

BH Bond Activation of Trimethylphosphineborane by Transition Metal Complexes: Synthesis of Metal Complexes Bearing Nonsubstituted Boryl–Trimethylphosphine, Cp**M*(CO)₃(BH₂•PMe₃) (M = Mo, W)

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Abstract: Photolysis of methylmolybdenum and tungsten complexes, Cp**M*(CO)₃Me (M = Mo, W), in the presence of BH₃•PMe₃ (**1**) afforded nonsubstituted boryl complexes Cp**M*(CO)₃(BH₂•PMe₃) (**2a**: M = Mo, **3a**: M = W) with concomitant evolution of methane. The structures of **2a** and **3a** were determined by single-crystal X-ray crystallography. The boryl group in these complexes adopts a tetra-coordinate geometry with coordination of trimethylphosphine to the boron atom. The tungsten–boron bond distance in **3a** is significantly longer than those of boryltungsten complexes with a tri-coordinate boryl group. The CO stretching bands in the IR spectra of **2a** and **3a** were observed at lower wavenumbers than those of the corresponding methyl complexes, indicating the pronounced polarization of the M–B bond, M(–)–B(+). Reactivity of the boryl complexes also featured the polar M–B bond. Boryl complexes having a nonsubstituted cyclopentadienyl ligand, Cp*M*(CO)₃(BH₂•PMe₃) (**2b**: M = Mo, **3b**: M = W) were generated by the similar photoreaction although they were thermally unstable.

Introduction

The first reports on the syntheses of transition-metal boryl complexes were documented by Nöth and Schmid in 1960s.^{1,2} However, the following development of chemistry of complexes having an M–B 2c2e bond has been quite slow and is far behind those of transition-metal silyl and phosphido compounds as well as alkyl derivatives. In the past decade, much attention was focused on boryl complexes.^{3–6} Chemistry of boryl complexes is closely related to metal-catalyzed boration and hydroboration of alkenes, alkynes, and conjugated polyenes.^{7–14} Quite recently, Waltz and Hartwig reported photoinduced selective function-

alization of alkanes by the use of a tungsten complex with a catecholboryl ligand, Cp*W(CO)₃Bcat' (cat' = 3,5-Me₂C₆H₂O₂).¹⁵ Thus, investigation of boryl complexes has become increasingly important. Most of boryl complexes reported so far possess a tri-coordinate boron atom. In many of them, the electron-deficiency of boron is compensated by π donor substituents such as catecholate, amino, or phenyl groups.^{5,6,16,17} The only fully

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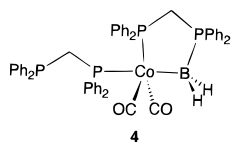
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characterized complex bearing a nonsubstituted boryl ligand is $(\eta^1\text{-dppm})(\text{OC})_2(\mu\text{-}\eta^2\text{-dppm})\text{CoBH}_2$ (**4**) (dppm = $\text{PPh}_2\text{CH}_2\text{-PPh}_2$).



In this complex, a PPh_2 moiety in one of the dppm ligands coordinates to the boryl group to bridge cobalt and boron.¹⁸ Consequently, the boron atom in the cobalt complex adopts a tetrahedral configuration. Adduct formation between a Lewis base and a boryl complex, to give $\text{CpM}(\text{CO})_3(\text{BCl}_2\cdot\text{NEt}_3)$ ($\text{M} = \text{Mo}, \text{W}$), can also be found in an early report of Nöth and Schmid although its detailed characterization and the crystal structure were not reported.^{1b}

Trimethylphosphineborane, $\text{BH}_3\cdot\text{PMe}_3$ (**1**), is one of the simplest boron compounds and is isoelectronic and isostructural with methane. Compound **1** is remarkably stable in comparison to other borane-Lewis base adducts, e.g., $\text{BH}_3\cdot\text{THF}$. Therefore, interaction of **1** with transition-metal complexes can be considered a model reaction of alkane activation.¹⁹ It is also important as a synthetic method of metal complexes with a boron hydride moiety. However, little is known of activation of tetra-coordinate (sp^3 -type) boranes. This makes a sharp contrast to chemistry of tri-coordinate boranes, of which, a number of catecholboryl complexes are prepared by means of oxidative addition of the BH bond in HBcat (cat = $o\text{-C}_6\text{H}_2\text{O}_2$).^{5,6} Fehlner and co-workers have reported the reaction of a tetra-coordinate borane, $\text{BH}_3\cdot\text{THF}$ with $\text{Co}_2(\text{CO})_8$.²⁰ In this reaction, cleavage of a BH bond takes place and a borylcobalt complex $\text{Co}(\text{CO})_4(\text{BH}_2\cdot\text{THF})$ is produced. This compound is, however, characterized only by ¹¹B NMR spectroscopy at low temperature due to thermal instability, and the details of its structure and reactivity are not clear.

We previously reported the photolysis of group 6 metal hexacarbonyls in the presence of **1**.²¹ In the product $[\text{M}(\text{CO})_5(\eta^1\text{-BH}_3\cdot\text{PMe}_3)]$ ($\text{M} = \text{Cr}, \text{W}$), **1** coordinates to the metal center through a B-H-M three-center two-electron bond. This bonding can be regarded as an "incomplete oxidative addition" of the BH of **1**. It is well-known that complexes with an electron-rich metal center display enhanced susceptibility toward oxidative addition. Therefore, by the use of electron-rich complexes, it is expected that a BH bond of **1** should be completely cleaved to form a direct M-B bond. From such a point of view, we explored the activation of **1** with use of molybdenum and tungsten complexes possessing a strongly electron-releasing pentamethylcyclopentadienyl (Cp^*) ligand under photolytic conditions. This work is also related to the BH and BB bond activation of $\text{B}_2\text{H}_4\cdot 2\text{PMe}_3$ by $\text{Co}_2(\text{CO})_8$, which produces a bridging borylene complex, $\text{Co}_2(\text{CO})_7(\mu\text{-BH}\cdot\text{PMe}_3)$.²² In this paper, we describe the syntheses, structures, spectroscopic features, and some chemical properties of new boryl complexes obtained by BH bond activation of **1**. Preparation of the boryl complexes with a nonsubstituted cyclopentadienyl ligand (Cp)

are also reported. Preliminary results on this work have been published previously.²³

Experimental Section

All manipulations were carried out under high vacuum or dry nitrogen atmosphere. Reagent-grade pentane, hexane, toluene, diethyl ether, and THF were distilled under a nitrogen atmosphere from sodium-benzophenone ketyl immediately before use. Benzene- d_6 was dried over a potassium mirror and transferred into NMR tubes under vacuum before use. $\text{BH}_3\cdot\text{PMe}_3$ (**1**),²⁴ $\text{Cp}^*\text{Mo}(\text{CO})_3\text{Me}$,²⁵ $\text{CpMo}(\text{CO})_3\text{Me}$,²⁶ $\text{Cp}^*\text{W}(\text{CO})_3\text{Me}$,²⁵ and $\text{CpW}(\text{CO})_3\text{Me}$ ²⁶ were prepared according to the literature. Me_3SiCl (Shin-etsu Chemicals) and MeI (Wako Pure Chemicals) were dried over CaH_2 and 4Å molecular sieves, respectively, and distilled. NMR spectra were recorded on a JEOL α -500 spectrometer. IR spectra were recorded on a Jasco FTIR-350 spectrometer. Mass spectra were obtained using a JEOL JMS-S600H spectrometer. Spectral data of new complexes are listed in Table 1 (¹H and ³¹P NMR), Table 2 (¹¹B NMR and IR), and Table 3 (¹³C NMR and MS).

Synthesis of $\text{Cp}^*\text{Mo}(\text{CO})_3(\text{BH}_2\cdot\text{PMe}_3)$ (2a**).** A solution of $\text{Cp}^*\text{Mo}(\text{CO})_3\text{Me}$ (203 mg, 0.62 mmol) and **1** (163 mg, 1.82 mmol) in diethyl ether (12 mL) was placed in a Pyrex glass tube (25 mm o.d.) equipped with a high-vacuum stopcock. The solution was irradiated for 50 min at 3 °C under static vacuum, using a 450 W medium-pressure Hg lamp. After irradiation, volatiles were removed, and the residue was extracted with hexane (12 mL) and filtered through a glass filter. The hexane extract was allowed to stand at -20 °C to afford $\text{Cp}^*\text{Mo}(\text{CO})_3(\text{BH}_2\cdot\text{PMe}_3)$ (**2a**) (44 mg, 0.11 mmol, 18%) as pale orange needles. Anal. Calcd for $\text{C}_{16}\text{H}_{26}\text{BMoO}_3\text{P}$: C, 47.56; H, 6.49. Found: C, 48.08; H, 6.43%.

Synthesis of $\text{Cp}^*\text{W}(\text{CO})_3(\text{BH}_2\cdot\text{PMe}_3)$ (3a**).** A hexane (12 mL) solution of $\text{Cp}^*\text{W}(\text{CO})_3\text{Me}$ (120 mg, 0.29 mmol) and **1** (52 mg, 0.58 mmol) was photolyzed for 80 min at 3 °C under static vacuum, using a 450 W medium-pressure Hg lamp. The resulting mixture was filtered through a glass filter. The filtrate was cooled to -20 °C to provide pale orange crystals along with a micro crystalline solid of unreacted **1**. Removal of **1** by evacuation at room temperature gave $\text{Cp}^*\text{W}(\text{CO})_3(\text{BH}_2\cdot\text{PMe}_3)$ (**3a**) (70 mg, 0.14 mmol, 49%). Anal. Calcd for $\text{C}_{16}\text{H}_{26}\text{BWO}_3\text{P}$: C, 39.06; H, 5.33. Found: C, 39.62; H, 5.52%.

Photolysis of $\text{CpMo}(\text{CO})_3\text{Me}$ in the presence of **1.** A benzene- d_6 (0.5 mL) solution of **1** (17 mg, 0.19 mmol) and $\text{CpMo}(\text{CO})_3\text{Me}$ (10 mg, 3.8×10^{-3} mmol) was photolyzed for 55 min at 5 °C in a Pyrex NMR tube flame-sealed under high vacuum. During the photolysis, the color of the solution changed from pale yellow to reddish brown. The ¹H, ¹¹B, ³¹P NMR spectra of the resulting solution indicated formation of $\text{CpMo}(\text{CO})_3(\text{BH}_2\cdot\text{PMe}_3)$ (**2b**) and methane (δ 0.14 ppm). However, complex **2b** so rapidly decomposed that the isolation was not achieved ($\tau_{1/2} \approx 2$ h at room temperature).

Synthesis of $\text{CpW}(\text{CO})_3(\text{BH}_2\cdot\text{PMe}_3)$ (3b**).** A toluene (10 mL) solution of $\text{CpW}(\text{CO})_3\text{Me}$ (162 mg, 0.47 mmol) and **1** (87 mg, 0.97 mmol) was irradiated for 70 min under vacuum at 5 °C. After removal of volatiles, the residue was extracted with pentane (10 mL). Cooling the extract provided a pale orange powder of $\text{CpW}(\text{CO})_3(\text{BH}_2\cdot\text{PMe}_3)$ (**3b**) (52 mg, 0.12 mmol, 25%). Elemental analysis of the product gave a poor result due to thermal instability ($\tau_{1/2} \approx \sim 20$ h at room temperature).

Reaction of **2a with HCl.** Gaseous hydrogen chloride (3×10^{-2} mmol) was introduced into a solution of **2a** (10 mg, 2.5×10^{-2} mmol) in benzene- d_6 (0.5 mL). ¹H and ¹¹B NMR spectra of the resulting solution revealed the quantitative formation of $\text{Cp}^*\text{Mo}(\text{CO})_3\text{H}$ ²⁷ and $\text{BH}_2\text{Cl}\cdot\text{PMe}_3$.²⁸

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Table 1. ^1H and ^{31}P NMR Spectral Data for the Boryl Complexes^a

compound	^1H NMR (500 MHz) δ/ppm			^{31}P NMR (202.4 MHz) δ/ppm
	$\eta\text{-C}_5\text{R}_5$	BH	PMe_3	
$\text{Cp}^*\text{Mo}(\text{CO})_3(\text{BH}_2\cdot\text{PMe}_3)$ (2a)	1.87	<i>b</i>	0.86 (d) $^2J(\text{PH}) = 11.0$ Hz	-2.4 (q) $^1J(\text{BP}) = 85$ Hz
$\text{CpMo}(\text{CO})_3(\text{BH}_2\cdot\text{PMe}_3)$ (2b)	4.91	<i>b</i>	0.89 (d) $^2J(\text{PH}) = 11.0$ Hz	-1.6 (br)
$\text{Cp}^*\text{W}(\text{CO})_3(\text{BH}_2\cdot\text{PMe}_3)$ (3a)	1.91	1.45 (br, q) $^1J(\text{BH}) = 110.0$ Hz	0.91 (d) $^2J(\text{PH}) = 11.0$ Hz	-1.3 (q) $^1J(\text{PB}) = 80$ Hz
$\text{CpW}(\text{CO})_3(\text{BH}_2\cdot\text{PMe}_3)$ (3b)	4.86	1.92 (br, q) $^1J(\text{BH}) = 110.7$ Hz	0.89 (d) $^2J(\text{PH}) = 11.0$ Hz	-2.2 (q) $^1J(\text{PB}) = 80$ Hz

^a The NMR spectra were measured in C_6D_6 . ^b The BH signals were too broad to be observed.

Table 2. ^{11}B NMR and IR Spectral Data for the Boryl Complexes

compound	^{11}B NMR ^a δ/ppm (160.4 MHz)	IR (KBr)/ cm^{-1}		$\Delta(\delta^{11}\text{B})^b$	$\Delta\nu(\text{CO})^c$
		$\nu(\text{BH})$	$\nu(\text{CO})$		
$\text{BH}_3\cdot\text{PMe}_3$ (1)	-37.0			0 (reference)	
$\text{Cp}^*\text{Mo}(\text{CO})_3(\text{BH}_2\cdot\text{PMe}_3)$ (2a)	-24.6 (dt) $^1J(\text{BH}) = 113$ Hz, $^1J(\text{BP}) = 85$ Hz	2402, 2369	1942, 1843	12.4	76
$\text{CpMo}(\text{CO})_3(\text{BH}_2\cdot\text{PMe}_3)$ (2b)	-27.8 (dt) $^1J(\text{BH}) = 115$ Hz, $^1J(\text{BP}) = 84$ Hz	<i>d</i>		9.8	<i>d</i>
$\text{Cp}^*\text{W}(\text{CO})_3(\text{BH}_2\cdot\text{PMe}_3)$ (3a)	-27.6 (dt) $^1J(\text{BH}) = 110$ Hz, $^1J(\text{BP}) = 80$ Hz	2390, 2362	1943, 1848	9.4	48
$\text{CpW}(\text{CO})_3(\text{BH}_2\cdot\text{PMe}_3)$ (3b)	-31.7 (dt) $^1J(\text{BH}) = 111$ Hz, $^1J(\text{BP}) = 80$ Hz	2414, 2382	1919, 1841	5.3	69

^a The NMR spectra were measured in C_6D_6 . ^b $\Delta(\delta^{11}\text{B}) = \delta^{11}\text{B}(\text{boryl complex}) - \delta^{11}\text{B}(\text{BH}_3\cdot\text{PMe}_3)$. ^c $\Delta\nu(\text{CO}) = \nu(\text{CO})_{\text{av}}[(\eta\text{-C}_5\text{R}_5)\text{M}(\text{CO})_3\text{Me}] - \nu(\text{CO})_{\text{av}}[(\eta\text{-C}_5\text{R}_5)\text{M}(\text{CO})_3(\text{BH}_2\cdot\text{PMe}_3)]$. The $\nu(\text{CO})$ vibrational frequencies of the methyl complexes are as follows: $\text{Cp}^*\text{Mo}(\text{CO})_3\text{Me}$ 2008, 1929 cm^{-1} ; $\text{Cp}^*\text{W}(\text{CO})_3\text{Me}$ 1998, 1888 cm^{-1} ; $\text{CpW}(\text{CO})_3\text{Me}$ 2004, 1894 cm^{-1} . ^d Owing to the thermal instability, **2b** could not be isolated, and its IR spectrum was not obtained.

Table 3. ^{13}C NMR and Mass Spectral Data for the Boryl Complexes

compd	^{13}C NMR (C_6D_6 , 125 MHz) δ/ppm	MS (EI) m/z
2a	10.5 (C_5Me_5), 13.9 (d, $^1J_{\text{PC}} = 38.4$ Hz, PMe_3), 102.4 (C_5Me_5), 229.3, 235.0 (br, CO)	406 (10, M^+), 378 (29, $\text{M}^+ - \text{CO}$), 350 (37, $\text{M}^+ - 2\text{CO}$), 318 (100, $\text{Cp}^*\text{Mo}(\text{CO})_3\text{H}^+$), 317 (85, $\text{Cp}^*\text{MoBH}_2^+$), 233 (16, Cp^*Mo^+)
2b^a	14.7 (d, $^1J_{\text{PC}} = 53.7$ Hz, PMe_3), 87.0 (Cp), 230.0, 236.0 (br, CO)	336 (4, M^+), 308 (30, $\text{M}^+ - \text{CO}$), 280 (35, $\text{M}^+ - 2\text{CO}$), 252 (20, $\text{M}^+ - 3\text{CO}$), 246 (100, the overlapping signal of isotopomers of $\text{CpMoBH}_2\text{PMe}_3^+$ and $\text{CpMo}(\text{CO})_3^+$), 204 (16, $\text{CpMo}(\text{CO})\text{BH}_2^+$)
3a	10.6 (C_5Me_5), 14.3 (d, $^1J_{\text{PC}} = 38.2$ Hz, PMe_3), 101.5 (C_5Me_5), 224.8, 235.4 (br, CO)	492 (39 M^+), 464 (64, $\text{M}^+ - \text{CO}$), 436 (100, $\text{M}^+ - 2\text{CO}$), 408 (36, $\text{M}^+ - 3\text{CO}$), 360 (28, $\text{Cp}^*\text{W}(\text{CO})\text{BH}_2^+$), 319 (30, Cp^*W^+)
3b	14.0 (d, $^1J_{\text{PC}} = 40.2$ Hz, PMe_3), 90.6 (Cp), 220.8, 226.0 (br, CO)	422 (11, M^+), 394 (14, $\text{M}^+ - \text{CO}$), 366 (14, $\text{M}^+ - 2\text{CO}$), 304 (57, $\text{Cp}^*\text{W}(\text{CO})_2^+$), 276 (41, $\text{Cp}^*\text{W}(\text{CO})^+$), 248 (100, CpW^+)

^a Because of its thermal instability, the mass spectrum of **2b** was recorded using the photolyzate of a hexane solution of $\text{Cp}(\text{CO})_3\text{Me}$ and $\text{BH}_3\cdot\text{PMe}_3$.

Reaction of 3a with HCl. The reaction of **3a** with HCl was monitored by the almost the same method as that of **2a** with HCl. The ^1H and ^{11}B NMR spectra indicated the formation of $\text{Cp}^*\text{W}(\text{CO})_3\text{H}^{27}$ and $\text{BH}_2\text{Cl}\cdot\text{PMe}_3$.²⁸

Reaction of $\text{Cp}^*\text{Mo}(\text{CO})_3\text{Me}$ with HCl. The reaction of $\text{Cp}^*\text{Mo}(\text{CO})_3\text{Me}$ with HCl was also carried out in the manner similar to that for **2a**. The ^1H NMR spectrum of the resulting solution indicated formation of a mixture including $\text{Cp}^*\text{Mo}(\text{CO})_3\text{Cl}$ and CH_4 .

Reaction of 2a with Me_3SiCl . A sample of **2a** (15 mg, 3.7×10^{-2} mmol) was dissolved in benzene-*d*₆ (0.5 mL), and Me_3SiCl (4.0×10^{-2} mmol) was introduced into the solution under vacuum. Quantitative formation of $\text{Cp}^*\text{Mo}(\text{CO})_3\text{SiMe}_3$ ²⁹ and $\text{BH}_2\text{Cl}\cdot\text{PMe}_3$ was shown by ^1H , ^{11}B , and ^{29}Si NMR spectra of the mixture.

Reaction of 3a with MeI. Complex **3a** and 2-fold excess of MeI were combined in C_6D_6 , and the resulting mixture was heated at 45 °C. After 24 h, formation of $\text{Cp}^*\text{W}(\text{CO})_3\text{Me}$ and $\text{BH}_2\text{I}\cdot\text{PMe}_3$ ²⁹ was observed in the ^1H and ^{11}B NMR.

Reaction of 2a with PMe_3 . To a solution of **2a** (10 mg, 2.5×10^{-2} mmol) in benzene-*d*₆ (0.5 mL) was introduced PMe_3 (0.25 mmol) under high vacuum. The color of the solution changed from pale yellow to deep yellow. The NMR spectra of the resulting mixture indicated the formation of $[\text{BH}_2\cdot 2\text{PMe}_3][\text{Mo}(\text{CO})_3\text{Cp}^*]$.³⁰

Reaction of 3a with PPhMe_2 . Reaction of **3a** with PPhMe_2 in benzene-*d*₆ was monitored by NMR spectroscopy. The ^1H , ^{11}B , and ^{31}P NMR spectra of the resulting solution indicated the formation of $[\text{BH}_2(\text{PMe}_3)(\text{PPhMe}_2)][\text{W}(\text{CO})_3\text{Cp}^*]$. Assignment of the NMR signals of the cation $[\text{BH}_2(\text{PMe}_3)(\text{PPhMe}_2)]^+$ was carried out by comparison of the spectra with those of independently prepared $[\text{BH}_2(\text{PMe}_3)(\text{PPhMe}_2)]\text{I}$.

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Preparation of $[\text{BH}_2(\text{PMe}_3)(\text{PPhMe}_2)]\text{I}$. To a solution of $\text{BH}_2\cdot\text{PMe}_3$ (338 mg, 1.56 mmol) in THF (8 mL) was added PPhMe_2 (242 mg, 1.75 mmol) at 0 °C with stirring to give a white precipitate. After 15 min of stirring, the cooling bath was removed and the mixture was further stirred for 30 min at room temperature. The solvent was evaporated under a reduced pressure, and the residue was washed with toluene (5 mL \times 3) and ether (5 mL \times 5). The resultant colorless solid of $[\text{BH}_2(\text{PMe}_3)(\text{PPhMe}_2)]\text{I}$ (518 mg, 1.46 mmol, 94%) was dried under vacuum. ^1H NMR (500 MHz, CDCl_3) δ 1.43 (q, br, $^1J_{\text{BH}} \approx 90$ Hz, 2H, BH), 1.63 (d, $^2J_{\text{PH}} = 11.5$ Hz, 9H, PMe_3), 2.05 (d, $^2J_{\text{PH}} = 11.5$ Hz, 6H, PPhMe_2), 7.55–7.57, 7.74–7.77 (m, PPhMe_2); $^{11}\text{B}\{^1\text{H}\}$ NMR (160.35 MHz, CDCl_3) δ -32.5 (tt, $^1J_{\text{BP}} \approx 90$ Hz, $^1J_{\text{BH}} \approx 90$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (202.35 MHz, CDCl_3) δ -7.7 (q, $^1J_{\text{BP}} \approx 90$ Hz, PMe_3), -3.7 (q, $^1J_{\text{BP}} \approx 90$ Hz, PPhMe_2). ^{13}C NMR (125 MHz, CDCl_3) δ 12.7 (dd, $^1J_{\text{PC}} = 44.1$ Hz, $^3J_{\text{PC}} = 4.1$ Hz, PPhMe_2), 13.0 (dd, $^1J_{\text{PC}} = 44.3$ Hz, $^3J_{\text{PC}} = 5.1$ Hz, PMe_3), 126.8 (dd, $^1J_{\text{PC}} = 66.9$ Hz, $^3J_{\text{PC}} = 5.1$ Hz, *ipso*-C), 130.4 (d, $J_{\text{PC}} = 11.3$ Hz, *o*-C), 131.2 (d, $J_{\text{PC}} = 9.3$ Hz, *m*-C), 133.2 (d, $J_{\text{PC}} = 3.0$ Hz, *p*-C). Anal. Calcd for $\text{C}_{11}\text{H}_{22}\text{BIP}_2$: C, 37.33; H, 6.27. Found: C, 36.87; H, 6.04%.

X-ray Crystal Structure Determination. Crystals of **2a** and **3a** were grown by cooling of their hexane solutions. Intensity data were collected on a Rigaku AFC-5 four-circle diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å). Data collection for **2a** was carried out at 0 °C, that for **3a** was carried out at -60 °C. Reflection data were corrected for Lorentz and polarization factors but not for absorption and extinction. Space groups were determined from systematic absences. Crystallographic and experimental data for these crystals are listed in Table 4.

The structures of all complexes were solved by the heavy atom method. All non-hydrogen atoms were located and refined applying anisotropic temperature factors. For **3a**, coordinates of hydrogen atoms bound to the boron atom were determined by difference Fourier synthesis and were refined isotropically. For **2a**, the hydrogen atoms

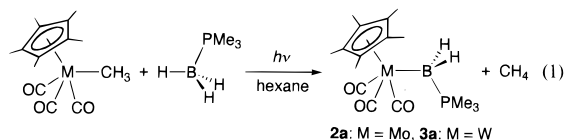
Table 4. Crystal Data for **2a** and **3a**

compd	(2a)	(3a)
sample	Cp*Mo(CO) ₃ (BH ₂ ·PMe ₃)	Cp*W(CO) ₃ (BH ₂ ·PMe ₃)
formula	C ₁₆ H ₂₆ BMoO ₃ P	C ₁₆ H ₂₆ BO ₃ PW
fw	404.09	491.95
color of cryst	pale orange	pale orange
temp/°C	0	-60
cryst system	tetragonal	
space group	P4 ₂ /m (no. 84)	
syst absence	(0 0 l): l = 2n + 1	
a/Å	12.773 (1)	12.709 (3)
c/Å	11.869 (3)	11.707 (6)
V/Å ³	1936.6 (5)	1890.9(12)
Z	4	4
d _{calcd} /g cm ⁻³	1.386	1.732
μ (Mo Kα)	8.26	9.10
cryst size/mm	0.30 × 0.30 × 0.5	0.20 × 0.25 × 0.3
radiation	MoKα (λ/Å = 0.71069)	
monochromator	graphite	
reflcn/measd	h, k, l	
2θ range/deg	3–75	3–60
scan mode	2θ – ω	
ω-scan width/deg	1.1 + 0.30 tanθ	1.1 + 0.30 tanθ
ω-scan rate/deg min ⁻¹	4.0	4.0
no. of unique data	5530	3131
no. of data used with F _o > 3σ(F _o)	2937	2380
no. of params refined	117	121
R1	0.049	0.033
Rw2	0.119	0.080
GoF	0.876	0.949
max resid electron dens	0.47	1.92

on boron were found and fixed. Coordinates of the hydrogen atoms of the methyl groups for both compounds were idealized by using a riding model. Atomic scattering factors for non-hydrogen atoms and hydrogen atoms were taken from refs 31 and 32, respectively. Calculations were performed using the programs SHELXS 86^{33a} and SHELXL 93.^{33b}

Results and Discussion

Syntheses and Structures of the Molybdenum and Tungsten Boryl Complexes. Photolysis of a methylmolybdenum or tungsten complex, Cp*M(CO)₃Me (M = Mo, W), in the presence of BH₃·PMe₃ (**1**) gave an orange-brown solution, from which nonsubstituted boryl complexes, Cp*M(CO)₃(BH₂·PMe₃) (**2a**: M = Mo, **3a**: M = W) were obtained. The boryl complexes **2a** and **3a** were isolated as pale orange crystals by recrystallization from hexane in 18 and 49% yields, respectively. The predominant side-products were [M(CO)₃Cp*]₂ and [M(CO)₂Cp*]₂. When these reactions were monitored by ¹H NMR spectroscopy, generation of methane was observed (eq 1). These reactions are quite rare examples of activation of a



BH bond in tetra-coordinate (sp³-type) borane to form metal

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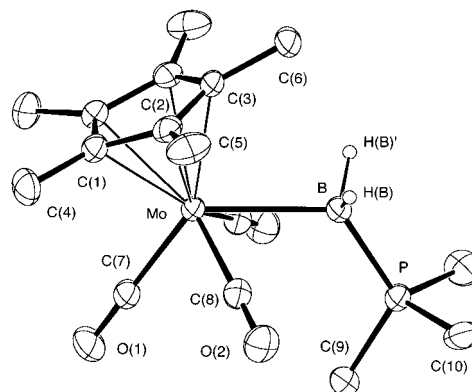


Figure 1. ORTEP diagram of Cp*Mo(CO)₃(BH₂·PMe₃) (**2a**) with thermal ellipsoids at the 30% probability level.

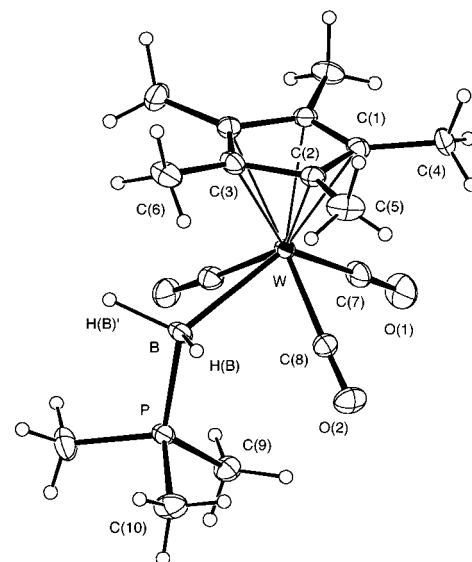


Figure 2. ORTEP diagram of Cp*W(CO)₃(BH₂·PMe₃) (**3a**) with thermal ellipsoids at the 30% probability level.

complexes having an M–B bond. The modest yields of **2a** and **3a** are attributed to the fact that these products are also light-sensitive. Similar reaction with use of BH₃·NMe₃ instead of **1** did not give boryl complexes. Related complexes with a tri-coordinate boryl group, Cp*W(CO)₃Bcat¹⁵ and CpM(CO)₃-BNMe₂B(Cl)NMe₂ (M = Mo, W),^{34,35} were synthesized by salt elimination reactions of the anions [W(CO)₃Cp*]⁻ and [M(CO)₃Cp]⁻ with the corresponding chloroboranes. Note that we have synthesized σ-borane complexes [M(CO)₅(η¹-BH₃·PMe₃)] (M = Cr, W)²¹ and a μ-borylene complex [Co₂(CO)₇(μ-BH·PMe₃)]²² during the course of study on coordination chemistry of lower borane-PMe₃ adducts. Although complexes with a boryl-trimethylphosphine adduct, BH₂·PMe₃, were the “missing link” between the borane complexes and the borylene complex, the success in the preparation of **2a** and **3a** has completed this vacancy. Characterization of the boryl complexes was accomplished by conventional spectroscopic and analytical methods as well as by X-ray crystallography.

The molecular structures of **2a** and **3a** are illustrated in Figures 1 and 2, respectively, with the atomic numbering schemes. Complex **2a** is the first structurally authenticated borylmolybdenum complex. Crystals of **2a** and **3a** are isomor-

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Table 5. Key Geometrical Parameters for **2a** and **3a**

	2a (M = Mo)	3a (M = W)
Distances (Å)		
M–B	2.497(5)	2.476(7)
P–B	1.949(5)	1.952(7)
M–CNT ^a	2.033(4)	2.025(4)
M–C(7)	1.960(5)	1.961(6)
M–C(8)	1.962(4)	1.964(5)
B–H(B)	1.18	1.18(6)
C(7)–O(1)	1.158(6)	1.153(8)
C(8)–O(2)	1.158(5)	1.158(6)
P–C(9)	1.814(5)	1.827(7)
P–C(10)	1.811(4)	1.803(6)
Angles (deg)		
B–M–CNT	112.82(12)	112.07(15)
M–B–P	121.4(2)	121.4(3)
C(7)–M–B	125.0(2)	126.1(2)
C(8)–M–B	67.21(12)	68.0(2)
C(7)–M–CNT	122.2(2)	121.9(2)
C(8)–M–NT	125.4(2)	125.24(14)
C(8)–M–C(8)′	105.8(2)	106.0(2)
C(7)–M–C(8)	80.98(13)	80.8(2)
M–B–H(B)	98.8	106(3)
H(B)–B–H(B)	109.4(4)	113(4)
P–B–H(B)	113.4	105(3)

^a CNT: centroid of Cp* rings.

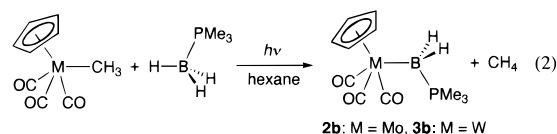
phous. Table 5 lists the summary of key geometrical parameters for **2a** and **3a**. These complexes have four-legged piano stool geometries as shown in Figures 1 and 2. The Cp*M(CO)₃ moiety and the boryl group, BH₂·PMe₃, are linked by a metal–boron σ bond, and no M–H–B interaction is included in the systems. They have a crystallographic mirror plane through the boron, central metal, and phosphorus atoms. The M–B axis adopts the *anti* conformation with respect to the Cp* and PMe₃ ligands, where the steric interaction is minimized. The M–B bond lengths are 2.497(5) (**2a**, M = Mo) and 2.476(7) (**3a**, M = W), respectively. These values are nearly identical to the sums of the half of the metal–metal interatomic distances in [M(CO)₃Cp]₂ (3.235(1) Å for M = Mo, 3.222(1) Å for M = W)³⁶ and half of the boron–boron bond length in B₂H₄·2PMe₃ (1.740(7) Å).³⁷ The W–B σ bond of **3a** is the longest one in boryltungsten complexes reported so far, and remarkably longer than those in tungsten boryl complexes with tri-coordinate boron, Tp*W(CO)₂{BEt(CH₂-*p*-C₆H₄Me)} (2.07(1) Å, where Tp* = tris(3,5-dimethylpyrazolyl)hydroborate),³⁸ Cp₂W(Bcat)′₂ (2.19(1) and 2.23(1) Å; cat′ = *o*-O₂C₆H₃-3-*t*Bu),³⁹ and Cp₂W(H)(Bcat) (2.190(7) Å).⁴⁰ In these compounds, the W–B bond has a partial double bond character, which arises from the overlap between the vacant p orbital of the tri-coordinate boron and the metal d orbital. On the other hand, the p orbital on boron in **2a** and **3a** is filled by coordination of the lone electron pair of PMe₃, and therefore, the boron atom cannot undergo effective back-donation from the metal center. In CpW(CO)₃B(NMe₂)B(Cl)NMe₂, which was synthesized by Braunschweig and co-workers, the W–B bond (2.370(8) Å) is substantially longer than those of the above tri-coordinate boryl complexes probably due to the π donation of the amino groups to the p orbitals of boron.³⁴ Nonetheless, the tungsten–boron bond distance in **3a** is even much longer than that. This is attributed to the strong polarization of the M–B bond in **2a** and **3a**, which can elongate the

M–B σ bond itself (vide infra). The positions of the hydrogen atoms on boron were determined by difference Fourier synthesis and refined for **3a**. For **2a**, they were found, but the positions were fixed. The B–H bond lengths are normal for terminal B–H bonds. The geometry around the boron atom is pyramidal, owing to coordination of PMe₃. The sum of the angles of M–B–H, M–B–H′, and H–B–H′ are 307° and 326° for **2a** and **3a**, respectively. The B–P interatomic distances (1.949(5) Å for **2a**, 1.952(7) Å for **3a**) are as expected for P→B dative interactions.

Boryl Complexes with a Nonsubstituted Cp ligand.

Syntheses of boryl complexes having a nonsubstituted cyclopentadienyl ligand were also sought. Irradiation of methyl complexes CpM(CO)₃Me in the presence of **1** in C₆D₆ and the following NMR measurements of the resulting solution indicated formation of the boryl complexes, CpM(CO)₃(BH₂·PMe₃) (**2b**: M = Mo, **3b**: M = W) and evolution of methane (eq 2). However, these compounds were thermally unstable, so that isolation in pure form was not successful.

The lifetimes $\tau_{1/2}$ were ~20 h (for **3b**) and ~2 h (for **2b**) under high vacuum.



Smith et al. have reported the reaction of GaMe₃ with CpW(CO)₃H, which results in multiple activation of the Ga–C bonds to afford CpW(CO)₃GaMe₂, [CpW(CO)₃]₂(μ_2 -GaMe), and [CpW(CO)₃]₃(μ_3 -Ga) besides CH₄.⁴¹ In the reaction of CpM(CO)₃H (M = Mo, W) with InMe₃, μ_3 -indium complexes [CpM(CO)₃]₃(μ_3 -In) are produced exclusively.⁴² We also reported that irradiation of CpFe(CO)₂SiMe₃ in the presence of RSiH₃ (R = *t*-Bu, CMe₂CMe₂H) gave silylene-bridged diiron complexes Cp₂-Fe₂(CO)₃(μ -SiHR).⁴³ In contrast, no evidence for multiple activations of BH bonds was obtained in these boron systems.

Spectroscopic and Chemical Properties of the Boryl Complexes. In the ¹H NMR spectra, the boryl complexes exhibit a sharp singlet and a doublet assignable to the Cp* and the PMe₃ ligand, respectively (Table 1). The BH signals of **3a** and **3b** resonate at 1.45 and 1.92 ppm, respectively, as a very broad quartet due to the quadrupolar moment of the ¹¹B nuclei. That of **2** was too broad to be observed. However, the existence of the BH protons is clearly evidenced by appearance of a triplet of doublets coupled with two protons and a phosphorus atom in the proton-coupled ¹¹B NMR spectrum. The trimethylphosphine-complexed boryl groups of **2** and **3** resonate at –24.6 to –31.7 ppm. These chemical shift values are clearly distinguishable from those of complexes with a tri-coordinate boryl group. The ¹¹B NMR signal of tri-coordinate boryl ligands is found at 30–121 ppm.^{5,6} At the same time, the δ^{11} B values of the boryl ligand of **2** and **3** are about 10 ppm higher (lower field) than that of the precursor **1** (Table 2). In ¹³C NMR spectra of alkyl complexes, we usually encounter upfield shifts of the α carbon signal relative to the parent alkane. For example, CpW(CO)₃Me exhibits the methyl signal at –35 ppm while methane resonates at –2 ppm.²⁵ Thus, the trend of chemical shifts in ¹¹B NMR

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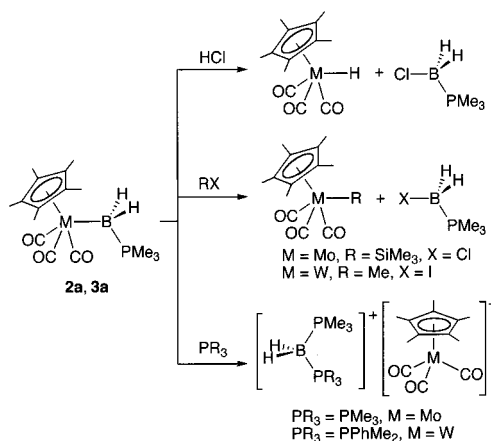
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spectroscopy of the boryl complexes is different from that of ^{13}C NMR of alkyl complexes, but it resembles that of ^{29}Si NMR of transition-metal silyl complexes, which also show marked downfield shifts of the silyl signals from the corresponding hydrosilanes.⁴⁴ The downfield shifts of the signal of the boryl ligands suggest that the M–B bond in the boryl complexes is polarized as $\text{M}(-)\text{--B}(+)$.

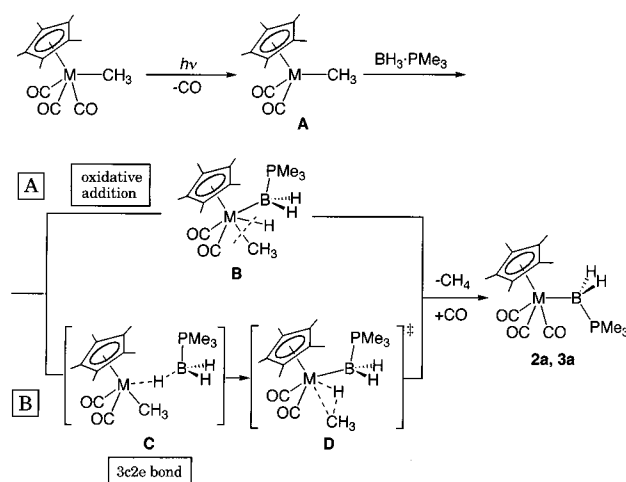
The $\nu(\text{CO})$ bands of **2a** and **3a** (1942 and 1843 cm^{-1} for **2a**; 1943 and 1848 cm^{-1} for **3a**) are found at remarkably lower wavenumbers than those observed for the corresponding methyl complexes, $\text{Cp}^*\text{M}(\text{CO})_3\text{Me}$ (2008 and 1929 cm^{-1} for $\text{M} = \text{Mo}$; 1998 and 1888 cm^{-1} for $\text{M} = \text{W}$). The $\Delta\nu(\text{CO})$ values, which are defined by the shift of the CO stretching bands of the boryl complexes relative to those of the methyl complexes (the average of the two $\nu(\text{CO})$ bands), are 76 and 48 cm^{-1} for molybdenum and tungsten systems, respectively. Complex **3b** also displays the $\nu(\text{CO})$ bands shifted to lower energy than $\text{CpW}(\text{CO})_3\text{Me}$ ($\Delta\nu(\text{CO}) = 69\text{ cm}^{-1}$, Table 2). The carbonyl-metallate anions $\text{Li}[\text{M}(\text{CO})_3\text{Cp}]$ ($\text{M} = \text{Mo}, \text{W}$), which consist of the carbonyl oxygen $\cdots\text{Li}$ contact ion pair and the solvent-separated ion pair, exhibit the $\nu(\text{CO})$ bands at $110\text{--}130\text{ cm}^{-1}$ lower energy in comparison to the methyl complexes, $\text{CpM}(\text{CO})_3\text{Me}$.^{45,46} Thus, the $\Delta\nu(\text{CO})$ values of the boryl complexes amount to approximately half of those of the anions. This finding is attributed to enhanced back-donation from the central metal to the CO ligands caused by the strong polarization of the M–B bond, $\text{M}(-)\text{--B}(+)$. This polarity is contrary to that in some tri-coordinate boryl complexes. In $\text{CpFe}(\text{CO})_2\text{Bcat}$ and $\text{CpFe}(\text{CO})_2\text{BPh}_2$, the Fe–B bond is polarized as $\text{Fe}(+)\text{--B}(-)$ owing to substantial back-donation from the iron d orbital to the vacant p orbital of boron, and the $\nu(\text{CO})$ stretching frequencies are higher than those of the methyl complexes.⁴⁷ In the $\text{CpMo}(\text{CO})_3\text{BR}'_2$ ($\text{R}' = \text{Cl}, \text{Ph}$) system, the positions of the $\nu(\text{CO})$ vibrational bands are also comparable to those of the halo complexes, $\text{CpMo}(\text{CO})_3\text{X}$ ($\text{X} = \text{Cl}, \text{I}$).^{1b}

The polarization of the M–B bond in the boryl complexes is also reflected in their reactivity (Scheme 1). Complexes **2a** and **3a** react with gaseous HCl to produce $\text{Cp}^*\text{M}(\text{CO})_3\text{H}$ and $\text{BH}_2\text{Cl}\cdot\text{PMe}_3$, quantitatively. We note that $\text{Cp}^*\text{Mo}(\text{CO})_3\text{Me}$ reacts with HCl to afford $\text{Cp}^*\text{Mo}(\text{CO})_3\text{Cl}$ and methane although the reaction is not very clean. Interaction of **2a** with Me_3SiCl gives $\text{Cp}^*\text{Mo}(\text{CO})_3\text{SiMe}_3$ along with the chloroborane. Similarly, **3a** slowly reacts with MeI to afford $\text{Cp}^*\text{W}(\text{CO})_3\text{Me}$ and the iodoborane. The Mo–B bond in **2a** is rapidly cleaved by attack of PMe_3 to afford a boronium salt $[\text{BH}_2\cdot 2\text{PMe}_3][\text{Mo}(\text{CO})_3\text{Cp}^*]$. Likewise, treatment of **3a** with PPhMe_2 yielded $[\text{BH}_2(\text{PMe}_3)(\text{PPhMe}_2)][\text{W}(\text{CO})_3\text{Cp}^*]$. In the reactions with phosphines, neither substitution of the carbonyl ligands nor phosphine exchange on the boryl group was observed. These results also demonstrate the pronounced polarization of the M–B bond. Thus, the M–B bond in these boryl complexes has a character like a contact ion pair composed of a cation $[\text{BH}_2\cdot\text{PMe}_3]^+$ and

Scheme 1



Scheme 2



an anion $[\text{M}(\text{CO})_3\text{Cp}^*]^-$.^{48,49} This notion is consistent with the long metal-boron distances in **2a** and **3a**. Fischer and co-workers have reported gallyl or indylmetal complexes with a highly polar metal–gallium or metal–indium bond.⁵⁰ The group 13 elements in these compounds adopt a tetra-coordinate configuration with an amine ligand.

Formation Mechanism of the Boryl Complexes. Possible mechanisms for the formation of **2a** and **3a** are described in Scheme 2. Irradiation of $\text{Cp}^*\text{M}(\text{CO})_3\text{Me}$ induces dissociative loss of a CO ligand to generate coordinatively unsaturated species $\text{Cp}^*\text{M}(\text{CO})_2\text{Me}$ (**A**).⁵¹ In path A, oxidative addition of a BH bond in **1** takes place to give a molybdenum or tungsten (IV) boryl(hydrido) intermediate (**B**). Reductive elimination of methane from **B** and following recoordination of CO afford the final products **2a** and **3a**. Path B is a concerted mechanism. In this pathway, **1** coordinates to the central metal in the 16 electron

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(49) In this point, the bonding in boryl complexes **2** and **3** is considerably different from that of base-stabilized silylene complexes $\text{M}=\text{SiR}_2\cdot\text{L}$, which look closely related to **2** and **3** in the electronic structure. In base-stabilized silylene complexes, the metal–silicon linkage has a substantial multiple bond character, and the coordination of the Lewis base to the silicon atom is labile in many cases. A short metal–silicon bond distance and a long silicon–donor atom bond length are found very frequently in those.

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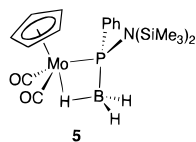
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intermediate **A** through a BH to form a M (II) intermediate **C**, which includes a B–H–M 3c2e bond. The concerted bond-rearrangement (**D**), liberation of methane, and following recoordination of CO produce the boryl complexes. These mechanisms are akin to the photoreactions of Cp'Fe(CO)₂SiMe₃ (Cp' = Cp or Cp*) with SiHR₃, which result in silyl exchange on the iron complex to produce Cp'Fe(CO)₂SiMe₃ and SiH–Me₃.^{43b,52,53} At present, we have no direct evidence to judge which mechanism A or B is preferable. Even when the reactions were monitored using NMR, no intermediate was detected. For the silyl exchange, the complete oxidative addition of an SiH bond to the unsaturated iron center has been clarified. An MO calculation on BH₃·PH₃,²¹ however, indicates that the BH σ* orbitals are energetically so high that oxidative addition of the B–H bond would be difficult. A related molybdenum borane-ether adduct complex, [Cp(CO)₂Mo(P(BH₃)Ph{N(SiMe₃)₂})] (**5**) should also be noted since it can be regarded as a chelate-stabilized derivative of the intermediate **C**.⁵⁴



Conclusion

New boryl complexes of molybdenum and tungsten were prepared by BH bond activation of **1**, which is an isoelectronic compound with methane. X-ray structural analysis showed that the M–B bond in these complexes is significantly longer than that in the tri-coordinate boryl complexes due to the lack of back-donation from the metal to the *p* orbital of boron. The spectroscopic features demonstrated that the M–B bond is strongly polarized in M(–)–B(+) fashion, which is contrary to alkyl complexes. The photoinduced alkyl–boryl exchange described here can be a new synthetic route to transition-metal boryl complexes.

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Supporting Information Available: Tables of crystallographic data for **2a** and **3a** (PDF). X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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