

Sulfur-Assisted Intermolecular Triphenylphosphine Dissociation of Thiocarbamoyl Ligand in Platinum(II). X-ray Structure of Complex $[\text{Pt}(\text{PPh}_3)_2(\eta^1\text{-SCNMe}_2)(\text{Cl})]$

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Treatment of $\text{Pt}(\text{PPh}_3)_4$ with *N,N*-dimethylthiocarbamoyl chloride, $\text{Me}_2\text{NC}(=\text{S})\text{Cl}$, in dichloromethane at $-20\text{ }^\circ\text{C}$ processes the oxidative addition reaction to produce platinum complex $[\text{Pt}(\text{PPh}_3)_2(\eta^1\text{-SCNMe}_2)(\text{Cl})]$, **2** with releasing two triphenylphosphine molecules. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of complex **2** shows the dissociation of the triphenylphosphine ligand to form diplatinum complex $[\text{Pt}(\text{PPh}_3)\text{Cl}]_2(\mu, \eta^2\text{-SCNMe}_2)_2$, **3** in which the two SCNMe_2 ligands coordinated through carbon to one metal center and bridging the other metal through sulfur. Complex **2** is characterized by X-ray diffraction analysis.

Keywords: *N,N*-dimethylthiocarbamoyl; Intermolecular; Dissociation; Platinum; X-ray diffraction.

INTRODUCTION

Metal complexes with the *N,N*-dimethylthiocarbamoyl, SCNMe_2 , ligands are known in Nb, Ta (VB)¹, Mo, W (VIB)², Ru, Rh, and Ir (VIII B)³ but platinum complex containing SCNMe_2 ligand has not been reported till now. We have recently been investigating the chemistry of *N,N*-dimethylthiocarbamoyl palladium complexes for the understanding of how the ligand interacts with the metal center and have shown⁴ the dissociation of either the chloride or the triphenylphosphine ligand of complex $[\text{Pd}(\text{PPh}_3)_2(\eta^1\text{-SCNMe}_2)(\text{Cl})]$ to form complex $[\text{Pd}(\text{PPh}_3)_2(\eta^2\text{-SCNMe}_2)][\text{Cl}]$ or the dipal-

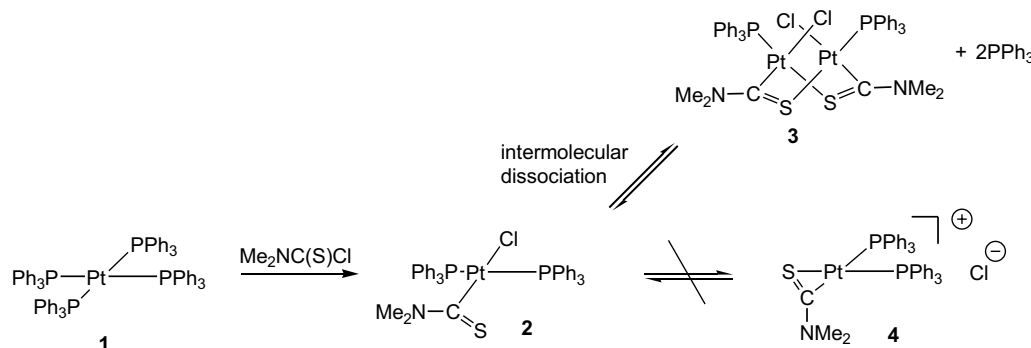
ladium complex $[\text{Pd}(\text{PPh}_3)\text{Cl}]_2(\mu, \eta^2\text{-SCNMe}_2)_2$.

In the context of our previous studies, we extended the research to the preparation and structure of platinum complex with the SCNMe_2 containing ligand.

RESULTS AND DISCUSSION

Treatment of $\text{Pt}(\text{PPh}_3)_4$, **1** with $\text{Me}_2\text{NC}(=\text{S})\text{Cl}$ in dichloromethane at $-20\text{ }^\circ\text{C}$ for 30 min yields the pale-yellow complex $[\text{Pt}(\text{PPh}_3)_2(\eta^1\text{-SCNMe}_2)(\text{Cl})]$, **2** (Scheme I). The air-stable pale-yellow compound **2** is soluble in di-

Scheme I



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methyl sulfoxide, dichloromethane, and insoluble in acetonitrile, methanol, *n*-hexane, and diethyl ether. The analytical data of **2** are in good agreement with the formulation. In the FAB mass spectra, one base peak with the typical Pt isotope distribution is in agreement with the $[M^+]$ molecular mass of **2**. The IR spectrum of **2** shows two stretching bands at 1480 and 1434 cm^{-1} for the C=N group. In the ^1H NMR spectrum, two methyl groups are observed at δ 2.27 and 2.67, and the corresponding resonances in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum appear at δ 39.1 and 46.3. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** shows one signal at δ 15.9 with satellites ($J_{\text{Pt-P}} = 1667.3$ Hz) due to ^{195}Pt nuclei. From the above description, it is clear that the thiocarbamoyl chloride oxidative addition to the starting complex **1** with releasing two PPh_3 molecules was observed. In complex **2**, two PPh_3 molecules and the thiocarbamoyl and chloride are in the *trans* position, respectively, and the thiocarbamoyl coordinated to the platinum metal through the carbon atom.

To confirm the geometry and the coordination mode of the thiocarbamoyl platinum compound, complex **2** is determined by X-ray diffraction analysis. A single crystal of **2** was grown by slow *n*-hexane diffusion into a dichloromethane solution at 4 °C. An ORTEP plot of **2** is shown in Fig. 1. Tables 1 and 2 contain crystal data and refinement details and selected bond distances and angles of **2**. In complex

Table 1. Crystal Data and Refinement Details for Complex **2**

| 2 | |
|--|---|
| chemical formula | $\text{C}_{39}\text{H}_{36}\text{ClNP}_2\text{SPd}$ |
| formula weight | 843.23 |
| crystal system | monoclinic |
| space group | $\text{P2}_1/\text{n}$ |
| <i>a</i> , Å | 12.7618(1) |
| <i>b</i> , Å | 18.6750(2) |
| <i>c</i> , Å | 14.9644(2) |
| α , deg | 90 |
| β , deg | 105.0026(5) |
| γ , deg | 90 |
| <i>V</i> , Å ³ | 3444.85(6) |
| <i>Z</i> | 4 |
| ρ_{calcd} , g cm^{-3} | 1.626 |
| μ , (Mo $\text{K}\alpha$), mm^{-1} | 4.333 |
| λ , Å | 0.71073 |
| <i>T</i> , K | 150(1) |
| θ range, deg | 1.78–27.50 |
| Independent rflns | 7907 |
| no. of variables | 407 |
| R^a | 0.030 |
| R_w^b | 0.064 |
| S^c | 1.013 |

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $R_w = [\sum w(|F_o| - |F_c|)^2]^{1/2}$; $w = 1/s^2(|F_o|)$.

^c Quality-of-fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{observed}} - N_{\text{parameters}})]^{1/2}$.

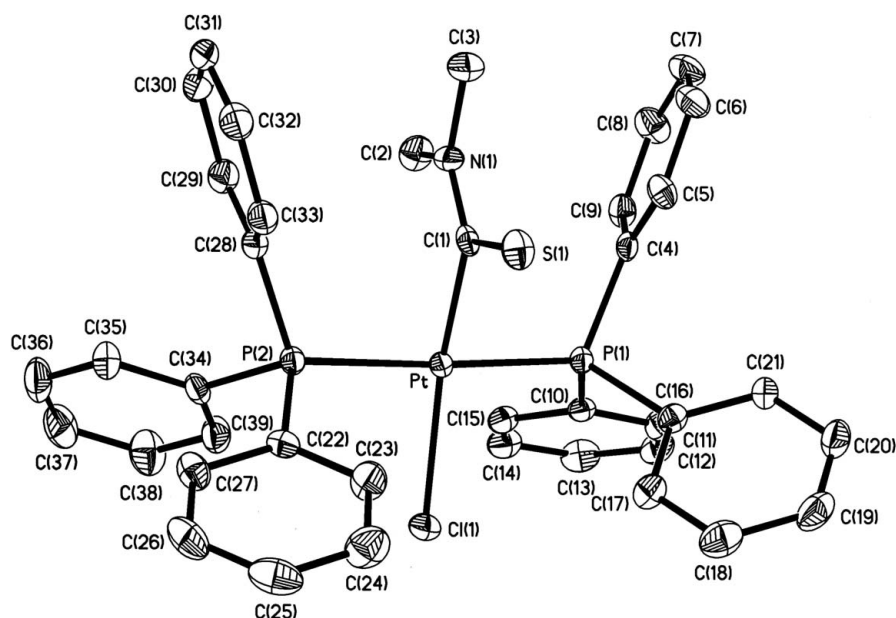


Fig. 1. An ORTEP drawing with 50% thermal ellipsoids and atom-numbering scheme for the complex $[\text{Pt}(\text{PPh}_3)_2(\eta^1\text{-SCNMe}_2)(\text{Cl})]$, **2**.

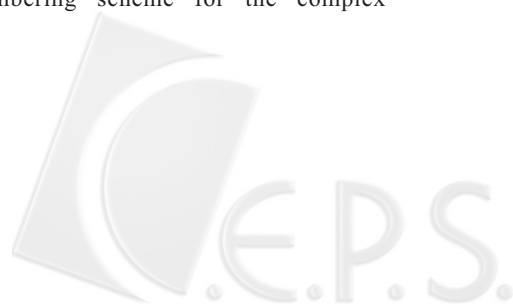


Table 2. Selected Interatomic Distances (Å) and Angles (deg) for **2**

| bond lengths | | bond angles | |
|--------------|-----------|----------------|------------|
| Pt-P(1) | 2.3115(8) | C(1)-Pt-Cl(1) | 166.93(10) |
| Pt-P(2) | 2.3226(8) | P(1)-Pt-P(2) | 176.44(3) |
| Pt-Cl(1) | 2.4142(8) | Cl(1)-Pt-P(1) | 90.17(3) |
| Pt-C(1) | 1.995(3) | Cl(1)-Pt-P(2) | 92.22(3) |
| C(1)-S(1) | 1.686(3) | C(1)-Pt-P(1) | 90.20(9) |
| C(1)-N(1) | 1.329(4) | C(1)-Pt-P(2) | 88.08(9) |
| C(2)-N(1) | 1.457(4) | S(1)-C(1)-Pt | 113.11(17) |
| C(3)-N(1) | 1.449(4) | S(1)-C(1)-N(1) | 123.0(2) |

2, the SCNMe₂ ligand is σ -bound to the Pt atom through the carbon atom of the thiocarbonyl group. The Pt atom and its neighboring atoms, P(1), P(2), Cl(1) and C(1) lie in a distorted squared plane. A least-squares plane calculation reveals the planarity of the P(2)P(1)C(1)Cl(1) core (largest deviation 0.031(1) Å). Two PPh₃ ligands are in *trans* position: P(1)-Pt-P(2), 176.44(3)°, while the SCNMe₂ ligand and chloride are *trans* to each other: C(1)-Pt-Cl(1), 166.93(10)°. The S-Pt bond distance of 3.036 Å in **2** indicates no bonding interaction between the sulfur atom and platinum metal atom. Within the SCNMe₂ ligand, the C-S (1.686(3) Å) and SC-N (1.329(4) Å) bond distances are typical for C-N and C-S bonds having partial double bond character and are certainly much shorter than the normal C-N (1.47 Å) and C-S (1.82 Å) single bonds.⁵ The Me-N bond distances (1.457(4) and

Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients for Important Atoms of **2**

| Atom | x | y | z | B _{eq} |
|-------|---------|---------|---------|-----------------|
| Pt | 4344(1) | 3061(1) | 2823(1) | 14(1) |
| Cl(1) | 4317(1) | 2264(1) | 4087(1) | 22(1) |
| S(1) | 5009(1) | 4622(1) | 2606(1) | 23(1) |
| P(1) | 6053(1) | 2651(1) | 2820(1) | 15(1) |
| P(2) | 2596(1) | 3463(1) | 2728(1) | 15(1) |
| N(1) | 4244(2) | 3844(2) | 1092(2) | 19(1) |
| C(1) | 4508(2) | 3877(2) | 2010(2) | 17(1) |
| C(2) | 3905(3) | 3183(2) | 581(3) | 25(1) |
| C(3) | 4336(3) | 4457(2) | 523(3) | 32(1) |
| C(4) | 6523(2) | 2873(2) | 1796(2) | 17(1) |
| C(10) | 6219(3) | 1677(2) | 2865(2) | 17(1) |
| C(16) | 7094(3) | 3028(2) | 3778(2) | 18(1) |
| C(22) | 2550(3) | 3929(2) | 3790(2) | 18(1) |
| C(28) | 2065(2) | 4111(2) | 1810(2) | 18(1) |
| C(34) | 1516(3) | 2791(2) | 2503(2) | 19(1) |

E. S. Ds. refer to the last digit printed.

1.449(4) Å) are normal for a single bond. The Pt-C(1) (1.995(3) Å) and Pt-Cl(1) (2.4142(8) Å) bond distances are consistent with the values reported for Pt^{II} complex.⁶

During the detection of the ³¹P{¹H} NMR spectra of **2** at 298 K in CDCl₃ for 2 h, two sets of triphenylphosphine resonances were observed. The two sets of resonances are assigned to the **2** (δ 15.9, $J_{\text{Pt-P}} = 1667.3$ Hz) and the dissociation

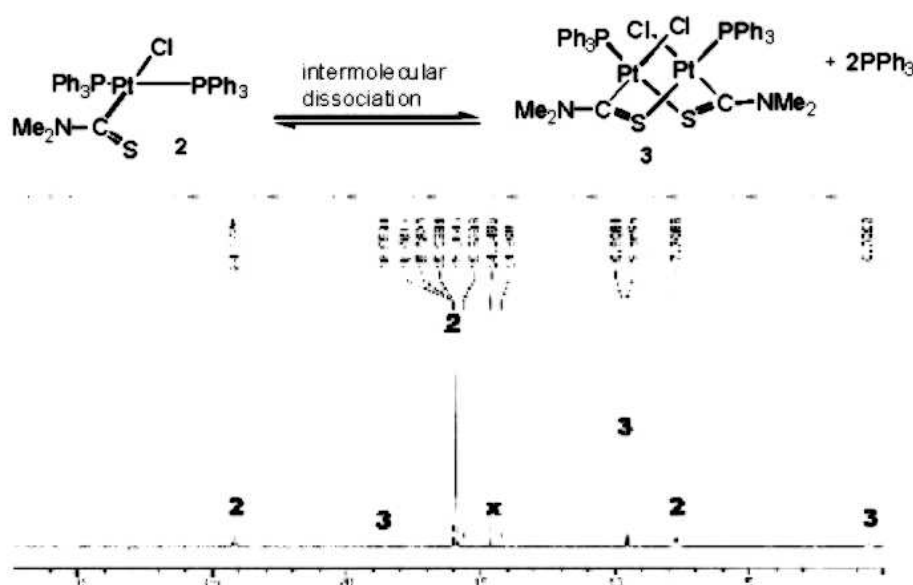


Fig. 2. ³¹P{¹H} NMR spectra of [Pt(PPh₃)₂(η¹-SCNMe₂)(Cl)], **2** and [Pt(PPh₃)Cl]₂(μ, η²-SCNMe₂)₂, **3** in CDCl₃ at 298 K for 2 h (X is the impurity).

of the triphenylphosphine ligand of **2** to form the diplatinum complex $[\text{Pt}(\text{PPh}_3)\text{Cl}]_2(\mu, \eta^2\text{-SCNMe}_2)_2$, **3** (δ 9.5, $J_{\text{Pt-P}} = 1826.0$ Hz) (Fig. 2). Continuously refluxing complex **2** in dichloromethane for 8 h produces complexes **2** and **3** with a ratio of 2:1 according to the integration of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. Complex **3** can be obtained as the final product by refluxing complex **2** in CHCl_3 for 8 h. This phenomena is similar to that of complex $[\text{Pd}(\text{PPh}_3)_2(\eta^1\text{-SCNMe}_2)(\text{Cl})]$.⁴ The analytical data of **3** are in good agreement with the formulation. In the FAB mass spectra, one base peak with the typical Pt dimer isotope distribution is in agreement with the $[\text{M}^+ - \text{Cl}]$ molecular mass of **3**. In the ^1H NMR spectrum of **3**, the four methyl protons of the SCNMe_2 ligand exhibit two resonances at δ 2.48 and δ 3.27. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3**, two singlet resonances appear at δ 39.8 and δ 48.7 and one singlet resonance appears at δ 213.6 for the carbon atom of the four methyl and thiocarbamoyl group, respectively. It is clear that complex **3** is a dimer with a two bridged thiocarbamoyl unit which coordinates through carbon to a one metal center and bridging the other metal through sulfur.

Complex $[\text{Pd}(\text{PPh}_3)_2(\eta^1\text{-CH}_2\text{SCH}_3)\text{Cl}]$ ⁷ and $[\text{Pd}(\text{PPh}_3)_2(\eta^1\text{-SCNMe}_2)(\text{Cl})]$ are the two reported examples that show the dissociation of triphenylphosphine or chloride ligand to form complexes $[\text{Pd}(\text{PPh}_3)(\eta^2\text{-CH}_2\text{SCH}_3)\text{Cl}]$ and $[\text{Pd}(\text{PPh}_3)_2(\eta^2\text{-CH}_2\text{SCH}_3)][\text{Cl}]$ and complexes $[\text{Pd}(\text{PPh}_3)(\eta^2\text{-SCNMe}_2)\text{Cl}]$ and $[\text{Pd}(\text{PPh}_3)_2(\eta^2\text{-SCNMe}_2)][\text{Cl}]$, respectively. During the detection period, no doublet resonances were observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. It is clear that no η^2 -thiocarbamoyl complex $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-SCNMe}_2)][\text{Cl}]$, **4** was observed. From the above description, the sulfur atom of the SCNMe_2 ligand assists intermolecular triphenylphosphine dissociation of **2** to form **3**. Reactions of **2** with nucleophiles are currently under investigation.

To compare with our previous study of the Pd analogues,^{4,8} significant differences between Pd and Pt complexes in solubility and stability are observed. Notably, the intermolecular triphenylphosphine dissociation reaction is spontaneous for Pd but requires heating for Pt complex. The thiocarbamoyl Pd complexes are more soluble than Pt complexes. Palladium(II) complexes are somewhat less stable in both the thermodynamic and the kinetic sense than their Pt(II) analogues but otherwise the coordination types are usually similar.

We employ thiocarbamoyl chloride ligand processing oxidative addition reaction in platinum complex to investigate the thiocarbamoyl bonding mode. Squared planar geometry, *trans*-position of the two phosphine ligands and the

thiocarbamoyl and chloride ligands, and η^1 -thiocarbamoyl bonding mode are confirmed by the first platinum crystal structure **2**. The sulfur atom of the SCNMe_2 ligand assists intermolecular triphenylphosphine dissociation of **2** to form **3**.

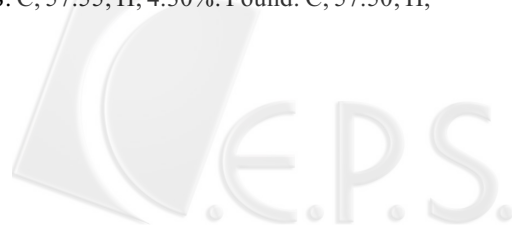
EXPERIMENTAL SECTION

General Procedures

All manipulations were performed under nitrogen using vacuum-line and standard Schlenk techniques. NMR spectra were recorded on an AM-500 WB FT-NMR spectrometer and are reported in units of parts per million with residual protons in the solvent as an internal standard (CDCl_3 , δ 7.24). IR spectra were measured on a Nicolet Avator-320 instrument and referenced to polystyrene standard, using cells equipped with calcium fluoride windows. MS spectra were recorded on a JEOL SX-102A spectrometer. Solvents were dried and deoxygenated by refluxing over the appropriate reagents before use. *n*-Hexane and diethyl ether were distilled from sodium-benzophenone. Acetonitrile and dichloromethane were distilled from calcium hydride, and methanol was distilled from magnesium. All other solvents and reagents were of reagent grade and used as received. Elemental analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instruments located at National Taiwan University. PtCl_2 was purchased from Strem Chemical, and $\text{Me}_2\text{NCS}_2\text{Cl}$ was purchased from Merck.

Preparation of $[\text{Pt}(\text{PPh}_3)_2(\eta^1\text{-SCNMe}_2)(\text{Cl})]$, **2**

CH_2Cl_2 (20 mL) was added to a flask (100 mL) containing $\text{Pt}(\text{PPh}_3)_4$ (1.243 g, 1.0 mmol) and $\text{Me}_2\text{NC}(\text{S})\text{Cl}$ (0.142 g, 1.15 mmol) at -20 °C. The stirred mixture was allowed to warm to room temperature for about 30 min. The solvent was concentrated to 10 mL, and 20 mL of diethyl ether was added to the solution. The pale-yellow solids were formed which were isolated by filtration (G4), washed with *n*-hexane (2×10 mL) and subsequently dried under vacuum yielding 0.83 g (98%) of $[\text{Pt}(\text{PPh}_3)_2(\eta^1\text{-SCNMe}_2)(\text{Cl})]$, **2**. Spectroscopy for **2**: IR (KBr, ν_{CN}): 1480 (m), 1434 (m) cm^{-1} . $^{31}\text{P}\{^1\text{H}\}$ NMR: δ 15.9 (s, PPh_3 , $J_{\text{Pt-P}} = 1667.3$ Hz). ^1H NMR: δ 2.27, 2.67 (s, 6H, NCH_3), 7.25-7.80 (m, 30H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 39.1, 46.3 (s, NCH_3), 127.8-134.9 (m, C of Ph), 209.0 (t, CS, $^2J_{\text{P-C}} = 5.7$ Hz). MS (FAB, NBA, m/z): 843 $[\text{M}^+]$, 807 $[\text{M}^+ - \text{Cl}]$, 719 $[\text{M}^+ - \text{Cl} - \text{SCNMe}_2]$, 545 $[\text{M}^+ - \text{Cl} - \text{PPh}_3]$. Anal. Calcd. for $\text{C}_{39}\text{H}_{36}\text{ClNP}_2\text{PtS}$: C, 57.55; H, 4.30%. Found: C, 57.50; H,



4.42.

Preparation of [Pt(PPh₃)Cl]₂(μ,η²-SCNMe₂)₂, **3**

CHCl₃ (20 mL) was added to a flask (100 mL) containing **2** (0.843 g, 1.0 mmol). The solution was refluxed for 8 h then diethyl ether (30 mL) was added to the solution and a yellow precipitate was formed. The precipitate was collected by filtration (G4), washed with *n*-hexane (2 × 10 mL) and then dried in vacuo yielding 0.45 g (78%) of **3**. Spectroscopy for **3**: ³¹P{¹H} NMR: δ 9.51 (t, PPh₃, *J*_{Pt-P} = 1826.0 Hz). ¹H NMR: δ 2.48, 3.27 (s, 6H, NCH₃), 7.28-7.80 (m, 30H, Ph). ¹³C{¹H} NMR: δ 39.8, 48.7 (s, NCH₃), 127.8-135.3 (m, C of Ph), 213.6 (s, CS). MS (FAB, NBA, *m/z*): 1125 [M⁺ - Cl]. Anal. Calcd for C₄₂H₄₂Cl₂N₂P₂S₂Pt₂: C, 43.41; H, 3.64; N, 2.41%. Found: C, 43.28; H, 3.58; N, 2.20.

Single-Crystal X-ray Diffraction Analysis of **2**

A single crystal of **2** suitable from X-ray diffraction analysis was grown by recrystallization from 20:1 *n*-hexane/CH₂Cl₂. The diffraction data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. The raw intensity data were converted to structure factor amplitudes and their esd's after correction for scan speed, background, Lorentz, and polarization effects. An empirical absorption correction, based on the azimuthal scan data, was applied to the data. Crystallographic computations were carried out on a Microvax III computer using the NRCC-SDP-VAX structure determination package.⁹

A suitable single crystal of **2** was mounted on the top of a glass fiber with glue. Initial lattice parameters were determined from 24 accurately centered reflections with θ values in the range from 1.78 to 27.50°. Cell constants and other pertinent data were collected and are recorded in Table 1. Reflection data were collected using the θ/2θ scan method. Three check reflections were measured every 30 min throughout the data collection and showed no apparent decay. The merging of equivalent and duplicate reflections gave a total of 27983 unique measured data in which 9389 reflections with I > 2σ(I) were considered observed. The structure was first solved by using the heavy-atom method (Patterson synthesis), which revealed the positions of metal atoms. The remaining atoms were found in a series of alternating difference Fourier maps and least-squares refinements. The quantity minimized by the least-squares program was ω(|F_o| - |F_c|)², where ω is the weight of a given operation. The analytical forms of the scattering factor tables for the neutral atoms

were used.¹⁰ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculations in their expected positions on the basis of idealized bonding geometry but were not refined in least squares. All hydrogens were assigned isotropic thermal parameters 1-2 Å² larger than the equivalent Biso value of the atom to which they were bonded. The final residuals of this refinement were *R* = 0.030 and *R_w* = 0.064. Selected bond distances and angles are listed in Table 2. Tables of thermal parameters and selected final atomic coordinates are given in the Supporting Information.

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