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Low-Coordinate Carbene Complexes of Nickel(0) and Platinum(0)[†]

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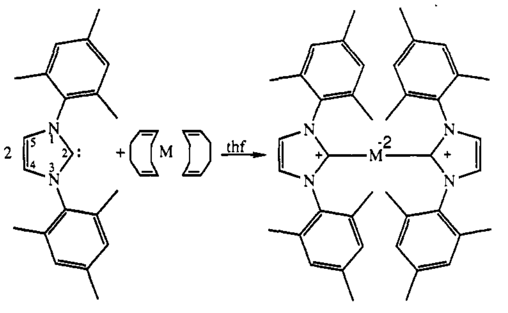
Abstract: The syntheses and characterizations of 2-coordinate homoleptic bis(carbene) adducts of 14-electron Ni(0) and Pt(0) are described. These carbene adducts are available directly from the reaction of the stable nucleophilic carbene 1,3-dimesitylimidazol-2-ylidene and the corresponding metal bis(cyclooctadiene) complexes. NMR data are consistent with the bis(carbene)–metal structures and suggest a higher degree of $d\pi$–$p\pi$ back-donation from the metal relative to closely related Cu(I), Ag(I), and Au(I) complexes. The X-ray crystal structures of both the nickel–carbene and platinum–carbene adducts are reported. The metals exhibit an essentially linear 2-coordinate geometry with the imidazole rings twisted 53° (Ni) and 51° (Pt) relative to one another.

Introduction

Low-coordinate nickel(0), palladium(0) and platinum(0) complexes are of interest because of their postulated intermediacy in various organometallic transformations. Two-coordinate phosphine (14-electron) complexes of these zerovalent transition-group-10 metals have been prepared and characterized in detail.[1-13] Carbene complexes of the transition-group-10 metals are well-known for higher oxidation states[14] but zerovalent complexes are rare.[15,16] A few 16e homoleptic tricoordinated transition-group-10 complexes derived from Ge(II) and Sn(II) ligands also have been reported.[17,18] We have previously reported the syntheses, characterizations, and isolation of stable nucleophilic carbenes[19-24] that are very convenient starting materials for studing previously inaccessible metal–carbene complexes. Homoleptic 2-coordinate copper(I) and silver(I) complexes that take advantage of stable carbenes with bulky substituents have been synthesized recently.[21] These new stable carbenes offer the potential for unusual coordination chemistry with zerovalent transition-metal centers.

Results and Discussion

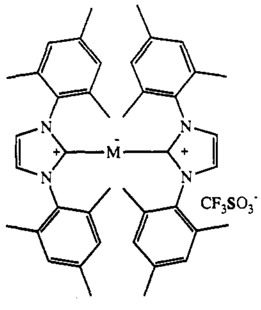
The reactions of bis(1,5-cyclooctadiene)nickel(0) or bis(1,5-cyclooctadiene)platinum(0) with 2 equiv of the carbene **1** in tetrahydrofuran (thf) proceeded smoothly to give the unusual carbene adducts **2a,b** in 70–80% yield (eq 1). The related copper(I), silver(I), and gold(I) complexes **3a,b**[21] and **4**[25] have been reported previously and serve as useful comparisons.



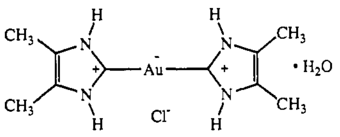
(1)

1

2a M = Ni
2b M = Pt



3a M = Cu
3b M = Ag



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The ^{13}C resonances for the former carbene centers shift upfield from δ 219.7 for **1** to δ 193.2 and 197.5 for **2a** and **2b**, respectively

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[†] In memory of Linus Amadeus.

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(1) Ugo, R.; LaMonica, G.; Cariati, F.; Cerini, S.; Conti, F. *Inorg. Chim. Acta* **1970**, *4*, 390.

(2) Otsuka, S.; Tani, K.; Kato, I.; Teranaka, O. *J. Chem. Soc., Dalton Trans.* **1974**, 2216.

(3) Englert, E.; Jolly, P. W.; Wilke, G. *Angew. Chem.* **1971**, *83*, 84.

(4) Jolly, P. W.; Jonas, K.; Kruger, C.; Tsay, Y. H. *J. Organomet. Chem.* **1971**, *33*, 109.

(5) Tanaka, M. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1992**, *48*, 739.

(6) Matsumoto, M.; Yoshioka, H.; Nakatsu, K.; Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1974**, *96*, 3322.

(7) Musuco, A.; Kuran, W.; Silvani, A.; Anker, M. W. *J. Chem. Soc., Chem. Commun.* **1973**, 938.

(8) Immirzi, A.; Musco, A. *J. Chem. Soc., Chem. Commun.* **1974**, 400.

(9) van der Linde, R.; der Jongh, R. O. *J. Chem. Soc. D.* **1971**, 563.

(10) Immirzi, A.; Musco, A.; Zambelli, P.; Carturan, G. *Inorg. Chim. Acta* **1975**, *13*, L13.

(11) Kudo, K.; Hidal, M.; Uchida, Y. *J. Organomet. Chem.* **1973**, *56*, 413.

(12) Otsuka, S.; Yoshida, T.; Matsumoto, M.; Nakatsu, K. *J. Am. Chem. Soc.* **1976**, *98*, 5850.

(13) Green, M.; Howard, J. A.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1975**, 3.

(14) Lappert, M. F. *J. Organomet. Chem.* **1988**, *358*, 185.

(15) Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Dalton Trans* **1977**, 2172.

(16) Gabor, B.; Krueger, C.; Marczinke, B.; Mynott, R.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1666.

(17) Hitchcock, P. B.; Lappert, M. F.; Misra, M. C. *J. Chem. Soc., Chem. Commun.* **1985**, 863.

(18) Herrmann, W. A.; Denk, M.; Behm, J.; Scherer, W.; Klingan, F.-R.; Bock, H.; Solouki, B.; Wagner, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *11*, 1485.

(19) Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361.

(20) Arduengo, A. J., III; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530.

(21) Arduengo, A. J., III; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. *Organometallics* **1993**, *12*, 3405.

(22) Arduengo, A. J., III; Dias, H. V. R.; Davidson, F.; Harlow, R. L. *J. Organomet. Chem.* **1993**, *462*, 13.

(23) Arduengo, A. J., III; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. *Inorg. Chem.* **1993**, *32*, 1541.

0002-7863/94/1516-4391$04.50/0

Table 1. Selected NMR Chemical Shifts (ppm δ) in **1**, **2**, and **3**[a]

nucleus	**1**[b]	**2a**[c]	**2b**[c]	**3a**[b]	**3b**[d]
$^{13}C_2$	219.7	193.2	197.5 ($^{1}J_{^{195}PtC}$ = 1218.0 Hz)	178.2	183.6 ($^{1}J_{^{107}AgC}$ = 188.0 Hz, $^{1}J_{^{109}AgC}$ = 208.6 Hz)
$^{13}C_{4(5)}$	121.3	118.1	118.6 ($^{3}J_{^{195}PtC}$ = 59.3 Hz)	124.2	124.2 ($^{3}J_{AgC}$ = 5.4 Hz)
$^{1}H_{4(5)}$	7.04 (6.91[c])	6.01 (6.41)[b]	6.10 (6.66)[b]	7.33	7.45[b] ($^{4}J_{AgH}$ = 1.5 Hz)
$^{15}N_{1(3)}$	−178.9	−193.2	−189.2	−180.8	−179.1 ($^{2}J_{^{107}AgN}$ = 6.3 Hz, $^{2}J_{^{109}AgN}$ = 7.2 Hz)
^{195}Pt or ^{109}Ag			−1196.1		642.4 ($^{4}J_{AgH}$ = 1.7 Hz)

[a] The numbering scheme for all compounds is as indicated for **1**. References are tetramethylsilane, $NH_4^{+15}NO_3^-$, $K_2{}^{195}PtCl_4$ set at 2887 ppm or 5 M $^{109}AgNO_3$. [b] In thf-d_8 solution. [c] In benzene-d_6 solution. [d] In pyridine-d_5 solution.

(Table 1). Upfield shifts for C_2 resonances in metal adducts relative to the free carbenes were also observed for magnesium,[22] zinc,[22] aluminum,[24] germanium,[23] copper,[21] silver,[21] and iodine[26] adducts. The imidazolium ion precursors of the stable imidazol-2-ylidenes bear a proton on C_2 and also show resonances for C_2 upfield of the carbenes.[19,20] However, the resonances for C_2 in **2a** and **2b** are not shifted as far upfield of the free carbene as the resonances for the closely analogous complexes of the transition group 11 metal cations, **3a** and **3b** (Table 1). The ^{15}N resonances for $N_{1(3)}$ in adducts **2a**,**b** are upfield from the resonance in the free carbene. The resonances for $C_{4(5)}$ are also upfield of the same nuclei in the free carbene and this shift is opposite to that observed in **3a** and **3b**. We have noted previously that the $H_{4(5)}$ resonances are particularly sensitive indicators of positive charge and delocalization in the imidazole ring.[19,27,28] There is a substantial upfield shift (~1 ppm in C_6D_6 and 0.5 ppm in thf-d_8) for the imidazole ring protons in **2a** and **2b** which is contrary to the shift observed for the copper(I) and silver(I) adducts. If the usual shift trends for the $H_{4(5)}$ resonances are followed, this upfield shift would reflect a localization and increase of electron density in the imidazole π-system. The increase in imidazole π-density suggests pπ–dπ back-donation from the nickel and platinum centers. Based on charge at the metal center, a greater degree of pπ–dπ back-donation could be expected for the zerovalent transition-group-10 metals compared to the group-11 monocations.

The nickel–carbene adduct **2a** was crystallized from hexanes to give crystals suitable for X-ray diffraction studies. The solid-state geometry of **2a** is depicted by the KANVAS[29] drawing in Figure 1. Selected bond distances and angles are given in Table 2 along with comparisons for free carbene **1**, silver adduct **3b**, and gold adduct **4**. The former carbene centers show ring-internal angles of 101.5° and 102.5°. These valence angles are not very different from the free carbene and are hence much smaller than the analogous angles in fully delocalized imidazolium ions.[30] This type of "near-carbene" angle has also been observed for a diethylmagnesium adduct.[22] The C–N bond distances (r_{avg} = 137.5 pm) at the former carbene center are longer than those in the free carbene which further indicates a retention of the carbene-like geometry in the imidazole ring. The C–Ni distances of 182.7 and 183.0 pm are the shortest we have observed for metal adducts of carbene **1** (*cf.* 210.2 pm, Ge[23]; 203.4 pm, Al[24]; 209.6 pm, Zn[22]; 227.9 pm, Mg[22]; 207.3 pm, Ag[21]). These nickel–carbon distances in **2a** are also slightly shorter than that in a 16e nickel(0) carbene complex (188.9 pm).[16] These short distances can be explained in terms of the dπ–pπ back-donation that is suggested by the ^1H NMR spectrum of **2a** but could also be rationalized in terms of sp hybridization at the linear 2-coordinate metal center. A strong hybridization effect on the geometry does not seem likely because the isostructural 14e bis(carbene)silver(I) complex does not show the same short metal–carbon distances.[21] The nickel atom of **2a** is nearly linear with a valence angle of 176.4°. The planes of the two imidazole rings are twisted 53° from coplanarity. This twist of the imidazole rings is somewhat larger than that observed in the silver complex **3b** (39.7°) and likely arises from steric interactions between the mesityl substituents on the nitrogens.

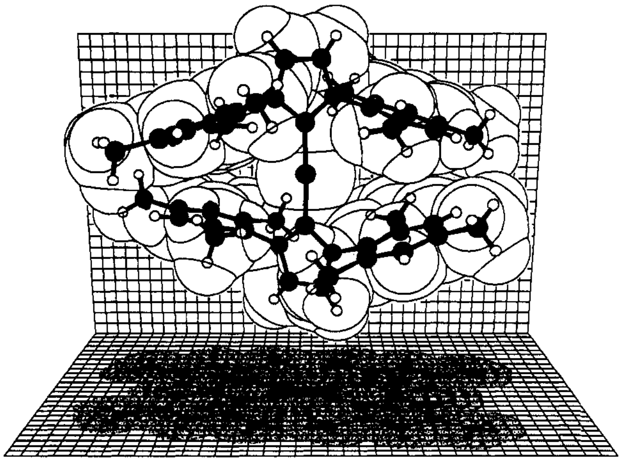

Figure 1. KANVAS[29] drawing of nickel complex **2a**.

Crystals of the platinum–carbene adduct **2b** suitable for X-ray diffraction studies were obtained by recrystallization from thf. The solid-state geometry of **2b** is depicted by the KANVAS[29] drawing in Figure 2. Selected bond distances and angles are given in Table 2. The former carbene centers show ring-internal angles of 103.1° and 102.1°. These valence angles again suggest a "near-carbene" geometry for the ligated carbene which is further supported by the long C–N bond distances (r_{avg} = 137.5 pm) to the former carbene center. The C–Pt distances of 195.9 and 194.2 pm are again short for metal–carbene distances and may reflect both pπ–dπ back-donation and the linear hybridization at the platinum center. Similar to the situation in the nickel complex, the planes of the two imidazole rings are twisted 51° from coplanarity.

The reactivity of both these 14e complexes with small ligands like ethylene, tetrafluoroethylene, and H_2 is high as might be expected. At this point no discrete addition compounds have been isolated but further studies are in progress.

Conclusion

The first 14e homoleptic bis(carbene)nickel(0) and bis(carbene)platinum(0) complexes have been isolated. The X-ray crystallographic structures of these two new complexes show a

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(24) Arduengo, A. J., III; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1992**, *114*, 9724.

(25) Britten, J. F.; Lock, C. J. L.; Wang, Z. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1992**, *C48*.

(26) Arduengo, A. J., III; Kline, M.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1991**, *113*, 9704.

(27) Arduengo, A. J., III; Burgess, E. M. *J. Am. Chem. Soc.* **1976**, *98*, 5021.

(28) Janulis, E. P., Jr.; Arduengo, A. J., III *J. Am. Chem. Soc.* **1983**, *105*, 3563.

(29) This drawing was made with the KANVAS computer graphics program. This program is based on the program SCHAKAL of E. Keller (Kristallographisches Institute der Universitat Freiburg, Germany), which was modified by A. J. Arduengo, III (E. I. du Pont de Nemours & Co., Wilmington, DE) to produce the back and shadowed planes. The planes bear a 50-pm grid and the lighting source is at infinity so that shadow size is meaningful.

(30) For structures of representative imidazolium ions see: (a) 1,3-dimethylimidazolium chloride (ref 20, supplementary material). (b) 1,3-di(1-adamantyl)imidazolium tetraphenylborate (ref 19, supplementary material). (c) 1,3-diphenylimidazolium perchlorate (Luger, P.; Ruban, G. *Z. Kristallogr.* **1975**, *142*, 177). (d) Langer, V.; Huml, K.; Reck, G. *Acta Crystallogr., Sect. B* **1982**, *38*, 298. (e) Abdul-Sada, A. K.; Greenway, A. M.; Hitchcock, P. B.; Mohammed, T. J.; Seddon, K. R.; Zora, J. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1753.

Table 2. Selected Bond Lengths (pm) and Angles (deg) in **2** and Related Structures[a]

property	**1**	**2a**	**2b**	**3b**[b]	**4**[c]	1,3-diphenyl-imidazolium ion[d]
$r(C_2–N_{1(3)})$	136.5(4), 137.1(4)	137.5(7), 137.4(7) 138.1(7), 136.9(7)	138.0(9), 137.4(10) 138.3(10), 136.4(10)	135.6(6), 136.0(6) 135.2(6), 135.5(6)	132.8(7), 135.3(9) 132.2(8), 133.1(8)	133.6
$r(C_4–C_5)$	133.1(5)	134.2(9), 132.4(9)	130.9(12), 132.7(12)	133.0(7), 132.9(7)	134.7(9), 131.0(10)	133.9
$r(N_{1(3)}–C_{5(4)})$	138.1(4), 137.8(4)	138.7(8), 137.8(8) 139.2(8), 139.3(8)	139.5(10), 140.5(11) 139.0(10), 138.4(10)	139.6(6), 139.8(6) 139.9(6), 139.0(6)	140.0(8), 138.1(8) 139.0(9), 139.8(8)	138.0
$r(N_{1(3)}$–mesityl)	144.1(4), 144.2(4)	144.6(8), 142.6(8) 142.7(8), 143.8(8)	143.5(10), 142.8(10) 142.8(10), 143.6(10)	143.7(6), 144.5(7) 143.4(6), 143.9(6)		143.2 (phenyl)
$r(C_2–M)$		182.7(6), 183.0(6)	195.9(8), 194.2(8)	206.7(4), 207.8(4)	201.2(6), 201.6(6)	
$\theta(N_1–C_2–N_3)$	101.4(2)	101.5(5), 102.5(5)	103.1(7), 102.1(7)	103.6(4), 104.8(4)	104.2(5), 104.0(5)	109.2
$\theta(C_{5(4)}–N_{1(3)}–C_2)$	112.8(3), 112.8(3)	112.4(5), 113.0(5) 111.5(5), 111.7(5)	110.5(7), 111.1(7) 111.2(7), 112.7(7)	111.1(4), 111.8(4) 110.6(4), 110.6(4)	111.9(5), 111.7(5) 112.4(6), 111.0(6)	108.0
$\theta(N_{1(3)}–C_{5(4)}–C_{4(5)})$	106.5(3), 106.5(3)	106.6(6), 106.5(6) 107.1(6), 107.2(6)	108.4(8), 106.9(8) 107.4(8), 106.6(8)	107.6(4), 105.9(5) 106.7(4), 107.3(4)	105.7(5), 106.4(6) 105.8(6), 106.8(6)	106.5
$\theta(C_2–N_{1(3)}$–mesityl)	121.8(2), 122.6(2)	123.0(5), 123.0(5) 124.2(5), 125.3(5)	123.4(6), 124.1(7) 123.8(7), 123.3(7)	125.4(4), 124.3(4) 126.3(4), 124.6(4)		126.6(phenyl)
$\theta(M–C_2–N_{1(3)})$		129.8(4), 128.7(5) 129.4(5), 128.0(5)	129.1(6), 127.7(6) 129.6(6), 128.2(6)	132.5(3), 123.7(3) 131.8(4), 123.4(3)	129.6(5), 126.1(4) 128.0(5), 128.1(4)	
$\theta(C_2–M–C_2)$		176.4(3)	177.4(3)	176.3(2)	175.8(2)	

[a] The numbering scheme for all compounds is as indicated for **1**. [b] See ref 21. [c] See ref 25. [d] See ref 30c.

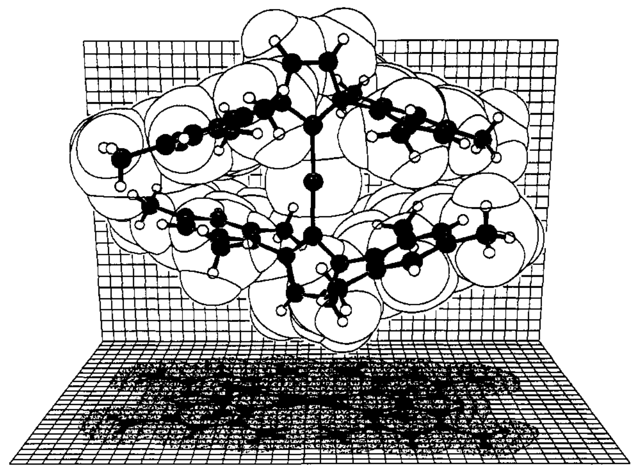

Figure 2. KANVAS[29] drawing of platinum complex **2b**.

near-linear geometry for the metal centers and imidazole ring structural parameters that are near the original free carbene geometry. Comparisons with isostructural 14e bis(carbene)silver suggests that the 2-coordinate linear geometry at the metal center and the resulting hybridization requirements are not sufficient to explain the short-metal carbon distances. The NMR spectra and short carbene–metal distances found for these compounds indicate that the imidazole moieties experience a degree of pπ–dπ back-donation that is higher than that observed in previously reported zinc, silver, and copper complexes. Further studies to explore the reactivity of the coordinatively unsaturated electron deficient metal complexes are underway.

Experimental Section

Reactions and manipulations were carried out under an atmosphere of dry nitrogen, either in a Vacuum Atmospheres drybox or using standard Schlenk techniques. Solvents were dried (using standard procedures),[31] distilled, and deoxygenated prior to use, unless otherwise indicated. Glassware was oven-dried at 160 °C overnight. The carbene **1** was prepared as previously described.[20] The bis(cyclooctadiene)metal complexes were purchased from Alfa Inorganics and used without further purification. The ^{1}H (300.75 MHz), ^{13}C (75.629 MHz), ^{19}F (282.987 MHz), ^{195}Pt (64.236 MHz), and ^{15}N (30.484 MHz) NMR spectra were recorded on a GE Omega 300WB spectrometer. NMR references are $(CH_3)_4Si$ (^{1}H, ^{13}C), $CFCl_3$ (^{19}F), $NH_4^+NO_3^-$ (^{15}N), and K_2PtCl_4 set at 2887 ppm (^{195}Pt). The ^{15}N DEPT experiments were run using the standard DEPT sequence[32] assuming a $J_{HN} \approx 7$ Hz with a θ pulse of 45°. The ^{195}Pt experiment was run using an inverse gated pulse sequence. Mass spectra were recorded on a VG-ZAB-E instrument using the FAB method and xenon gas. Melting points were obtained on a Thomas-Hoover capillary apparatus and were not corrected. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

2,2′-Bis(1,3-dimesitylimidazol-2-ylidene)nickel(0) (2a). Bis(1,5-cyclooctadiene)nickel(0) (0.107 g, 0.389 mmol) was dissolved in thf (30 mL). A solution of **1** (0.236 g, 0.778 mmol) in thf (20 mL) was slowly added at room temperature. A very dark colored solution was obtained. After the mixture was stirred for 20 min the volatiles were removed in vacuo. The solid was redissolved in 5 mL of hexane and cooled at –25 °C to give 0.215 g (83%) of **2a** as dark violet crystals, mp 174 °C. ^{1}H NMR (thf-d_8) δ 1.87 (s, 12 H, *o*-CH_3), 2.35 (s, 6 H, *p*-CH_3), 6.41 (s, 2 H, NCH), 6.75 (s, 4 H, *m*-H); ^{1}H NMR (C_6D_6) δ 2.08 (s, 12 H, *o*-CH_3), 2.30 (s, 6 H, *p*-CH_3), 6.01 (s, 2 H, NCH), 6.81 (s, 4 H, *m*-H); ^{13}C NMR (C_6D_6) δ 18.35 (s, *o*-CH_3), 21.31 (s, *p*-CH_3), 118.06 (s, NCH), 128.70 (s, Mes C-3,5), 135.40 (s, Mes C-2,6), 136.09 (s, Mes C-4), 138.64 (s, Mes C-1), 193.22 (s, NCN); ^{15}N NMR (C_6D_6) δ –193.92. FAB-MS 666.32 (M^+), 362.08 ($M^+ - 1$). Anal. Calcd for $C_{42}H_{48}N_4Ni$: C, 75.57; H, 7.25; N, 8.39. Found: C, 75.20; H, 7.16; N, 8.45.

2,2′-Bis(1,3-dimesitylimidazol-2-ylidene)platinum(0) (2b). Bis(1,5-cyclooctadiene)platinum(0) (0.205 g, 0.498 mmol) was partially dissolved in hexane (30 mL) and a solution of **1** (0.304 g, 1.0 mmol) in hexane (10 mL) was added slowly. A yellow colored solid was obtained. This mixture was stirred for 30 min and then the solid product was separated by filtration and dried in vacuo to give 0.280 g (70%) of **3** as yellow powder, mp 247 °C. ^{1}H NMR (thf-d_8) δ 1.84 (s, 12 H, *o*-CH_3), 2.36 (s, 6 H, *p*-CH_3), 6.66 (s, 2 H, NCH), 6.72 (s, 4 H, *m*-H); ^{1}H NMR (C_6D_6) δ 2.04 (s, 12 H, *o*-CH_3), 2.32 (s, 6 H, *p*-CH_3), 6.10 (s, 2 H, NCH), 6.81 (s, 4 H, *m*-H); ^{13}C NMR (C_6D_6) δ 18.78 (s, $^5J_{C^{195}Pt} = 37.84$ Hz, *o*-CH_3), 21.33 (s, *p*-CH_3), 118.60 (s, $^3J_{C^{195}Pt} = 59.31$ Hz, NCH), 128.55 (s, Mes C-3,5), 135.67 (s, Mes C-2,6), 136.19 (s, Mes C-4), 138.61 (s, Mes C-1), 197.45 (s, $^1J_{C^{195}Pt} = 1217.98$ Hz); ^{15}N NMR (C_6D_6) δ –189.21; ^{195}Pt NMR (C_6D_6) δ –1196.08. FAB-MS: 803.35 (M^+). Anal. Calcd for $C_{42}H_{48}N_4Pt$: C, 62.75; H, 6.01; N, 6.97. Found: C, 63.10; H, 5.87; N, 6.97.

X-ray Crystal Structure of Bis(1,3-dimesitylimidazol-2-ylidene)-nickel(0) (2a). Crystal data: $C_{42}H_{48}N_4Ni$, orthorhombic, space group *Pbca* (No. 61), $a = 1720.2(2)$ pm, $b = 1877.2(2)$ pm, $c = 2281.3(3)$ pm; $T = -125$ °C, $Z = 8$, fw = 667.58, $D_c = 1.204$ g cm^{-3}, μ(Mo) = 5.60 cm^{-1}. Crystal description: black block (0.43 × 0.34 × 0.50 mm) grown from a saturated hexane solution of **2**. A total of 8335 reflections were collected; $4.2° \leq 2\theta \leq 53.0°$; data octants – + –; ω-scan method, scan width = 1.20° ω, scan speed 3.90–11.70 deg min^{-1}, on a Syntex R3 diffractometer with graphite monochromator using Mo Kα radiation (λ = 71.073 pm). Typical half-height peak width = 0.31° ω; two standards collected 91 times, adjusted for a 8% decrease in intensity (196 omitted), 4.1% variation in azimuthal scan, no absorption correction. With 3620 unique reflections of intensity greater than 3.0σ, the structure was solved by automated Patterson analysis (PHASE) and refined by full-matrix least squares on *F*. Anomalous terms for Ni were included, weights $\propto$

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(31) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: New York, 1985.

(32) Doddrell, D. M.; Pegg, D. T.; Bendall, M. R. *J. Magn. Reson.* **1982**, *48*, 323.

$[\sigma^2(I) + 0.0009I^2]^{-1/2}$. The asymmetric unit consisted of one molecule in a general position. Hydrogen atoms idealized with r_{C-H} = 95 pm. There were 424 parameters (data/parameter ratio = 8.54) with all non-hydrogen atoms anisotropic and all hydrogens in fixed positions. The final R factors were R = 0.066, R_w = 0.071. The error of fit was 2.29, max Δ/σ = 0.03. The final difference Fourier showed the largest residual density to be 0.98 10^{-6} e pm^{-3} near the Ni atom. Further details of the crystal structure are available in the supplementary material.

X-ray Crystal Structure of Bis(1,3-dimesitylimidazol-2-ylidene)platinum(0) (2b). Crystal data: $C_{42}H_{48}N_4Pt$, orthorhombic, space group *Pbca* (No. 61), a = 1712.6(3) pm, b = 1918.9(9) pm, c = 2290.4(3) pm; T = –65 °C, Z = 8, FW = 803.96, D_c = 1.419 g cm^{-3}, μ(Mo) = 37.98 cm^{-1}. Crystal description: gold parallelopiped (0.35 × 0.30 × 0.35 mm) grown from a thf solution of **3** (evaporation). A total of 8592 reflections were collected, 1.8° $\leq 2\theta \leq$ 60.0°, data octants + + +, ω scan method, scan width = 1.20–2.20°, scan speed = 1.50–5.00 deg min^{-1}, on a Enraf-Nonius CAD4 diffractometer with graphite monochromator using Mo Kα radiation (λ = 71.073 pm). Typical half-height peak width = 0.14° ω, two standards collected 42 times, adjusted for a 2% decrease in intensity, 6.0% variation in azimuthal scan, no absorption correction. With 3536 unique reflections of intensity greater than $3\sigma(I)$, the structure was solved by automated Patterson analysis (PHASE) and refined by full-matrix least squares on F. Anomalous terms for Pt were included, weights $\propto$ $[\sigma^2(I)+0.0009I^2]^{-1/2}$. The asymmetric unit consisted of one molecule in a general position. Hydrogen atoms idealized with r_{C-H} = 95 pm. There were 424 parameters (data/parameter ratio = 8.54) with all non-hydrogen atoms anisotropic and all hydrogens in fixed positions. The final R factors were R = 0.036, R_w = 0.034. The error of fit was 1.23, max Δ/σ = 0.05. The final difference Fourier showed the largest residual density to be 0.76 10^{-6} e pm^{-3} near the Pt atom. Further details of the crystal structure are available in the supplementary material.

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Supplementary Material Available: Tables of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances, and bond angles in **2a** and **2b** and ORTEP drawings (18 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.