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Hydrogen Migrations in Rhodium Silyl Complexes: Silylene Intermediates vs Oxidative Addition/Reductive Elimination[†]

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Reaction of $(PMe_3)_4RhMe$ with H_2SiPh_2 results in elimination of CH_4 and generation of the rhodium silyl complex $(Me_3P)_4RhSiHPh_2$ (**1**; 62% isolated yield). Compound **1**, which appears to adopt a trigonal bipyramidal geometry with the silyl group in an axial position, is in equilibrium with the 16-electron complex $(Me_3P)_3RhSiHPh_2$ (**2**). Reaction of $(Me_3P)_3RhCl$ with $(THF)_2LiSiHMes_2$ (Mes = 2,4,6-trimethylphenyl) in toluene resulted in formation of the metalated species $\mathit{fac}\text{-}(\mathrm{Me_3P})_3\overline{\mathrm{Rh(H)Si(H)(Mes)C_6H_2Me_2C}}\mathrm{H_2}$ (**3**), which was characterized by X-ray crystallography. Compound **3** was also prepared by the reaction of $(Me_3P)_4RhMe$ with H_2SiMes_2. The reaction of $(Me_3P)_4RhMe$ with 1 equiv of D_2SiMes_2 in toluene resulted in distribution of deuterium between the Rh−H, SiH, $RhCH_2$, and *o*-Me positions of **3**. Since the rate of this equilibration is not reduced in the presence of excess PMe_3, we propose that successive Si−H and C−H reductive-elimination/oxidative-addition cycles are responsible for the deuterium-scrambling process.

Introduction

A primary focus of studies on transition-metal silicon compounds has long been development of chemistry for metal-bound silylene ligands.[1,2] Possible applications in catalysis have largely driven this interest,[2] and significant progress toward defining the properties and reactivities of silylene complexes ($L_nM{=}SiR_2$) has been made in recent years.[3,4] Several routes to metal complexes of divalent silicon are now established, and initial reactivity studies have been reported.[4] However, direct observation of an intramolecular migration leading to a silylene complex has not been reported, although numerous reports suggest this possibility on the basis of indirect evidence.[5,6] A detailed understanding of how silylene complexes might arise via migratory rearrangements is key to developing this area further, since catalytic processes based on transition-metal silylene intermediates would undoubtedly involve such migrations.[2]

We have been interested in observing 1,2- and 1,3-migrations which might generate unsaturated silicon centers in transition-metal silicon compounds. Our approach has involved the use of coordinatively unsaturated, electron-rich metal complexes that may initiate 1,2-migrations of a group from silicon to the metal center. In related rhodium and iridium complexes, this strategy has resulted in observation of several complex rearrangements, which probably involve silylene intermediates.[6] Although intermediates of this type are

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[†] Dedicated to Professor Warren Roper, on the occasion of his 60th birthday.

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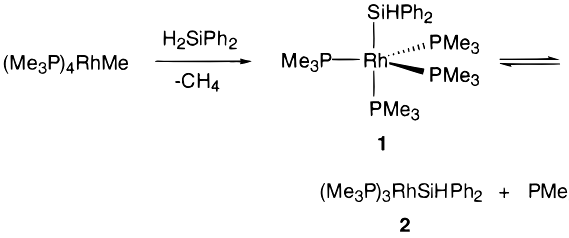
often invoked to explain observed rearrangements or conversions in transition-metal−silicon systems, definitive proof for their existence remains lacking, and alternative mechanisms (most notably, based on oxidative-addition/reductive-elimination sequences) are often more likely. In this contribution, we describe rearrangements in a rhodium silyl complex which are in fact most likely due to processes of the latter type.

Results and Discussion

Addition of 1 equiv of H_2SiPh_2 to $(Me_3P)_4RhMe$ in pentane resulted in gas evolution and formation of an orange solution from which an orange powder was isolated in 62% yield. The ^1H NMR spectrum of this compound (benzene-d_6) indicates the absence of a methyl ligand, and a new singlet at δ 5.50 is attributed to an Si−H functionality (the latter resonance appears as a complex multiplet at ≤ -60 °C). The resonance for the PMe_3 ligands appears as a doublet at δ 1.09 ($^2J_{HP} = 3.6$ Hz), and the integrated intensities in the spectrum suggest formulation of the compound as $(Me_3P)_4RhSiHPh_2$ (**1**; eq 1).



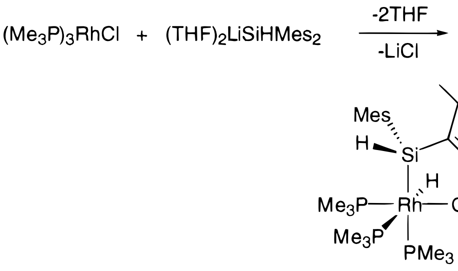
(1)

Variable-temperature ^{31}P NMR studies suggest fluxional behavior attributed to two or more independent processes. A broad signal in the ^{31}P NMR spectrum at δ −26.1 is observed at room temperature, and cooling to −60 °C (toluene-d_8) revealed two resonances at −8.43 and −26.21, in an approximate ratio of 1:3. Both resonances are still somewhat broad at this temperature, with the upfield peak appearing as an unresolved multiplet and the other peak as a doublet. This pattern was observed previously for $(PMe_3)_4RhMe$[7] and is consistent with a trigonal-bipyramidal structure with the silyl group in an axial position. Continued cooling of the solution of **1** gives rise to further broadening of the signals, and at −100 °C, three separate resonances are present as a sharp signal at δ −63.2 (assigned to free PMe_3) and broad resonances at −9.2 and −34.5 ppm (2:1 ratio; Rh−P and P−P couplings are obscured), which are assigned to exchanging phosphine ligands of square-planar **2**.

Although Rh(I) silyl complexes are in general somewhat rare,[6,8−10] a few compounds of the type $(PMe_3)_3RhSiR_3$ have been reported. Milstein prepared $(PMe_3)_3RhSiMe_2Ph$, which displays C−F activation chemistry,[9] and our group has reported the thermally unstable complex $(PMe_3)_3RhSiMe_2SiMe(SiMe_3)_2$.[6] The square-planar complex $(PMe_3)_3RhSiPh_3$ has also been prepared via the reaction of $(PMe_3)_{3,4}RhMe$ with $HSiPh_3$.[10] To our knowledge, the five-coordinate complex $(PMe_3)_4RhSiPh_3$ was not observed in the latter system, possibly due to steric crowding about rhodium. In an analogous iridium system, the hydride $(PMe_3)_4IrH$ was reported to react with Ph_2SiH_2 to give the Ir(III) silyl hydride *fac*-$(PMe_3)_3IrH_2(SiHPh_2)$.[11]

Compound **1** is somewhat thermally sensitive, decomposing to several unidentified hydride complexes upon heating to 70 °C (1 h, benzene-d_6). The presence of greatly complicated Si−H and aryl regions in the ^1H NMR spectrum suggests that metalations of the phenyl rings may represent major decomposition pathways.[12] Attempts to induce hydride migration from silicon to rhodium by removal of a phosphine ligand with $B(C_6F_5)_3$ resulted in formation of a red-black solution and several unidentified products (by ^1H NMR spectroscopy).

In an attempt to observe clean hydrogen-migration chemistry, we examined a related rhodium silyl complex with sterically demanding mesityl groups. Reaction of $(Me_3P)_3RhCl$ with $(THF)_2LiSiHMes_2$ (Mes = 2,4,6-trimethylphenyl) in toluene resulted in formation of a light yellow solution, from which colorless crystals of a new product (**3**) were isolated after workup. The presence of both Rh−H (δ -9.90) and Si−H (δ 5.76) resonances in the ^1H NMR spectrum of **3**, and five separate methyl signals, suggested the structure shown in eq 2. Note that a similar intramolecular C−H activation of a mesityl-substituted silyl group in an iridium(III) system was recently reported by Tobita and Ogino.[13]



(2)

3

The structure of **3** was confirmed by X-ray diffraction (Figure 1). The Rh−Si distance of 2.365(7) Å is slightly longer than that reported for *mer*-$RhCl(H)(SiHPh_2)(PMe_3)_3$ (2.313(4) Å),[14] and hydrogen atoms on rhodium and silicon were located and refined to provide Rh−H and Si−H distances of 1.541(3) and 1.456(3) Å, respectively. The small Si−Rh−C(1) angle of 80.16(7)° is indicative of some strain in the five-membered ring. Note that the substitution pattern about Rh is analogous to that in *fac*-$(Me_3P)_3Ir(CH_3)(H)(SiPh_3)$, formed via oxidative addition of $HSiPh_3$ to $(PMe_3)_3IrMe$.[15] Although **3** possesses two stereo centers, only one diastereomer of the product was observed. Compound **3** is considerably more stable than **1** and decomposes over

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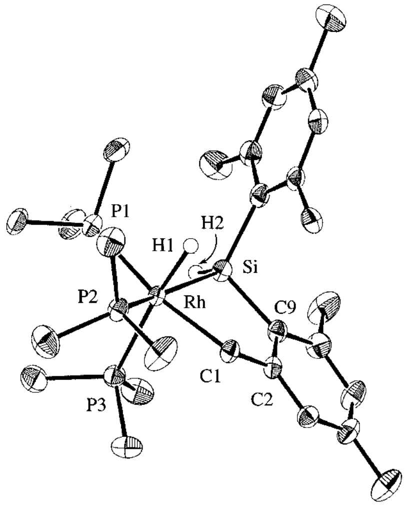

Figure 1. Molecular structure of **3**.

2 days at 80 °C (benzene-d_6) to a variety of uncharacterized products.

As expected, **3** may also be prepared via the reaction of $(Me_3P)_4RhCl$ with $(THF)_2LiSiHMes_2$ and by the reaction of $(Me_3P)_4RhMe$ and H_2SiMes_2. The former reaction may involve the intermediate $(Me_3P)_4RhSiHMes_2$, which is analogous to **1**. However, no intermediates were observed by monitoring the latter reaction at 0 °C in toluene-d_8 by ^{31}P NMR spectroscopy, suggesting that loss of PMe_3 and metalation are extremely rapid at this temperature. Unfortunately, at significantly lower temperatures, the reaction is too slow to be monitored conveniently by NMR spectroscopy. A large excess (ca. 30 equiv) of PMe_3 does not generate $(Me_3P)_4RhSiHMes_2$, as determined by ^1H and ^{31}P NMR spectroscopy.

To investigate the mechanism of the process in eq 2, we examined the reaction of $(Me_3P)_4RhMe$ with 1 equiv of D_2SiMes_2 in toluene. After 30 min at room temperature, exclusive formation of *fac*-$(Me_3P)_3Rh(H)Si(D)(Mes)C_6H_2Me_2CH_2$ was observed (by ^1H and $^2H\{^1H\}$ NMR spectroscopy). Over 1 day, however, scrambling of hydrogen into the Si−H position is observed (by ^1H NMR spectroscopy), and $^2H\{^1H\}$ NMR spectroscopy demonstrated that deuterium had washed into the Rh−H (δ −12.35), $RhCH_2$ (δ 3.40), and *o*-Me (δ 2.84, 2.45, 2.23) positions of **3**. On the basis of integrated intensities for the deuterium resonances, it appears that this deuterium scrambling gives a statistical distribution of deuterium over the Rh−H, Si−H, $RhCH_2$, and *o*-Me sites.

Several mechanisms for hydrogen exchange are possible, some of which are illustrated in Scheme 1. Dissociation of PMe_3 would create a 16-electron intermediate, which could undergo a 1,2-hydrogen shift to produce a silylene (or carbene) intermediate. Alternatively, hydrogen scrambling may occur via oxidative-addition/reductive-elimination cycles involving Si−H and C−H bond activations. Since these two general mechanisms may be distinguished by the phosphine concentration dependence on the rate of scrambling, we simultaneously monitored two scrambling reactions (by $^2H\{^1H\}$ NMR spectroscopy), one of which occurred in the presence of ca. 40 equiv of PMe_3. No difference in the rates of rearrangement was observed ($t_{1/2} \approx 6$ h), implying that phosphine dissociation is not required for hydrogen scrambling. We therefore propose that Si−H and C−H reductive-elimination/oxidative-addition cycles lead to the observed hydrogen migration reactions. Note that C−H bond reductive elimination, coupled with bond rotations in the resulting $-CH_2[3,5\text{-}Me_2(2\text{-}SiHMes)\text{-}C_6H_2]$ ligand, would distribute deuterium to the *o*-Me positions of the mesityl groups. Caulton has recently proposed that exchange of Si−H and Ru−H sites in the 16-electron complex $RuH(SiHPh_2)(CO)(P^tBu_2Me)_2$ takes place via a similar mechanism, albeit at a much faster rate (ca. 1 s^{-1}).[16] Attempts to observe the square-planar intermediates shown in Scheme 1, by monitoring the reaction by ^{31}P NMR spectroscopy at −80 °C, were not successful. Although the relative rates of Si−H vs C−H reductive elimination are difficult to measure with certainty, similar rates are implied by the ^2H NMR signals, all of which appear throughout the equilibration in a ratio commensurate with a statistical distribution of deuterium.

Conclusion

In this work, we have identified relatively simple migration reactions in a rhodium silyl complex. On the basis of the mechanistic information available, it appears that these reactions occur via oxidative-addition/reductive-elimination steps. An alternative mechanism, based on 1,2-migration of hydrogen from silicon to rhodium, seems much less likely, on the basis of the absence of a phosphine dependence on the rate of hydrogen scrambling in **3**. This conclusion is also supported by the known chemical properties reported for transition-metal silyl complexes.[1] Thus, whereas reductive-elimination/oxidative-addition cycles are facile and commonly observed, direct observation of a 1,2-migration reaction that produces a silylene ligand has not yet been reported. Our efforts to observe such migrations are continuing.

Experimental Section

All manipulations were performed under an inert atmosphere using standard Schlenk techniques. Dry, oxygen-free solvents were employed throughout. Diethyl ether, pentane, and THF were distilled from sodium/benzophenone and stored under nitrogen. Benzene-d_6 and toluene-d_8 were distilled from Na/K alloy. The compounds $(Me_3P)_4RhMe$,[7] $(Me_3P)_3RhCl$,[17] $(THF)_2LiSiHMes_2$,[18] and H_2SiMes_2[19] were prepared according to known procedures. The silane D_2SiMes_2 was prepared by the reduction of Cl_2SiMes_2[20] with $LiAlD_4$ in diethyl ether. Diphenylsilane was purchased from Aldrich and used as received. Elemental analyses were performed by the microanalytical laboratory at the University of California, Berkeley. IR samples were prepared as KBr pellets, and all absorptions are reported in units of cm^{-1}. $^2H\{^1H\}$ spectra were

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Scheme 1

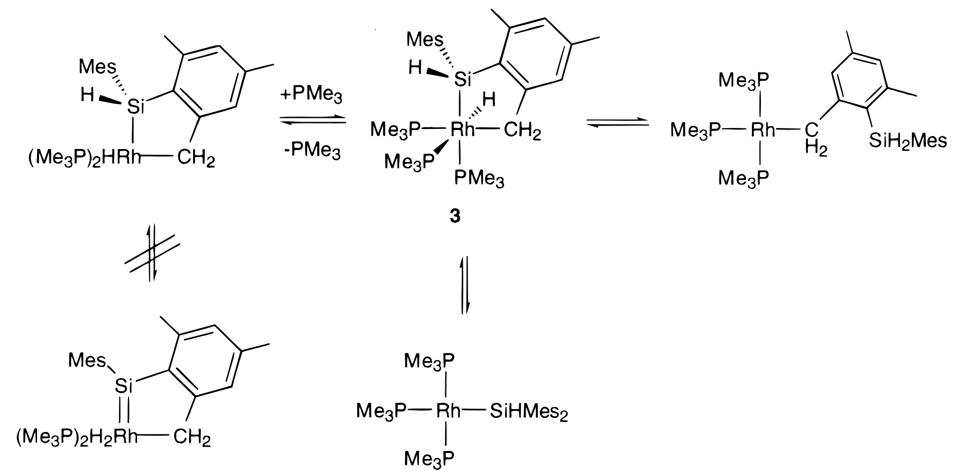

Table 1. Selected Bond Distances (Å) and Angles (deg) for 3

(a) Bond Distances			
Rh−Si	2.3651(1)	C(1)−C(2)	1.514(4)
Rh−P(1)	2.302(1)	C(2)−C(9)	1.402(4)
Rh−P(2)	2.328(1)	Si−C(9)	1.886(3)
Rh−P(3)	2.354(2)	Rh−H(1)	1.514(3)
Rh−C(1)	2.172(3)	Si−H(2)	1.456(3)
(b) Bond Angles			
P(1)−Rh−Si	169.00(8)	C(2)−C(9)−Si	113.3(2)
P(2)−Rh−Si	96.77(3)	Rh−Si−C(9)	103.49(8)
P(3)−Rh−Si	160.62(3)	P(1)−Rh−P(3)	98.13(3)
P(1)−Rh−P(2)	97.84(3)	Si−Rh−C(1)	80.16(7)
P(2)−Rh−P(3)	99.26(3)	Rh−C(1)−C(2)	117.9(2)
P(2)−Rh−C(1)	88.92(8)	P(3)−Rh−C(1)	89.29(7)
P(1)−Rh−Si	90.38(3)	C(1)−C(2)−C(9)	119.4(2)

Table 2. Crystal and Data Collection Parameters for 3

(a) Crystal Parameters	
formula	$RhSiP_3C_{27}H_{40}$
fw	598.60
cryst color, habit	colorless block
cryst size, mm	0.20 × 0.20 × 0.30
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a, Å	9.1148(1)
b, Å	17.8498(1)
c, Å	19.4996(3)
β, deg	100.055(1)
V, Å^3	3123.80(5)
Z	4
D(calc), g cm^{-3}	1.272
μ(Mo Kα), cm^{-1}	7.50
temp, K	151
(b) Data Collection	
diffractometer	Siemens SMART
radiation	Mo Kα (λ = 0.710 69 Å)
scan type	ω (0.30° per frame)
scan rate, s per frame	20
total no. of rflns collected	12 976
no of unique rflns	4872 (R_{int} = 0.027)
no. of observns	3905 ($I > 3.00\sigma(I)$)
(c) Refinement	
rflns/param ratio	9.02
$R(F)$, %	2.3
$R(wF)$, %	3.0
goodness of fit indicator	1.27
max peak in final diff map, e Å^{-3}	0.29
min peak in final diff map, e Å^{-3}	−0.28

obtained with samples dissolved in toluene, and all other spectra were recorded on samples in benzene-d_6 solution.

$(Me_3P)_4RhSiHPh_2$ (1). To a solution of $(PMe_3)_4RhMe$ (0.200 g, 0.474 mmol) in 10 mL of pentane was added a pentane solution (5 mL) of H_2SiPh_2 (0.090 g, 0.488 mmol) over a period of ca. 1 min. The reaction mixture immediately changed from bright yellow to orange, with accompanying evolution of gas. After the mixture was stirred for 15 min, the solvent was removed under reduced pressure to leave an orange residue, which was crystallized from 5 mL of pentane at −78 °C to give 0.173 g (62%) of the product as an orange powder. Anal. Calcd for $RhSiP_4C_{24}H_{47}$: C, 48.82; H, 8.02. Found: C, 48.50; H, 8.23. Mp: 100−102 °C dec. ^1H NMR (benzene-d_6, 400 MHz, 25 °C): δ 1.09 (d, $^2J_{HP} = 4.8$ Hz, 36 H, PMe_3), 5.50 (s, 1 H, Si−H), 7.21 (t, 1 H, Ph), 7.31 (t, 2 H, Ph), 8.03 (d, 2 H, Ph). ^1H NMR (toluene-d_8, 400 MHz, −60 °C): δ 0.89 (s, axial PMe_3), 1.16 (s, equatorial PMe_3), 5.56 (m, SiH), 7.29 (t, Ar H), 7.41 (t, Ar H), 8.10 (d, Ar H). $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.6 MHz): δ 23.5 (br s, PMe_3), 126.5 (s, Ph), 127.0 (s, Ph), 137.7 (s, Ph), 149.7 (s, Ph). $^{31}P\{^1H\}$ NMR (benzene-d_6, 121.5 MHz, 25 °C): δ −26.1 (br s). $^{31}P\{^1H\}$ NMR (toluene-d_8, 121.5 MHz, −60 °C): δ −26.21 (br d, $^1J_{PRh} = 158$ Hz, equatorial PMe_3), −8.43 (m, axial PMe_3). $^{31}P\{^1H\}$ NMR (toluene-d_8, 121.5 MHz, −100 °C): δ −63.2 (s, free PMe_3), −34.5 (br s), −9.2 (br s). IR (KBr): 2909 s, 2856 s, 2005 s, 1324 m, 1292 s, 1256 s, 1151 s, 1124 m, 1092 m, 934 s, 764 m, 678 w, 621 w.

***fac*-$(Me_3P)_3Rh(H)SiH(Mes)C_6H_2Me_2CH_2$ (3).** A toluene solution (15 mL) of $(THF)_2LiSiHMes_2$ (0.342 g, 0.818 mmol) was added to a solution of $(Me_3P)_3RhCl$ (0.300 g, 0.818 mmol) in 15 mL of toluene. Stirring the resulting mixture for 5 h resulted in formation of a light yellow solution and an off-white precipitate. The solvent was removed under reduced pressure, the resulting residue was then extracted into Et_2O (2 × 10 mL). Concentration of the combined extracts to ca. 10 mL and cooling to −78 °C gave 0.361 g (75%) of pure **3**. Anal. Calcd for $RhSiP_3C_{27}H_{40}$: C, 55.10; H, 6.85. Found: C, 54.94; H, 7.01. Mp: 145−150 °C dec. ^1H NMR (benzene-d_6, 400 MHz): δ −9.90 (dq, $^1J_{HRh} = 160$, $^2J_{HP} = 10$ Hz, 1 H, RhH), 0.87 (d, $^2J_{HP} = 6.4$ Hz, 9 H, PMe_3), 1.00 (d, $^2J_{HP} = 5.6$ Hz, 9 H, PMe_3), 1.03 (d, $^2J_{HP} = 6.8$ Hz, 9 H, PMe_3), 2.21 (s, 3 H, Me), 2.32 (s, 3 H, Me), 2.45 (s, 3 H, Me), 2.67 (s, 3 H, Me), 3.03 (s, 3 H, Me), 3.45 (br s, 2 H, CH_2), 5.76 (m, 1 H, Si−H), 6.75 (s, 1 H, Ar H), 6.82 (s, 1 H, Ar H), 7.01 (s, 1 H, Ar H), 7.23 (s, 1 H, Ar H). $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.6 MHz): δ 18.3 (m, PMe_3), 21.2 (s, Me), 21.5 (s, Me), 22.2 (s, Me), 23.7 (m, PMe_3), 23.9 (m, PMe_3), 25.64 (s, Me), 25.7 (s, Me), 34.9 (m, CH_2), 125.9 (s, Ph), 126.2 (s, Ph), 128.2 (s, Ph), 128.6 (s, Ph), 128.8 (s, Ph), 130.0 (s, Ph), 136.1 (s, Ph), 136.6 (s, Ph), 141.9 (s, Ph), 142.1 (s, Ph), 142.4 (s, Ph), 141.9 (s, Ph), 146.8 (s, Ph). $^{31}P\{^1H\}$ NMR (toluene-d_8, 121.5 MHz): δ −21.07 (dt, $^1J_{PRh} = 82.6$ Hz, $^2J_{PP} = 25.9$ Hz), −18.18 (dt, $^1J_{PRh} = 93.9$ Hz), −12.41 (dt, $^1J_{PRh} = 89.1$ Hz). IR (KBr): 2962 s, 2902 s, 2059 m, 1967 m, 1552 w, 1432 m, 1417 m, 1299 m, 1282 m, 943 s, 846 s, 782 s, 598 w, 551 w.

X-ray Crystal Structure Determination for 3. A colorless trapezoidal crystal was mounted on a glass fiber using Paratone N hydrocarbon oil. X-ray data were collected using a Siemens SMART diffractometer with a CCD area detector. The preliminary orientation matrix and unit cell parameters were determined by collecting 60 10-second frames, followed by spot integration and least-squares refinement. A hemisphere of data was collected at a temperature of −112 ± 1 °C using ω scans of 0.30° and a collection time of 20 s per frame. Frame data were integrated using SAINT and corrected for Lorentz and polarization effects. An absorption correction was applied using XPREP ($\mu R = 0.08$, $T_{\max} = 0.90$, $T_{\min} = 0.82$). The 12 976 reflections which were integrated were averaged in point group $2/m$ to yield 4872 unique reflections ($R_{\mathrm{int}} = 0.027$). No decay correction was necessary. The space group was determined to be $P2_1/n$ (No. 14). The structure was solved using direct methods (SIR92) and refined by full-matrix least-squares methods using teXsan software. The non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were included at calculated positions but not refined. The number of variable parameters was 433, giving a data/parameter ratio of 9.02. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.29 and −0.28 e/Å^3: $R = 0.023$, $R_w = 0.030$, GOF = 1.27. Selected bond distances and angles are given in Table 1, and crystal and data collection parameters are given in Table 2.

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Supporting Information Available: Tables of crystal, data collection, and refinement parameters, bond distances and angles, and anisotropic displacement parameters (7 pages). Ordering information is given on any current masthead page.

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