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## Communications

# Dicyclometalated Mononuclear Bis(carbene)platinum(IV) Complexes

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*Summary: The consecutive reaction of bis(arylisocyanide)platinum(II) complex* ***1*** *with a primary amine and then chloroform gave novel dicyclometalated mononuclear bis(carbene)platinum(IV) complex* ***2*** *having an octahedral structure, which may be formed via monocyclometalated bis(carbene)platinum(II) complex* ***3*** *and dicyclometalated bis(carbene)platinum(IV) complex* ***4****.*

Mononuclear platinum−carbene complexes are dominated by zero- and divalent platinum complexes.[1] The vast majority of them contain at least one heteroatom attached to the carbenoid carbon, that is, the so-called Fischer-type carbene complexes. One of preparative methods available for the Fischer-type carbene complexes is the nucleophilic attack of alcohols, amines, or thiols on isocyanide complexes.[2] In contrast to platinum(II)−carbene complexes, very few platinum(IV)−carbene complexes are known,[3] although many alkylplatinum(IV) derivatives[4] have appeared and their chemistry has been investigated in detail. Clark reported the first platinum(IV)−alkoxy−carbene complex,[3a] and Muir and Chatt showed the first molecular structure of a cationic platinum(IV)−carbene complex by X-ray crystallographic studies.[3e,f] On the other hand, metalation on aromatic groups in transition metal complexes is generally induced by reduction or oxidation. Although the intramolecular ortho-metalation on an aromatic group is well-known for transition metal

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[1] (a) For pre-1982 references, see: Hartley, F. R. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982, Vol. 6, p 502. (b) Barefield, E. K.; Carrier, A. M.; Sepelak, D. J.; Van Derveer, D. C. *Organometallics* **1982**, *1*, 103. (c) Lappert, M. F. *J. Organomet. Chem.* **1988**, *358*, 185, and references therein. (d) Gaber, B.; Krueger, C.; Marczinke, B.; Mynott, R.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1666. (e) Fehlhammer, W. P.; Bliss, T.; Fucho, J.; Holzmann, G. Z. *Naturforsch. B* **1992**, *47*, 79. (f) Michelin, R. A.; Bertani, R.; Mozzon, M.; Bombieri, G.; Benetollo, F.; Silva, M. F. C. G.; Pombeiro, A. J. L. *Organometallics* **1993**, *12*, 2372. (g) Ardvengo, A. J.; Gamper, S. F.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1994**, *116*, 4391.

[2] For example: (a) Badley, M. E. M.; Chatt. J.; Richards, R. L.; Sim, G. A. *Chem. Commun.* **1969**, 1322. (b) Larkin, G. A.; Scott, R. P.; Wallbridge, M. G. H. *J. Organomet. Chem.* **1972**, *37*, C21. (c) Miller, J. S.; Balch, A. L. *Inorg. Chem.* **1972**, *11*, 2069. (d) Rouschias, G.; Shaw, B. L. *J. Chem. Soc. A* **1971**, 2097. (e) Burke, A.; Balch, A. L.; Enemark, J. H. *J. Am. Chem. Soc.* **1970**, *92*, 2555. (f) Michelin, R. A.; Zanotto, L.; Braga, D.; Sabatino, P.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 85. (g) Fehlhammer, W. P.; Metzner, R.; Luger, P.; Dauter, Z. *Chem. Ber.* **1995**, *128*, 1061. (h) Kernbach, U.; Lügger, T.; Hahn, F. E.; Fehlhammer, W. P. *J. Organomet. Chem.* **1997**, *541*, 51.

[3] (a) Chisholm, M. H.; Clark, H. C. *J. Chem. Soc., Chem. Commun.* **1971**, 1484. (b) Cetinkaya, B.; Lappert, M. F.; Turner, K. *J. Chem. Soc., Chem. Commun.* **1972**, 851. (c) Balch, A. L. *J. Organomet. Chem.* **1972**, *37*, C19. (d) Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1973**, *12*, 362. (e) Muir, K. W.; Walker, R.; Chatt, J.; Richards, R. L.; Royston, G. H. D. *J. Organomet. Chem.* **1973**, *56*, C30. (f) Walker, R.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1975**, 272. (g) Hartshorn, A. J.; Lappert, M. F.; Turner, K. *J. Chem. Soc., Dalton Trans.* **1978**, 348. (h) Rendina, L. M.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 1030.

[4] (a) Thayer, J. S. *Organomet. Chem. Rev.* **1970**, *5*, 53. (b) Abel, E. W.; Orrell, K. G.; Stephenson, D. *J. Organomet. Chem.* **1989**, *373*, 401, and references therein. (c) Abel, E. W.; Orrell, E. W.; Scanlan, S. P.; Stephenson, D.; Keminitt, T.; Levason, W. *J. Chem. Soc., Dalton Trans.* **1991**, 591, and references therein. (d) Abel, E. W.; Beckett, M. A.; Bates, P. A.; Hurshouse, M. B. *Polyhedron* **1988**, *7*, 1855. (e) Chaudhury, S.; Jain, V. K.; Jakkal, V. S.; Venkatasubramanian, K. *J. Organomet. Chem.* **1992**, *424*, 115, and references therein. (f) Hill, G. S.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 1209, and references therein.

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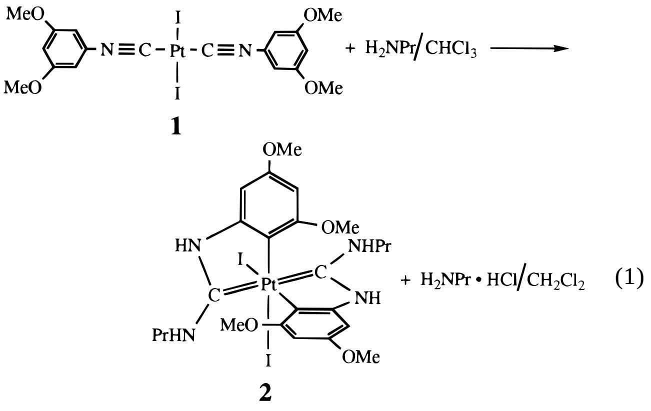
complexes with N-[5] and P-donor[6] ligands, there have been few examples of ortho-metalation occurring in carbene complexes to give metalated carbene complexes.[7,8]

We now report the formation of a novel dicyclometalated mononuclear bis(carbene)platinum(IV) complex from the reaction of *trans*-diiodobis(3,5-dimethoxyphenylisocyanide)platinum(II) (**1**) with a primary amine in chloroform (eq 1). This new complex is the first doubly metalated bis(carbene)metal complex.



(1)

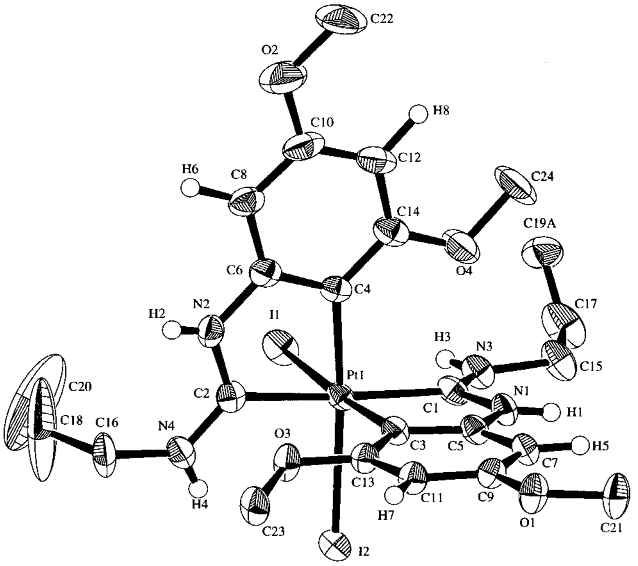


**Figure 1.** ORTEP drawing of complex **2**. Selected bond distances (Å) and angles (deg): Pt(1)−C(1), 2.050(7); Pt(1)−C(2), 2.057(7); Pt(1)−C(3), 2.039(6); Pt(1)−C(4), 2.037(6); Pt(1)−I(1), 2.7417(5); Pt(1)−I(2), 2.7514(6); I(1)−Pt(1)−I(2), 91.56(2); C(1)−Pt(1)−C(2), 174.8(3); C(3)−Pt(1)−C(4), 89.5(2).

To a solution of $PtI_2\{CNC_6H_3(OMe)_2\}$ (**1**) (0.228 g, 0.3 mmol) in chloroform (35 mL) was added propylamine (0.32 mL, 3.0 mmol). After stirring for 48 h at room temperature, precipitates formed were separated from the reaction mixture by filtration and recrystallized from chloroform−acetone to give complex **2** as pale yellow crystals (0.112 g, 42% yield) (eq 1). Both of the isocyanide ligands coordinated to Pt(II) underwent 1,2-addition of the amine to the N≡C bond with transformation to a carbenoid bond, and simultaneously intramolecular metalation occurred at phenyl rings on both the carbene ligands to give a unique dicyclometalated bis(carbene) complex of tetravalent platinum. Based on spectral and elemental analyses, novel platinum(IV)−carbene complex **2** was identified.[9] In the IR spectra of **2**, absorptions due to $\nu$(N−H) and $\nu$(N=C) are observed at 3304 and 3270, and 1541 $cm^{-1}$, respectively, and the absorption due to $\nu$(N≡C) at 2202 $cm^{-1}$ in **1** disappears. The $^1H$ NMR spectrum of **2** in acetone-$d_6$ shows a very simple pattern, suggesting that the complex may have a symmetrical structure. In the $^{13}C\{^1H\}$ NMR spectrum, the carbene carbon atom appears at $\delta$ 185 ppm with attendant $^{195}Pt$ satellite signals ($J_{Pt=C}$ = 733 Hz), the $^{13}C$ shielding of which is similar to that of cationic Pt(IV)−carbene complexes such as $[PtClMe_2(CHNMe_2)(^tBu_2bpy)]Cl$ ($\delta$ 185 in $CD_2Cl_2$)[4f] and is significantly higher than that observed for typical Fischer-type carbene complexes ($\delta$ 190−210 ppm).[8,10] The metalated carbon atom of the phenyl group is observed at $\delta$ 106 ppm and flanked by $^{195}Pt$ satellite signals ($J_{Pt-C}$ = 850 Hz). The $^{195}Pt$ NMR spectrum of **2** shows a single peak at −1935 ppm (versus an external $K_2PtCl_4$ reference), which is in a lower field than that of the divalent platinum complex **1** ($\delta$ −3808 ppm), suggesting the Pt atom in **2** to be in a higher oxidation state.

The structure of **2** has been finally confirmed by an X-ray crystallographic study.[11] Figure 1 depicts the ORTEP drawing, which reveals that **2** adopts an octahedral configuration of a central tetravalent platinum coordinated by two cis iodine atoms, two cis metalated carbons on the aromatic rings, and two trans (diamino)carbene ligands. The Pt=C bond distances (2.050(7) and 2.057(7) Å) are considerably longer than generally expected M=C double bonds but normal for a trans Pt=

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[9] **2**: 42% yield, mp 270 °C (decomp); IR (KBr) 3304, 3270 ($\nu_{N-H}$), 1575 ($\nu_{C=N}$) $cm^{-1}$; $^1H$ NMR (600 MHz, acetone-$d_6$) $\delta$ = 9.72 (satellite, $J_{Pt-H}$ = 53 Hz, 2H, H1, and H2), 8.19 (br s, 2H, H3, and H4), 6.21 (s, 2H, H5, and H6), 5.75 (s, 2H, H7, and H8), 3.62 (s, 6H, OMe × 2), 3.58 (m, 4H, $NCH_2CH_2CH_3$ × 2), 3.53 (s, 6H, OMe × 2), 1.82 (m, 4H, $NCH_2CH_2CH_3$ × 2), 1.11 (t, $J$ = 7.25 Hz, 6H, $NCH_2CH_2CH_3$ × 2); $^{13}C$ NMR (600 Hz, acetone-$d_6$): $\delta$ 185.2 (Pt=C, $J_{Pt-C}$ = 733 Hz), 160.7 (C−O), 159.6 (C−O), 153.0 (N−*C*, phenyl), 105.6 (Pt−C, $J_{Pt-C}$ = 850 Hz), 93.5 (C−H, phenyl), 93.1 (C−H, phenyl), 56.1 (OMe), 55.3 (OMe), 46.5 ($NCH_2CH_2CH_3$), 22.5 ($NCH_2CH_2CH_3$), 11.8 ($NCH_2CH_2CH_3$). Mass ($FAB^+$): 892 (M), 765 [M-127(I)]. Anal. Calcd for $C_{24}H_{34}N_4O_4I_2Pt$: C, 32.34; H, 3.84; N, 6.28; I, 28.47. Found: C, 32.26; H, 4.06; N, 6.27; I, 28.41.

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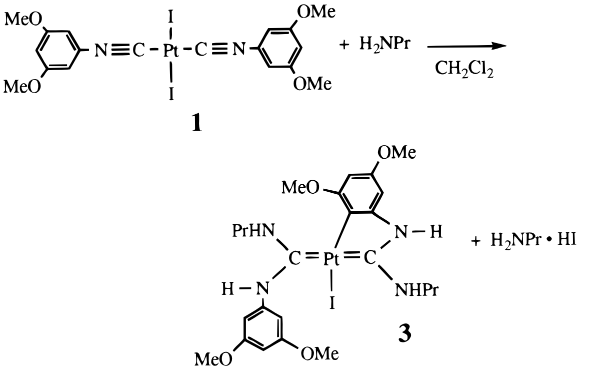
[11] Crystal data for **2**·$2CHCl_3$: $C_{26}H_{36}N_4O_4Cl_6I_2Pt_1$;_pale yellow crystals (0.45 × 0.18 × 0.13 mm), triclinic, space group $P\bar{1}$ (no. 2); $a$ = 12.494(2) Å, $b$ = 13.917(3) Å, $c$ = 12.251(3) Å; $\alpha$ = 97.69(2)°, $\beta$ = 99.25(2)°, $\gamma$ = 115.49(1)°, $V$ = 1847.9(7) $Å^3$, $Z$ = 2, $D_c$ = 2.031 g $cm^{-3}$, $F(000)$ = 1076.0, $\mu$ (Mo K$\alpha$) = 59.22 $cm^{-1}$. The data were collected on a Rigaku AFC5R diffractometer at −78 °C. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. The final cycle of full-matrix least-squares refinement was based on 6825 observed reflections ($I > 3.00\sigma(I)$) and converged with unweighted and weighted agreement factors of $R$ = 0.041, $R_w$ = 0.042.

C bond,[2a,8,10b,12] of which the longer Pt−C carbene bond is due to the delocalization of $\pi$-electrons over Pt═C═(N<)$_2$ bonds, as frequently observed for the Fischer-type carbene complexes. The shorter bond distances (C(1)−N(1), 1.336 Å; C(1)−N(3), 1.315 Å) than normal C−N bond ones (ca. 1.45 Å) in **2** also support the $\pi$-electron delocalization. On the other hand, two five-membered metallacycles share approximately the same planes with aromatic rings, and the dihedral angle is 88.5°. By a close inspection of the structure, it seems like a metallaspiro compound.

The stoichiometry of reaction 1 (eq 1) indicates that the formation of dicyclometalated bis(carbene)platinum **2** from complex **1** must require acceptors for two protons coming from phenyl rings to be metalated. During the course of our study on the mesogenic carbene compounds,[13] we found that an ortho-metalation reaction occurred to give a neutral ortho-metalated bis(diaminocarbene)platinum(II) complex when bis(arylisocyanide)platinum(II) was reacted with a primary amine.[8] Similarly, when complex **1** was reacted with propylamine in CH$_2$Cl$_2$, monometalated bis(carbene)platinum(II) **3** and H$_2$NPr·HI were formed in 90% yield (eq 2).



**1**

**3**

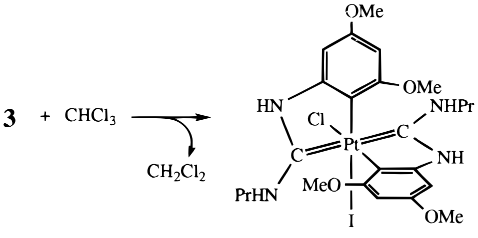
(2)

In this reaction a proton acceptor is an iodide anion coordinated on the platinum atom in **1**, and the resulting HI was captured by the amine to form the ammonium iodide. On treatment of isolated **3** again with H$_2$NPr·HI in CH$_2$Cl$_2$ no reaction was observed, but in CHCl$_3$ complex **2** was obtained in 38% yield (eq 3),

$$\mathbf{3} + \mathrm{H_2NPr\cdot HI} + \mathrm{CHCl_3} \longrightarrow \mathbf{2} + \mathrm{H_2NPr\cdot HCl} + \mathrm{CH_2Cl_2} \qquad (3)$$

suggesting that monometalated bis(carbene)platinum **3** may be one of intermediates leading to **2** and that chloroform participates in the reaction. When **1** was reacted with propylamine in chloroform, H$_2$NPr·HCl was obtained as white powders from the reaction residue after isolation of **2**. To clarify the participation of chloroform, we traced the reaction of **1** with propylamine in CDCl$_3$ by $^1$H NMR spectroscopy and found the formation of CDHCl$_2$ accompanied with formation of **2** and H$_2$NPr·HCl.

On the other hand, complex **3** reacted with CHCl$_3$ to give (chloro)(iodo)dicyclometalated bis(carbene)platinum **4**[14] (29% yield, eq 4), which was converted to **2** quantitatively on treatment with H$_2$NPr·HI in acetone (eq 5).



**4**

(4)

$$\mathbf{4} + \mathrm{H_2NPr\cdot HI} \xrightarrow[\text{acetone}]{} \mathbf{2} + \mathrm{H_2NPr\cdot HCl} \qquad (5)$$

Unfortunately the formation of complexes **2** and **4** in eqs 1, 3, and 4 was always accompanied by unidentified complexes. This may be one of the causes for the somewhat low yields of **2** and **4**. The reaction mechanism of eq 1 seems to be rather complicated, but the above experimental evidence suggests that the reaction proceeds stepwise through intermediates **3** and **4**, and the proton acceptors may be iodine and dichloromethyl species. The reaction of eq 4 did not occur in the dark, implying that a radical process may be involved in the step affording **2** from **3** with chloroform. A detailed study on the mechanism is now in progress.

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**Supporting Information Available:** Tables of crystal data and details of the structure solution, positional and displacement parameters, and bond distances and angles (22 pages). Ordering information is given on any current masthead page.

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[14] **4**: 29% yield, mp 282 °C (decomp); IR (KBr) 3245, 3199 ($\nu_{\mathrm{N-H}}$), 1581 ($\nu_{\mathrm{C=N}}$) cm$^{-1}$; $^1$H NMR (600 MHz, acetone-$d_6$) $\delta = 9.74$ (satellite, $J_{\mathrm{Pt-H}} = 53$ Hz, 2H, H1′, and H2′), 8.19 (br s, 2H, H3′, and H4′), 6.21 (s, 2H, H5′, and H6′), 5.75 (s, 2H, H7′, and H8′), 3.62 (s, 6H, OMe × 2), 3.58 (m, 4H, NC$H_2$CH$_2$CH$_3$ × 2), 3.54 (s, 6H, OMe × 2), 1.79 (m, 4H, NCH$_2$C$H_2$CH$_3$ × 2), 1.11 (t, $J = 7.25$ Hz, 6H, NCH$_2$CH$_2$C$H_3$ × 2). Mass (FAB$^+$): 801 (M), 765 [M − 35.5(Cl)], 674 [M − 127(I)]. Anal. Calcd for C$_{24}$H$_{34}$N$_4$O$_4$IClPt: C, 36.03; H, 4.28; N, 7.00; I + Cl, 20.29. Found: C, 36.31; H, 4.07; N, 6.94; I + Cl, 20.24.