Platinumbis(azido)dpff Compound: Preparation, Structure, and Reactivity to Isocyanides of \([\text{Pt}(\text{dpff})(\text{N}_3)_2]\) (dpff = 1,1'-Bis(diphenylphosphino)ferrocene)

Wan Sung Kim, Yong-Joo Kim,† and Soon W. Lee*

Department of Chemistry (BK21), Sungkyunkwan University, Natural Science Campus, Suwon 440-746, Korea
†Department of Chemistry, Kangnung National University, Kangnung 210-702, Korea
Received March 28, 2002

Key words: Isocyanides, dppe, Bis(azide), Platinum

The chemistry of the azido \((\text{N}_3^-)\) ligand coordinated to late transition metals has received continual interests because of interesting magnetic, structural, and reactivity properties, including the 1,3-dipolar cycloaddition to give heterocycles and the thermal or photochemical N–N bond cleavage to give metal–imido \((\text{M}=\text{N}^-)\) compounds. In particular, group 10 metal–azido compounds containing phosphine or amine ligands have been intensely studied owing to their novel reactivity such as the formation of metal nitrides or clusters.

Recently, we have reported the preparations, structures, and properties of several azido or bis(azido) compounds of Pd(II) and Pt(II) containing small tertiary phosphines. In particular, we found that cis-[M(N$_3$)$_2$(PR)$_3$] \((M = \text{Pd} \text{ or Pt}; \text{PR} = \text{PMe}_3 \text{ or PEt}_3)\) reacted with 2 equiv of isocyanide \((\text{RC}=\text{N})\) to give trans-[M(CN$_4$(R))$_2$(PR)$_3$]. Moreover, the reaction of 2,6-dimethylphenyl isocyanide with cis-[Pd(N$_3$)$_2$(PR)$_3$] \((\text{PR} = \text{PMe}_3, \text{PEt}_3, \text{or PMePh}_2)\) led to trans-[Pd(CN$_4$(R))(N=C= NC$_6$H$_4$-2,6-Me$_2$)(PR)$_3$] with the liberation of N$_2$, which contains a C-coordinated tetrazolato ligand and a carbodiimido ligand. These results suggest that the reactivity of [M(N$_3$)$_2$(PR)$_3$] \((M = \text{Pd} \text{ or Pt})\) depends at least on the type of the organic isocyanide. As an extension of our work, we have investigated the preparation and reactivity of the platinum–bis(azido) compound containing the dpff ligand \((1,1'\text{-bis(diphenylphosphino)}\text{ferrocene})\). We employed this sterically demanding, chelating phosphate ligand (dpff) due to its steric bulk that might lead to the formation of desirable bis(carbodiimido) compounds rather than either bis(tetrazolato) compounds or those containing one tetrazolato and one carbodiimido. The dpff ligand is one of the efficient stabilizing agents for transition metal-catalyzed cross-coupling reactions as well as a redox-active ligand for electrochemical studies. Herein we report the preparation, structural characterization, and reactions with isocyanides of Pt(dpff)(N$_3$)$_2$.

**Experimental Section**

Unless otherwise stated, all reactions have been performed with standard Schlenk line and cannula techniques under argon. Air-sensitive solids were manipulated in a glove box filled with argon. [PtCl$_2$(SM$_2$)$_2$], 1,1'-bis(diphenylphosphino)-ferrocene (dpff = Fe(η$_2$-C$_5$H$_4$PP)$_2$), and [PtCl$_2$(dpff)] were prepared by literature methods.

$^1$H-, $^{13}$C-$^1$H NMR spectra were recorded with a Varian Unity Inova 500 MHz spectrometer. IR spectra were recorded with a Nicolet 205 FTIR spectrophotometer. Elemental analyses were performed by the Korea Basic Science Institute.

**Preparation of [Pt(N$_3$)$_2$(dpff)] (1).** Compound 1 was prepared in one of the following two methods.

**Method 1.** A mixture of [PtCl$_2$(dpff)] \((0.10 \text{ g, 0.122 mmol})\) and NaN$_3$ \((0.016 \text{ g, 0.250 mmol})\) in 30 mL of CH$_2$Cl$_2$ was stirred at room temperature for 48 h. The orange-brown solution was filtered and then evaporated under vacuum. The residue was washed with diethyl ether \((20 \text{ mL} \times 2)\) and hexane \((20 \text{ mL} \times 2)\), and then dried under vacuum to give 0.055 g of 1 \((0.067 \text{ mmol}, 55\%)\).

**Method 2.** [PtCl$_2$(dpff)] \((0.10 \text{ g, 0.122 mmol})\) and Mg \((0.014 \text{ g, 0.35 mmol})\) in 30 mL of THF were cooled to 0 °C. After 10 min, neat (CH$_3$)$_3$SiN$_3$ \((0.2 \text{ mL, 1.47 mmol})\) was added slowly to this solution. The mixture was stirred at 50 °C in a water bath for 60 h. The orange-brown solution was filtered and then evaporated under vacuum. The residue was washed with diethyl ether \((20 \text{ mL} \times 2)\) and hexane \((20 \text{ mL} \times 2)\) and then dried under vacuum to give 0.034 g of 1 \((0.041 \text{ mmol, 34\%)}.\)

$^1$H-NMR \((\text{CDCl}_3)\): δ 7.41-7.79 \((20\text{H}), 4.21 \text{ (d, } 2\text{H}), 4.39 \text{ (d, } 4\text{H}), 1.39 \text{ (d, } 3\text{H})\). IR: 2052 cm$^{-1}$.'
(cyclohexyl), 26.0 (cyclohexyl). \( ^3 \text{P} \{^1 \text{H}\} \text{-NMR (CDCl}_3 \}: \delta 10.92 (\text{J}_{PP} = 2259 \text{ Hz}), \text{mp: 170-172 °C} \). \( ^{19} \text{F} \text{-NMR (CDCl}_3 \): \delta 0.0425 (0.0533, 0.0297) \text{ cm}^{-1} \). Anal. Calcd for \text{CaH}_6\text{N}_5\text{P}_2\text{FeCl}: C, 54.81; H, 4.75; N, 10.65. Found: C, 55.12; H, 5.18; N, 10.32.

Preparation of \([\text{Pt(CN} \cdot \text{Bu)}_{2}(\text{dppf})] \) (3). This compound was prepared similar to compound 2. Compound 1 (0.03 g, 0.036 mmol) was treated with excess tert-butyll isocyanide (0.1 mL, 0.884 mmol) to give 0.028 g of compound 3 (0.028 mmol, 78%). \(^1 \text{H} \text{-NMR (CDCl}_3 \): \delta 6.70-8.27 (m, 20H), 4.40 (d, 2H), 4.87 (d, 2H), 3.84 (d, 2H), 4.24 (d, 2H), 1.18 (s, 9H, \text{-Bu}), 59.4 (\text{C}_3), 77.9-72.7 (\text{C}_\text{H}_2), 59.4 (\text{C}_{Me_3}), 30.6 (\text{C}_{Me_3}), \quad \delta 10.80 (\text{J}_{PP} = 2295 \text{ Hz}), \text{mp: 169-171 °C} \). IR (KBr): 2236, 2002, 1524 cm\(^{-1} \). Anal. Calcd for \text{CaH}_6\text{N}_5\text{P}_2\text{FeCl}: C, 54.81; H, 4.74; N, 10.36.

X-ray structure determination. All X-ray data were collected with the use of a Siemens P4 diffractometer equipped with a Mo X-ray tube and a graphite-crystal monochromator. Details on crystal and intensity data are given in Table 1. The orientation matrix and unit-cell parameters were determined by least-squares analyses of the setting angles of 28 (for 1), 31 (for 2-\text{CHCl}_3), or 23 (for 3-\text{CHCl}_3) reflections in the range of 15.0° < 2θ < 25.0°. Three check-reflections were measured every 100 reflections throughout data collection and showed no noticeable variations in intensity. Intensity data were corrected for Lorentz and polarization effects. Decay corrections were also made. The intensity data were empirically corrected for absorption with y-scan data. All calculations were carried out with the use of SHELXTL programs.

All crystal structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms in the two co-crystallized chloroform molecules in 2-\text{CHCl}_3 were not located. All remaining hydrogen atoms were generated in ideal positions and refined in a riding model.

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center, CCDC No. 182496 for 1, 182495 for 2-\text{CHCl}_3, and 182494 for 3-\text{CHCl}_3. Copies of this information may be obtained free of charge from: The director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Table 1. X-ray data collection and structure refinement

<table>
<thead>
<tr>
<th>No. of reflections measured</th>
<th>6293</th>
<th>8538</th>
<th>8387</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of reflections unique</td>
<td>5972</td>
<td>8280</td>
<td>7946</td>
</tr>
<tr>
<td>No. of reflections with ( I &gt; 2 \sigma(I) )</td>
<td>5557</td>
<td>5717</td>
<td>7412</td>
</tr>
<tr>
<td>No. of parameters refined</td>
<td>398</td>
<td>624</td>
<td>533</td>
</tr>
</tbody>
</table>

\( 2\theta \) range (°) 3.5-50.0, 3.5-50.0, 3.5-50.0

scan type \( \omega \) \( \omega \) \( \omega \)

scan speed variable variable variable

GOF (goodness-of-fit on \( E^2 \)) 1.077 0.990 1.049

Max., min. in \( \Delta P (\varepsilon \text{ Å}^3) \) 2.200, 0.665, 1.225, -2.222, -0.662, -0.746

R 0.0425 0.0533 0.0297

\( wR_2 = \frac{\Sigma [w(Fo^2 - Fe^2)2]^2/\Sigma [w(Fo^2)]^2]^{1/2} \)

Notes

1 + \text{HCl (in Et}_2\text{O) \rightarrow [PtCl}_2\text{(dppf)]} (2)

Structure of compound 1 The molecular structure of 1 is shown in Figure 1, which displays two azido (N\(_3\)) and one

Results and Discussion

Preparation of \([\text{Pt(N}_3)_2(\text{dppf})] \) (1). The platinum-bis(azido)-dppf compound (1) can be prepared in two ways. In dichloromethane at room temperature, \([\text{PtCl}_2(\text{dppf})] \) reacts with an inorganic azide (\text{NaN}_3) to give compound 1 (eq 1). In a refluxing THF, the reaction of \([\text{PtCl}_2(\text{dppf})] \) with an organic azide (Me\(_3\text{SiN}_3\)) in the presence of Mg also leads to the formation of 1. However, the latter reaction requires more vigorous conditions (the reducing agent Mg, the refluxing THF, and a longer reaction time) and gave a lower yield.

Interestingly, the platinum-bis(azido) compound 1 is thermally stable in the solid state and in solution. For example, 1 melts at 247-249 °C without the liberation of N\(_2\). The IR spectrum of 1 shows a strong absorption band at 2052 cm\(^{-1} \) corresponding to the azido group. On treatment with excessive HCl in diethyl ether, compound 1 is converted back to the starting material (eq 2).
The two Cp rings are not perfectly parallel but twisted from each other with the dihedral angle of 4.6(3)°. The torsion angle of Pt1--Pt--P2 is 61.87(4)°, and the distance of P1···P2 is 34.1(3)°, indicating that the two Cp rings adopt a gauche (or staggered) conformation. For comparison, the ideal torsion angles for the gauche and eclipsed conformations are 36° and 72°, respectively. Both distances of Fe--Ct (Ct: a centroid of the Cp ring) are 1.641 Å, and the angle of the Ct1 plane, defined by N1, N4, P1, P2, and Pt1, is roughly planar with the average atomic displacement of 0.1551 Å. The bond angles (174.9(8)° and 174.0(9)°) of N in the azido ligands (173-180°). The distance of Pt···Fe is 4.222(1) Å, which clearly rules out direct interactions between the two metals. On the other hand, as stated above, cis-[M(N3)2(PR3)] reacted with isocyanide to give either trans-[M(CN4(R))(PR3)] or trans-[Pd(CN4(R))(N=C=N-R)(PR3)] with the change in the configuration from cis to trans. In addition, cis-[M(N3)(dppe)] (dppe = Ph2PCH2-CH2PPh2), which contains the chelating bidentate ligand (dppe) similar to compound 1, reacted with 2,6-dimethylphenyl isocyanide to a bis(carbodiimido) compound, cis-[M(N=C=N-C6H3-2,6-Me2)2(dppe)]. Considering the steric bulk of the dppe and dppf ligands, it might be deduced that the steric factor does not play a dominant role in deriving the reaction to form bis(carbodiimido) compounds in our system.

Reactions of 1 with isocyanides. When [PtCl2(dppe)] is directly treated with isocyanide, no reaction occurs. On the other hand, the platinum–bis(dppe) compound 1 reacts with tert-butyl and cyclohexyl isocyanides to give sterically congested compounds (2 and 3), which contain two C-bonded tetrazolate rings and one dppe ligand (eq 3). This reaction is somewhat unusual because the reaction might have given either a mono(carbodiimido) or even a bis(carbodiimido) compound to relieve the steric hindrance in the product. Analogous cycloaddition reactions of platinum–bis(dppe) compounds with isocyanides were previously studied by Beck and co-workers. According to their works, the reactions of compounds of Pd(II), Cu(I), Ag(I), and Au(I) having terminal or bridging azido ligands with Cs2; or CF3CN gave the compounds containing the N-coordinated tetrazolate ring. On the other hand, cis-[M(N3)2(PR3)] reacted with isocyanide to give either trans-[M(N3)2(PR3)] or cis-[Pd(N3)(R)(N=C=N-R)(PR3)] with the change in the configuration from cis to trans. In addition, cis-[M(N3)(dppe)] (dppe = Ph2PCH2-CH2PPh2), which contains the chelating bidentate ligand (dppe) similar to compound 1, reacted with 2,6-dimethylphenyl isocyanide to a bis(carbodiimido) compound, cis-[M(N=C=N-C6H3-2,6-Me2)2(dppe)]. Considering the steric bulk of the dppe and dppf ligands, it might be deduced that the steric factor does not play a dominant role in deriving the reaction to form bis(carbodiimido) compounds in our system.

Structures of 2 and 3. The molecular structures of 2 and 3 are shown in Figures 2 and 3, respectively. Each compound has two C-bonded tetrazolate rings and one bidentate dpff ligand. The coordination sphere of each Pt can be described as distorted square-planar. The equatorial plane, defined by two tetrazolate-ring carbon atoms, two phosphorus atoms, and the Pt metal, is essentially planar with the average atomic displacement of 0.073 Å for 2 or 0.004 Å for 3.

Two heterocyclic five-membered tetrazolate rings in each compound are essentially planar with the average atomic displacement of 0.001-0.008 Å. These two rings are mutually perpendicular with the dihedral angles of 76.5(3)°-85.5(2)°. The substituents [cyclohexyl (2) or tert-butyl (3)] on the two tetrazolate rings seem to orient as far as possible. The relative orientation of the substituents probably result from the steric congestion due to the steically demanding tetrazolato ligands formed in the reaction. The two Cp rings in compounds 2 and 3, as in compound 1, are twisted from each other with the dihedral angle of 5.2(4)° (2) or 4.4(4)° (3). As expected, the conformation of the two Cp rings in the dpff ligand severely deviates from the gauche conformation with the P1–C1–C6–P2 torsion angle of 51.4(6)° or 52.7(3)°. The Fe–Ct distances are 1.657 Å and 1.661 Å (2) or 1.648 Å and 1.649 Å (3). The Ct1–Fe–Ct2 (Ct1: C1–C5; Ct2: C6–C10) angle is 169.13° (2) or 179.51° (3). The P–Fe–P bite angle is 64.53(6)° (2) or 65.10 (3)° (3), and the P1–P2 distance is 3.617(3) Å (2) or 3.637(1) Å (3). The long Pt–Fe (4.344(1) Å or 2 Å) 4.331(1) Å (3) distance indicates no direct interactions between the two metals.

In summary, we have prepared a platinum–bis(azido)dpff compound, [Pt(N3)2(dppf)], which was treated with isocy-anide (RNC: R = t-Bu or C6H11) to give a bis(terazolato) compound, [Pt(CN2–R2)(dpff)]. All compounds have been structurally characterized by X-ray diffraction.

Acknowledgment. This work is based on research sponsored by the Korea Research Foundation Grant (KRF-2001-015-DP0262).

References