the trans influence of L. The Au−Cl bond distance (2.239(3) Å) in **9** is significantly shorter than the corresponding in Cl−Au−PPh$_3$ of 2.279(3) Å.[25] This is in agreement with the greater trans influence of PPh$_3$ than that of an isocyanide. The bond angles Cl(1)−Au(1)−C(21), Au(1)−C(21)−N(1), and C(21)−N(1)−Cl(2) are 175.4(4)°, 175.1(12)°, and 172.7(13)°, respectively. Although similar distortion is observed in complex **2**, the distortion is greater than those for other gold(I) complexes.[26] The overall result is that the molecule of **9** has a little bent rather than linear geometry. Complex **9** is readily converted to the gold(I) thiolate of triisocyanide by the reaction between **9** and sodium phenylthiolate (Scheme 5). Its composition is readily confirmed by analytical and spectroscopic data. A similar gold(I) selenolate complex has been reported by reaction of [Au$_2$Cl$_2$(μ-dppf)] with PhSeSiMe$_3$.[27]

Isocyanide Ligation at Luminescent Re(I) and Pt(II) Complexes. As there has been considerable interest in polynuclear metal complexes bearing multiluminescent units

(22) Holovics, T. C.; Robinson, R. E.; Weintrob, E. C.; Toriyama, M.; Lushington, G. H.; Barybin, M. V. *J. Am. Chem. Soc.* **2006**, *128*, 2300.

(23) Schneider, W.; Angermaier, K.; Sladek, A.; Schmidbauer, H. *Naturforsch.* **1996**, *51b*, 790.

(24) (a) Sarapu, A. C.; Fenske, R. F. *Inorg. Chem.* **1975**, *14*, 247. (b) Jia, G.; Payne, N. C.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1993**, *12*, 4771.

(25) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

(26) Humphrey, S. M.; Mack, H.-G.; Redshaw, C.; Elsegood, M. R. J.; Young, K. J. H.; Mayer, H. A.; Kaska, W. C. *Dalton Trans.* **2005**, 439.

(27) Canales, S.; Crespo, O.; Gimeno, M. C.; Jones, P. G.; Laguna, A. *Inorg. Chem.* **2004**, *43*, 7234.
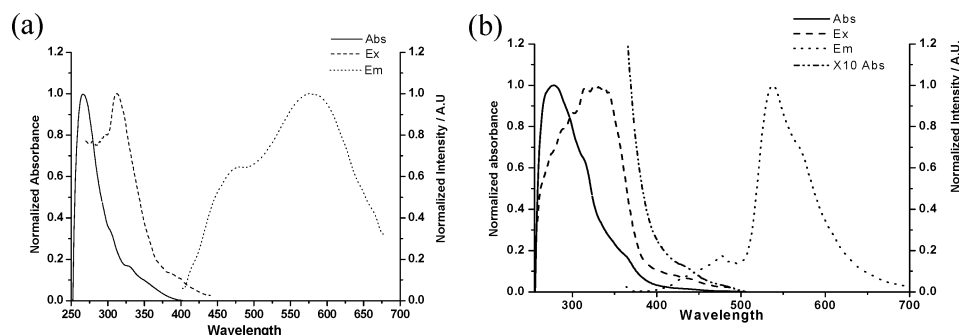
Figure 5. UV−vis absorption and emission spectrum of **11** (a) and **12** (b) in CH$_2$Cl$_2$/DMF at 298 K (λ_{em}= 350 nm, normalized intensity, concentration = 1.0 × 10^{-5} M). Excitation spectra monitored at (a) 560 and (b) 570 nm.

capable of performing light-induced processes, we attempted to synthesize such complexes using the multidentate isocyanide ligand. The trinuclear Re(I) complex **11** can be prepared by refluxing [Re(bpy)(CO)$_3$(CH$_3$CN)]PF$_6$ with **5** in THF and purified by crystallization from CH$_2$Cl$_2$/Et$_2$O solution (Scheme 6). The identity of the new rhenium compound has been established by NMR, IR, FAB-MS spectrometry, and elemental analysis. Compound **11** shows a strong C≡N absorption at 2196 cm^{-1} and three strong C≡O stretching absorptions at 2062 and 1902 cm^{-1}. The observation of two strong bands in the C≡O stretching mode confirms that the three carbonyl groups are in a facial arrangement with C_{3v} local symmetry.[11a,28] The FAB-MS spectrum of **11** exhibits a peak at *m/z* 1879 displaying the expected isotopic profile of the [M − 2PF$_6$]$^+$ cation. As the facile displacement of the chloride group from [(C^N^N)PtCl] (HC^N^N= 6-phenyl-2,2′-bipyridine) by isocyanide has been well documented,[29] we thought that the reaction of [(C^N^N)PtCl] with triisocyanide ligand **5** occurred to afford the trinuclear platinum complex. As expected, we prepared the trinuclear complex with three [(C^N^N)Pt] moieties by coordinating to the triisocyanide ligand. Complex **12** is air and moisture stable at room temperature. The FAB-MS spectrum of **12** reveals a peak at *m/z* 2181 corresponding to [M$^+$ − ClO$_4$]. The characteristic IR absorption for υ(C≡N) in **12** appears at 2155 cm^{-1}, which is comparable to that of [(C^N^N)Pt-(C≡N^{t}Bu)]ClO$_4$ (2207 cm^{-1}).[29a] All ^{1}H and ^{13}C NMR data of **12** are consistent with the proposed molecular structure.

Photophysical Properties. The photophysical parameters obtained from compounds **10**−**12** and free ligand **5** are summarized in Table 2. Ligand **5** exhibits three intense bands in the 225−320 nm region. The absorption spectra of complexes **10**−**12** shows a series of intense absorptions at <330 nm which can be assigned to $\pi \rightarrow \pi^*$ transitions localized on C^N^N or diimine ligands and free ligand. The lower energy bands which appear from ∼340 nm and extend past 410 nm are assigned to M → ligand (M = Au, Re, Pt) charge-transfer (MLCT) absorption bands with reference to previous spectroscopic work on related complexes.[9b,11,29] Weak bands at 352 (**11**) and 363 nm (**12**) with extinction coefficients (ϵ) on the order of 10^4 M^{-1} cm^{-1} and the close resemblance of excitation spectra at 345 (**11**) and 352 nm (**12**) to the low-energy tail at ca. 400−500 nm in the electronic absorption spectrum are supportive of a MLCT origin. In the case of **11**, a solvent-sensitive band maximizes

at 342 nm in DMF, 348 nm in MeOH, and 368 nm in THF. The bathochromic shift with decreasing solvent polarity indicates additional support for the assignment to the MLCT bond. The different MLCT bands of compounds **10**−**12** associated with transitions to the diimine or C^N^N ligands and free ligand are substantially overlapping, and it is not possible to assign their accurate positions.

All complexes **10**−**12** are emissive in solution at room temperature. Complex **12** in CH$_2$Cl$_2$/DMF solution at 298 K shows a broad emission band (λ_{max}= 542 nm) in the region of 500−700 nm, while complex **11** (λ_{max}= 568 nm) under the same condition exhibits a much broader emission band with a shoulder peak at 475 nm relative to complex **12**. The nature of these emission bands can be assigned to a MLCT excited state.[30] Similar assignments in absorption and emission have been described for the related acetylide complexes, such as those of Pt(II) and Re(I), which were isoelectronic to the isocyanide.[31] Measurement of the solid-state emission spectrum of **10** at 77 K revealed a broad featureless band centered at 604 nm. A lifetime of 124 ns for the emission band is detected. The relatively long lifetime of the 604 nm emission is consistent with its assignment to a triplet metal-centered state. The emission spectra of **11** (Figure 5a) and **12** (Figure 5b) exhibit a broad center at 568 and 542 nm, respectively, which is attributable to the triplet MLCT emission, typical of [(bpy)Re(CO)$_3$][11b] and Pt(II)(diimine) complexes.[30] Of note is that the high emission quantum yield of **11** and **12** may be rationalized by the strong ligand field of isocyanide which increases the energy of ligand-field excited states. Similar phenomena were observed in the Pt-(II) complexes with isocyanide ligands.[29b]

Conclusions

In summary, a novel triisocyanide ligand **5** was prepared. The ligand was found to be an effective reactant to coordinate

(28) Gamelin, D. R.; George, M. W.; Glynn, P.; Grevels, F.-W.; Johnson, F. P. A.; Klotzbücher, W.; Morrison, S. L.; Russell, G.; Schaffner, K.; Turner, J. J. *Inorg. Chem.* **1994**, *33*, 3246.
(29) (a) Lai, S.-W.; Chan, M. C.-W.; Cheung, K.-K.; Che, C.-M. *Organometallics* **1999**, *18*, 3327. (b) Lai, S.-W.; Lam, H.-W.; Lu, W.; Cheung, K.-K.; Che, C.-M. *Organometallics* **2002**, *21*, 226.
(30) Chan, S.-C.; Chan, M. C. W.; Wang, Y.; Che, C.-M.; Cheung, K.-K.; Zhu, N. *Chem. Eur. J.* **2001**, *7*, 4180.
(31) (a) Yam, V. W.-W.; Tao, C.-H.; Zhang, L.; Wong, K. M.-C.; Cheung, K.-K. *Organometallics* **2001**, *20*, 453. (b) Tao, C.-H.; Zhu, N.; Yam, V. W.-W. *Chem. Eur. J.* **2005**, *11*, 1647. (c) Chong, S. H.-F.; Lam, S. C.-F.; Yam, V. W.-W.; Zhu, N.; Cheung, K.-K. *Organometallics* **2004**, *23*, 4924.

to various metal complexes through the isocyanide ligation. Ligand **5** readily reacts with 16-electron rhodium complex, (η^5-Cp*)Rh(Cab$^{s,s'}$) to afford the trimetallic addition product **6**. Such trirhodium

complex can also be prepared by the cleavage reaction between the rhodium dimer [Cp*RhCl$_2$]$_2$ and **5**, followed by the reaction of Li$_2$Cab$^{s,s'}$. The trimetallic chromium complex **8** shows slightly weak Cr → C≡N back-bonding. Trimetallic gold complex bearing ligand **5** can be prepared by the displacement reaction of (dimethylsulfide)gold(I) chloride with **5**. The trimetallic Re(I) and Pt(II) complexes of **5** exhibit interesting photophysical properties. The emission spectra of both complexes exhibit a broad band centered at 540−570 nm, due to the triplet MLCT emission. Work will involve the synthesis of a hexaisocyanide ligand, multiisocyanide with porphyrin unit, and their metal complexes.

Experimental Section

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques. THF, toluene, diethyl ether, and hexane were distilled from sodium benzophenone. Methylene chloride, CHCl$_3$, MeOH, and EtOH were distilled under nitrogen from P$_2$O$_5$. The ^{1}H, ^{13}C, and ^{11}B NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.00, 75.44, and 96.00 MHz, respectively. ^{11}B NMR chemical shifts are reported relative to BF$_3$·O(C$_2$H$_5$)$_2$, used as an external reference, with a negative sign indicating an upfield shift. The absorption spectra were recorded on a Perkin-Elmer Lambda 25 UV−visible spectrophotometer. IR spectra were recorded on a Biorad FTS-165 spectrometer. Mass spectra were recorded on a JEOL JMS-SX 102A instrument. Elemental analyses were performed with a Carlo Elba Instruments CHNS-O EA 1108 analyzer. Triphosgene, acetic anhydride, formic acid, 2,6-diisopropyl-4-iodoaniline, and chloro(dimethylsulfide)-gold(I) were purchased from Aldrich Chemical Co. 1,3,5-Triethynylbenzene,[33] (η^5-Cp*)Rh(Cab$^{s,s'}$),[13] [Re(bpy)-(CO)$_3$–(AN)]PF$_6$,[34] (C^N^N)PtCl,[35] and Li$_2$(Cab$^{s,s'}$)[20] were prepared according to literature methods.

1,4-Bis(4-isocyano-3,5-diisopropylpheny)buta-1,3-diyne (1). A mixture of 4-isocyanophenylacetylene (0.24 g, 0.31 mmol), CuCl$_2$ (0.083 g, 0.62 mmol), and NaOAc (0.13 g, 0.62 mmol) in THF (10 mL) in a Schlenk flask was heated to reflux for 12 h. The THF was then evaporated in vacuo. The residue was extracted with CH$_2$Cl$_2$. The pure product was isolated by column chromatography on silica gel using CH$_2$Cl$_2$/hexane (1:1) as the eluent in 84% yield. mp: 236 °C. ^{1}H NMR (CDCl$_3$): δ 7.32 (s, 4H), 3.35 (h, 4H, J_{HH} = 6.6 Hz, C*H*), 1.27 (d, 24H, J_{HH} = 6.6 Hz, C*H$_3$*). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 170.9, 145.6, 145.4, 128.1, 127.2, 122.7, 125.0, 81.9, 30.4, 22.6. IR (KBr pellet, cm^{-1}): 2050 (v(C≡C)), 2124 (v(C≡N)). Anal. Calcd for C$_{30}$H$_{32}$N$_2$: C, 85.67; H, 7.67. Found: C, 85.34; H, 7.71

[{((η^5-Cp*)Rh(Cab^{s,s})(CNC$_6$H$_2^i$Pr$_2$-2,6))$_2$-C≡C}-1,2] (2). To a stirred toluene solution (5 mL) of **1** (0.049 g, 0.07 mmol) was added (η^5-Cp*)Rh(Cab$^{s,s'}$) (0.1 g 0.22 mmol) dissolved in toluene (5 mL) at 0 °C. The solution was allowed to warm to room

temperature. The solution was stirred for 2 h. The pure complex **2** was isolated by silica gel chromatography (eluent: CH$_2$Cl$_2$/hexane = 1:6) as an orange crystalline solid in 92% yield. mp: 282 °C. ^{1}H NMR(CDCl$_3$): δ 7.39 (s, 4H), 3.51 (h, 4H, J_{HH} = 6.6 Hz, C*H*), 1.81 (s, 30H), 1.32 (d, 24H, J_{HH} = 6.6 Hz, C*H$_3$*). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 172.8, 146.3, 135.7, 127.7, 126.2, 122.9, 103.0, 94.0, 81.8, 30.1, 23.6, 9.4. IR (KBr pellet, cm^{-1}): 2085 (v(C≡C)), 2578 (v(B−H)), 2162 (v(C≡N)). FAB-MS: m/z 1113 [M$^+$]. Anal. Calcd For C$_{62}$H$_{94}$B$_{20}$N$_2$O$_2$S$_4$Rh$_2$: C, 53.95; H, 5.61. Found: C, 53.56; H, 5.32.

1,3,5-Tris[(4-amino-3,5-diisopropylphenyl)ethynyl]benzene (3). A mixture of triethynylbenzene (0.15 g, 1 mmol), 2,6-diisopropyl-4-iodoaniline (1.52 g, 5 mmol), Pd(PPh$_3$)$_4$ (0.10 g, 0.09 mmol), CuI (0.017 g, 0.09 mmol), and degassed NEt$_3$ (10 mL) in THF (10 mL) in a Schlenk flask was heated to reflux for 72 h. The resulting reaction mixture was extracted with CH$_2$Cl$_2$. Compound **3** was purified by chromatography on silica gel using CH$_2$Cl$_2$/hexane (1:1) as the eluent in 72% yield. mp: 165 °C. ^{1}H NMR (CDCl$_3$): δ 7.58 (s, 3H), 7.22 (s, 6H), 3.92 (br, 6H, N*H$_2$*), 2.88 (h, 6H, J_{HH} = 6.6 Hz, C*H*), 1.29 (d, 36H, J_{HH} = 6.6 Hz, C*H$_3$*). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 141.8, 132.3, 130.6, 124.6, 117.4, 112.2, 93.8, 86.0, 28.3, 22.5. IR (KBr pellet, cm^{-1}): 2123(v(C≡C)). Anal. Calcd for C$_{48}$H$_{57}$N$_3$: C, 85.28; H, 8.50. Found: C, 85.15; H, 8.37.

1,3,5-Tris[(4-formamido-3,5-diisopropylphenyl)ethynyl]benzene (4). A mixture of acetic anhydride (3 mL) and formic acid (3 mL) was heated for 2 h at 50−60 °C. Then the solution was cooled to room temperature. Compound **3** (0.45 g, 0.67 mmol) dissolved in diethyl ether (20 mL) was slowly added to this solution. The resulting solution was stirred for 12 h at room temperature and neutralized with aqueous sodium carbonate. The organic phase was dried over MgSO$_4$. After filtration and evaporation of the solvent, the product **4** was obtained as a white solid in 85% yield. mp: 208 °C. ^{1}H NMR (CDCl$_3$): δ 8.49 (s, 3H, C*H*O), 7.71 (s, 3H), 7.31 (s, 6H), 6.74 (s, 3H, N*H*), 3.21 (h, 6H, J_{HH} = 6.6 Hz, C*H*), 1.24 (d, 36H, J_{HH} = 6.6 Hz, C*H$_3$*). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 163.8, 147.1, 130.5, 129.2, 127.8, 124.2, 123.4, 90.4, 88.3, 28.6, 23.4. IR (KBr pellet, cm^{-1}): 1684 (v(C=O)), 2088 (v(C≡C)). Anal. Calcd for C$_{51}$H$_{57}$N$_3$O$_3$: C, 80.60; H, 7.56. Found: C, 80.38; H, 7.45.

1,3,5-Tris[(4-isocyano-3,5-diisopropylphenyl)ethynyl]benzene (5). To a stirred THF solution (20 mL) of **2** (0.24 g, 0.31 mmol) and NEt$_3$ (5 mL) was added a solution of triphosgene (0.18 g, 0.60 mmol) in THF (10 mL) at −78 °C. The mixture was warmed to room temperature and stirred for 12 h. The mixture was evaporated under reduced pressure to remove THF and NEt$_3$. The reaction mixture was extracted with CHCl$_3$. Compound **5** was purified by chromatography on silica gel using CH$_2$Cl$_2$/hexane (1: 1) as the eluent in 72% yield. mp: 236 °C. ^{1}H NMR (CDCl$_3$): δ 7.71 (s, 3H), 7.32 (s, 6H), 3.36 (h, 6H, J_{HH} = 6.9 Hz, C*H*), 1.31 (d, 36H, J_{HH} = 6.9 Hz, C*H$_3$*). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 170.3, 145.5, 130.8, 123.9, 123.0, 118.3, 116.8, 90.3, 89.2, 28.2, 22.5. IR (KBr pellet, cm^{-1}): 2091 (v(C≡C)), 2109 (v(C≡N)). FAB-MS: m/z 705 [M$^+$]. Anal. Calcd for C$_{51}$H$_{51}$N$_3$: C, 86.77: H, 7.28. Found: C, 86.33; H, 7.14.

[{(η^5-Cp*)Rh(Cab^{s,s})(CNC$_6$H$_2^i$Pr$_2$-2,6-C≡C-3)}$_3$C$_6$H$_3$-1,3,5] (6). (A) To a stirred toluene solution (5 mL) of **5** (0.049 g, 0.07 mmol) was added (η^5-Cp*)Rh(Cab$^{s,s'}$) (0.10 g, 0.22 mmol) dissolved in toluene (5 mL) at 0 °C. The solution was allowed to warm to room temperature. The solution was stirred for 3 h. The pure compound **6** was isolated by silica gel chromatography (eluent: CH$_2$Cl$_2$/hexane (1:10)) as a yellow solid in 92% yield.

(B) An alternative procedure of complex **6** from complex **7**: To a stirred THF solution (5 mL) of Li$_2$Cab$^{s,s'}$ (0.01 g, 0.045 mmol) was added complex **7** (0.05 g, 0.03 mmol) dissolved in THF (5

(32) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583.
(33) Leininger, S.; Stang, P. J.; Huang, S. *Organometallics* **1998**, *17*, 3981.
(34) Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952.
(35) Cheung, T. C.; Cheung, K. K.; Peng, S. M.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1996**, 1645.

mL) at 0 °C. The solution was stirred for 6 h at 0 °C. Purification of complex **6** was described above (A). The isolated yield was 62%. mp: 280 °C. ^{1}H NMR (CDCl$_3$): δ 7.76 (s, 3H), 7.39 (s, 6H), 3.53 (h, 6H, J_{HH} = 6.9 Hz, C*H*), 1.82 (s, 45H), 1.35 (d, 36H, J_{HH} = 6.9 Hz, C*H$_3$*). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 173.2, 146.4, 136.1, 127.6, 124.5, 123.9, 103.1, 93.5, 91.2, 89.9, 28.9, 22.9, 9.5. ^{11}B NMR (CDCl$_3$): δ −6.4 (d, 5B, J_{BH} = 135 Hz), −10.2 (d, 3B, J_{BH} = 120 Hz), −16.2 (d, 2B, J_{BH} = 140 Hz). IR (KBr pellet, cm^{-1}): 2093 (v(C≡C)), 2154 (v(C≡N)), 2582 (v(B−H)). FAB-MS: m/z 2044 [M$^+$]. Anal. Calcd for C$_{126}$H$_{135}$N$_3$S$_6$Rh$_3$: C, 69.02; H, 6.21. Found: C, 68.78; H, 6.09.

[{(η^5-Cp*)RhCl$_2$(CNC$_6$H$_2$^{i}Pr$_2$-2,6-C≡C-3)}$_3$C$_6$H$_3$-1,3,5] (7). To a stirred CH$_2$Cl$_2$ solution (10 mL) of [Cp*RhCl$_2$]$_2$ (0.05 g, 0.081 mmol) was added ligand **5** (0.038 g, 0.054 mmol) in CH$_2$Cl$_2$ (10 mL) at room temperature. The solution was stirred for 1 h. The solvent was removed in vacuo and washed with Et$_2$O (20 mL). The pure product **7** was obtained by recrystallization with CH$_2$-Cl$_2$/hexane as an orange solid in 82% yield. mp: 327 °C. ^{1}H NMR (CDCl$_3$): δ 7.72 (s, 3H), 7.33 (s, 6H), 3.46 (h, 6H, J_{HH} = 6.6 Hz, C*H*), 1.85 (s, 45H), 1.32 (d, 36H, J_{HH} = 6.6 Hz, C*H$_3$*). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 172.4, 144.8, 137.2, 126.8, 124.2, 123.7, 104.6, 93.2, 90.6, 89.2, 27.4, 22.4, 9.8. IR (KBr pellet, cm^{-1}): 2096 (v-(C≡C)), 2160 (v(C≡N)). Anal. Calcd for C$_{81}$H$_{96}$N$_3$Cl$_6$Rh$_3$: C, 59.57; H, 5.93. Found: C, 59.38; H, 5.81.

[{Cr(CO)$_5$(CNC$_6$H$_2$^{i}Pr$_2$-2,6-C≡C-3)}$_3$C$_6$H$_3$-1,3,5] (8). A stirred THF solution (30 mL) of Cr(CO)$_6$ (0.096 g, 0.43 mmol) was irradiated using a Hg immersion lamp (150 W) at room temperature for 3.5 h until the solution turned orange. Then ligand **5** (0.10 g, 0.14 mmol) in THF (5 mL) was added to the orange solution. The solution was stirred for 30 min at room temperature. The solvent was evaporated in vacuo, and excess Cr(CO)$_6$ was removed by vacuum sublimation. The pale yellow residue was extracted with diethyl ether (20 mL × 3). Compound **8** was purified by chromatography on silica gel using CH$_2$Cl$_2$/hexane (1:3) as an eluent in 70% yield. mp: 176 °C. ^{1}H NMR (CDCl$_3$): δ 7.72 (s, 3H), 7.33 (s, 6H), 3.26 (h, 6H, J_{HH} = 7.2 Hz, C*H*), 1.35 (d, 36H, J_{HH} = 7.2 Hz, C*H$_3$*). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 214.5, 214.2, 170.3, 145.5, 134.5, 128.4, 126.9, 124.4, 123.9, 90.3, 89.2, 29.9, 22.6. IR (KBr pellet, cm^{-1}): 2121 (v(C≡N)), 2090 (v(C≡C)), 2051 (v(C≡O)), 1957 (v(C≡O)). Anal. Calcd for C$_{64}$H$_{47}$Cr$_3$N$_3$O$_{15}$: C, 61.30; H, 3.78. Found: C, 60.81; H, 3.61.

[{AuCl(CNC$_6$H$_2$^{i}Pr$_2$-2,6-C≡C-3)}$_3$C$_6$H$_3$-1,3,5] (9). To a stirred CH$_2$Cl$_2$ solution (10 mL) of Au(SMe$_2$)Cl (0.026 g, 0.009 mmol) was added ligand **5** (0.021 g, 0.003 mmol) in CH$_2$Cl$_2$ (10 mL) at room temperature. The solution was stirred for 6 h. The solvent was removed in vacuo and washed with Et$_2$O (10 mL × 3). The pure product **9** was obtained by recrystallization with CH$_2$Cl$_2$/Et$_2$O as a white crystalline solid in 84% yield. mp: 361 °C. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.73 (s, 3H), 7.41 (s, 6H), 3.24 (h, 6H, J_{HH} = 6.9 Hz, C*H*), 1.29 (d, 36H, J_{HH} = 6.9 Hz, C*H$_3$*). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 170.8, 147.0, 136.2, 127.6, 126.2, 123.8, 122.1, 90.4, 89.9, 30.2, 22.0. IR (KBr pellet, cm^{-1}): 2090 (v(C≡C)), 2202 (v(C≡N)). Anal. Calcd for C$_{51}$H$_{51}$N$_3$Cl$_3$Au$_3$: C, 43.65: H, 3.66. Found: C, 43.41; H, 3.52.

[{AuSPh(CNC$_6$H$_2$^{i}Pr$_2$-2,6-C≡C-3)}$_3$C$_6$H$_3$-1,3,5] (10). Under nitrogen NaSC$_6$H$_5$ (0.016 g, 0.121 mmol) was added to a stirred THF (10 mL) and MeOH (10 mL) solution of **9** (0.053 g, 0.0378 mmol). After stirring for 1 h, the solution was evaporated and washed with MeOH (5 mL × 2). The pure product **10** was obtained by recrystallization with CH$_2$Cl$_2$/Et$_2$O as an orange crystal in 84% yield. mp: 324 °C. ^{1}H NMR (CDCl$_3$): δ 7.76 (s, 3H), 7.68 (d, 6H, J_{HH} = 6.6 Hz), 7.35 (s, 6H), 7.13 (m, 6H), 7.02 (t, 3H, J_{HH} = 6.6 Hz), 3.27 (h, 6H, J_{HH} = 6.6 Hz, C*H*), 1.33 (d, 36H, J_{HH} = 6.6

Hz, C*H$_3$*). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 171.2, 156.8, 146.6, 146.0, 134.1, 131.7, 128.6, 127.4, 125.9, 123.7, 122.3, 90.5, 89.7, 30.9, 23.7. IR (KBr pellet, cm^{-1}): 2096 (v(C≡C)), 2186 (v(C≡N)). Anal. Calcd for C$_{69}$H$_{66}$N$_3$S$_3$Au$_3$: C, 51.01: H, 4.10. Found: C, 50.84; H, 4.02.

[{Re(bpy)(CO)$_3$(CNC$_6$H$_2$^{i}Pr$_2$-2,6-C≡C-3)}$_3$C$_6$H$_3$-1,3,5]-(PF$_6$)$_3$ (11). A mixture of [Re(bpy)(CO)$_3$(CH$_3$CN)]PF$_6$ (0.14 g, 0.23 mmol) and **5** (0.05 g, 0.07 mmol) in THF (20 mL) was heated to reflux under nitrogen for 12 h. The solvent was removed in vacuo and washed with ethanol (3 mL × 3). The pure product **11** was obtained by crystallization by vapor diffusion of Et$_2$O into a CH$_2$-Cl$_2$ solution of the product as a pale yellow crystal in 43% yield. mp: 168 °C. ^{1}H NMR (CDCl$_3$): δ 9.07 (d, 6H, J_{HH} = 4.2 Hz), 8.20 (d, 6H, J_{HH} = 7.5 Hz), 8.08 (m, 6H), 7.71 (s, 3H), 7.55 (m, 6H), 7.37 (s, 6H), 3.12 (h, 6H, J_{HH} = 6.6 Hz, C*H*), 1.25 (d, 36H, J_{HH} = 6.6 Hz, C*H$_3$*). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 196.1, 191.9, 156.0, 154.8, 147.6, 146.9, 140.3, 140.0, 127.8, 127.4, 123.6, 123.2, 122.6, 91.8, 89.6, 30.7, 22.7. IR (KBr pellet, cm^{-1}): 1902, 2062 (v(C≡O)), 2092 (v(C≡C)), 2196 (v(C≡N)). FAB-MS: m/z 1879 [(M − 2PF$_6$)]$^+$. Anal. Calcd for C$_{90}$H$_{84}$F$_{18}$N$_9$O$_9$P$_3$Re$_3$: C, 44.31; H, 3.39. Found: C, 44.51; H, 3.47.

[{Pt((N^N^C))(CNC$_6$H$_2$^{i}Pr$_2$-2,6-C≡C-3)}$_3$C$_6$H$_3$-1,3,5]-(ClO$_4$)$_3$ (12). To a stirred solution of [(C^N^N)PtCl] (0.20 g, 0.44 mmol) in CH$_3$CN (10 mL) and CH$_2$Cl$_2$ (10 mL) was added **5** (0.103 g, 0.146 mmol) in CH$_2$Cl$_2$ (5 mL) at room temperature. The color of the mixture changed to red after 30 min. The solution was stirred for 2 h. To that solution was added excess LiClO$_4$ in CH$_3$CN (15 mL). On addition of Et$_2$O (20 mL) to that solution, the yellow product **12** precipitated out. The product was collected and washed with Et$_2$O (10 mL × 3) in 72% yield. mp: 276 °C. ^{1}H NMR (CD$_2$-Cl$_2$): δ 8.62 (d, 6H, J_{HH} = 7.5 Hz), 8.44 (m, 6H), 8.16 (d, 6H, J_{HH} = 6.6 Hz), 7.87 (m, 6H), 7.75 (m, 6H), 7.69 (s, 3H), 7.35 (s, 6H), 7.20 (d, 3H, J_{HH} = 6.9 Hz), 3.35 (h, 6H, J_{HH} = 6.9 Hz, C*H*), 1.36 (d, 36H, J_{HH} = 6.9 Hz, C*H$_3$*). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 164.0, 156.5, 155.1, 146.9, 145.8, 144.0, 143.6, 142.2, 141.7, 137.6, 137.1, 134.7, 134.5, 129.3, 127.4 127.1, 126.7, 126.0, 124.9, 124.2, 123.3, 120.9, 120.5, 90.3, 89.9, 30.2, 21.9. IR (KBr pellet, cm^{-1}): 2093 (v(C≡C)), 2155 (v(C≡N)). FAB-MS: m/z 2181 [M − ClO$_4$]$^+$. Anal. Calcd for C$_{99}$H$_{84}$N$_9$Cl$_3$O$_{12}$Pt$_3$: C, 59.90; H, 4.27. Found: C, 59.98; H, 4.34.

Emission and Lifetime Measurements. Emission spectra were recorded on a Perkin-Elmer LS-50 spectrophotometer with a Hamamatsu R928 photomultiplier. Luminescence lifetimes were measured with a Quanta Ray DCR-3 pulsed Nd:YAG laser system (355 nm, time resolution, 0.5 ns). Luminescence quantum yields were performed on a Perkin-Elmer LS-50 spectrophotometer using the method of Demas and Crosby with [Ru(bpy)$_3$]$^{2+}$ [36] as the quantum yield standard (Φ = 0.029).

X-ray Crystallography. Suitable crystals of **2**, **8**, and **9** were grown by THF/hexane, CH$_2$Cl$_2$/hexane, and CH$_2$Cl$_2$/Et$_2$O, respectively. All X-ray data of compounds **2**, **8**, and **9** were collected using graphite-monochromated Mo Kα radiation (λ = 0.7173 Å) with a Bruker AXS SMART CCD area-detector diffractometer. The orientation matrix and unit cell parameters of **2**, **8**, and **9** were determined by least-squares analyses of the setting angles of the range 3.88° < 2θ < 56.62°, 2.36° < 2θ < 56.74°, and 2.78° < 2θ < 56.68° with 8803, 8144, and 4445 reflections, respectively. Three check reflections were measured every 100 reflections throughout data collection and showed no significant variation in intensity. Intensity data were collected with Ψ-scan data. All calculations were carried out with the SHELXL-97 program. The structure was

---

(36) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.

solved by the direct method. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the calculated positions. The SQUEEZE procedure in PLATON takes care of the contribution of disordered solvents such as THF (complex **2**), hexane (complex **8**), and diethyl ether (complex **9**) to the calculated structure factors by back-Fourier transformation of the continuous density found in a masked region of the difference map. The masked region is defined as the solvent accessible void left by the ordered part of the structure.[37]

Supporting Information Available: Crystallographic data in CIF format for **2**, **8**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0620900

(37) See the SQUEEZE instruction at http://www.cryst.chem.uu.nl/platon.