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Ring Opening with Phosphorus–Carbon Bond Cleavage and Coupling in the Reaction of 1,2,3-Triphenylphosphirene (C_2Ph_3P) with $[Ru_3(CO)_{12}]$: X-ray Structure of $[Ru_3(CO)_8(\mu_3-C_4Ph_6P_2)]$

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Summary: The title complex $[Ru_3(CO)_8(\mu_3-\eta^4-PhPCPh-CPhPPhCPhCPh)]$ is obtained along with $[Ru_4(CO)_{11}(\mu_4-PPh)(\mu_4-PhC_2Ph)]$ by reaction of $[Ru_3(CO)_{12}]$ with 1,2,3-triphenylphosphirene in refluxing tetrahydrofuran. The trinuclear cluster was characterized by NMR and IR spectroscopy, and its structure was determined by X-ray analysis. The dark red crystals are monoclinic, $P2_1/c$, $Z = 4$, $a = 15.439(3)$ Å, $b = 12.654(2)$ Å, $c = 23.313(3)$ Å, $\beta = 105.833(9)^\circ$. The structure was solved by direct methods and refined to $R = 0.022$, $R_w = 0.026$ for 3939 reflections with $[F > 4.0\sigma(F)]$. The molecule is a 48-electron cluster which contains two opened and coupled phosphirene rings acting as an 8-electron donor ligand to a $Ru_3(CO)_8$ unit.

Phosphirene rings are potentially very useful precursors to a range of organometallic ligands, acetylenes, phosphinidenes, and various linked systems. Reactions of phosphirene rings $PhPCPh=CPh$ with mononuclear transition metal complexes can lead to insertion of metal fragments like $[M(PR_3)_2]$ ($M = Pd$, $R = Et$; $M = Pt$, $R = Et$, Ph , $dppe$) into a P–C bond of the phosphirene ring.¹ Metal carbonyl complexes in which the phosphirene ring acts as a normal tertiary phosphine have been reported recently. Under forcing conditions, P–C bond cleavage occurs and CO or alkenes are inserted into a pentacarbonyl(phosphirene)metal skeleton ($M = Cr$, Mo , W).² We have recently examined a related heterocycle, 1-phenylphosphole, and found that simple substitution compounds $[M_3(CO)_{12-x}(PhPC_4H_4)_x]$ ($x = 1$ or 2 , $M = Os$) are formed initially with the heterocycle η^1 -coordinated through the P atom,³ which is the commonly found mode of coordination for phospholes. By thermal treatment of these simple substitution products, oxidative addition occurs with P–C bond cleavage to afford ring-opened clusters $[Os_3(CO)_9(PhPC_4H_4)]$ and $[Os_3(CO)_8(PhPC_4H_4)]$ in which the coordination of the P atom can be considered in terms of a μ -phosphido group as part of an eight-electron donating ligand, differently coordinated in the two clusters.

Here we report the results of the reaction of 1,2,3-triphenylphosphirene with $[Ru_3(CO)_{12}]$ in refluxing dry THF. A tetranuclear product was shown by spectroscopic and analytical data to be the pentagonal-bipyramidal *closo*- $[Ru_4(CO)_9(\mu-CO)_2(\mu_4-PPh)(\mu_4,\eta^2-PhC_2Ph)]$, **1**, already described by Carty as a product from the reaction of the phosphinidene complex $[Ru_4(CO)_{13}(\mu_3-PPh)]$ with diphenylacetylene.⁴ However the main product was the new cluster $[Ru_3(CO)_8(C_4Ph_6P_2)]$, complex **2**, which was formed by ring-opening and coupling of two phosphiridene rings. Complex **2** has been characterized by X-ray diffraction analysis, elemental analysis, and NMR and IR spectroscopy.

Results and Discussion

The reaction of $[Ru_3(CO)_{12}]$ with 1,2,3-triphenylphosphirene in refluxing THF yields complexes **1** (12%) and **2** (44%) that are shown in Scheme 1. Complex **1** was shown by analytical and spectroscopic methods to be the same compound that was formed previously by reaction of PhC_2Ph with the phosphinidene cluster $[Ru_4(CO)_{13}(\mu_3-Ph)]$ and structurally characterized.⁴ The phosphiridene is likely to coordinate initially through the P atom in the cluster $[Ru_3(CO)_{11}(C_2Ph_3P)]$, **A** (Scheme 1). Ring-opening would then give compound **B**, which structurally corresponds directly to the known compound $[Os_3(\mu-CO)(CO)_9(\mu_3-MePC_6H_4)]$, formed from $PMePh_2$ and $[Os_3(CO)_{12}]$,⁵ and an iron analogue, $[Fe_3(\mu-CO)(CO)_9(\mu_3-RPCR'=CR'')]$, in which $R = C_6H_4OMe-4$, $R' = H$, and $R'' = Ph$, is also known.⁶

Neither of the suggested intermediates **A** and **B** was detected experimentally. Reaction of **B** with $[Ru_3(CO)_{12}]$ to add a $Ru(CO)_2$ unit would give the known cluster **C**, which has been shown to decarbonylate under our reaction conditions to give the isolated product **1**. The main product is the 48-electron cluster **2**, which we believe to be formed by interception of the proposed intermediate **B** of 1,2,3-triphenylphosphirene. A moderate increase in the yield of **2** was obtained (**2**, 52%; **1**, 10%) by carrying out the reaction in a 2:1 ligand:cluster mole ratio. Spectroscopic and analytical results on **2**

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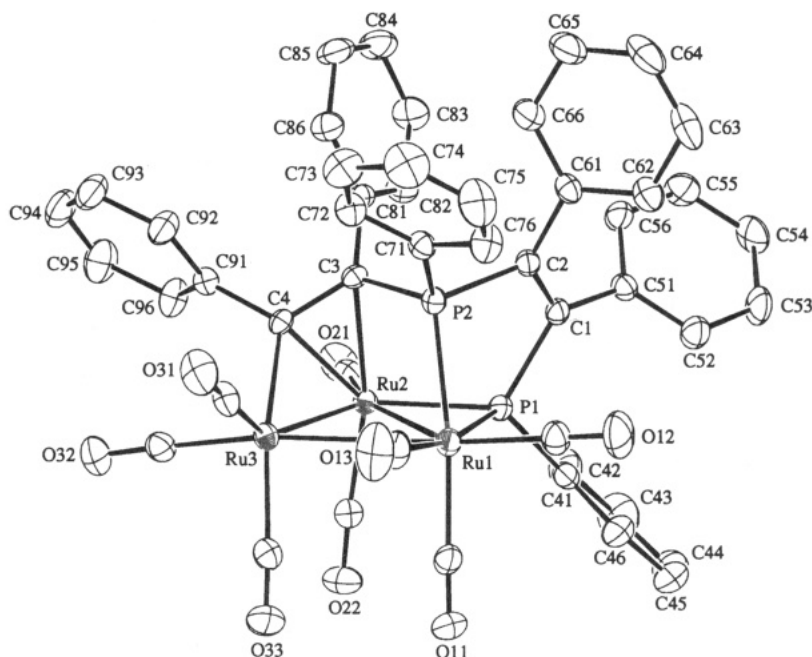
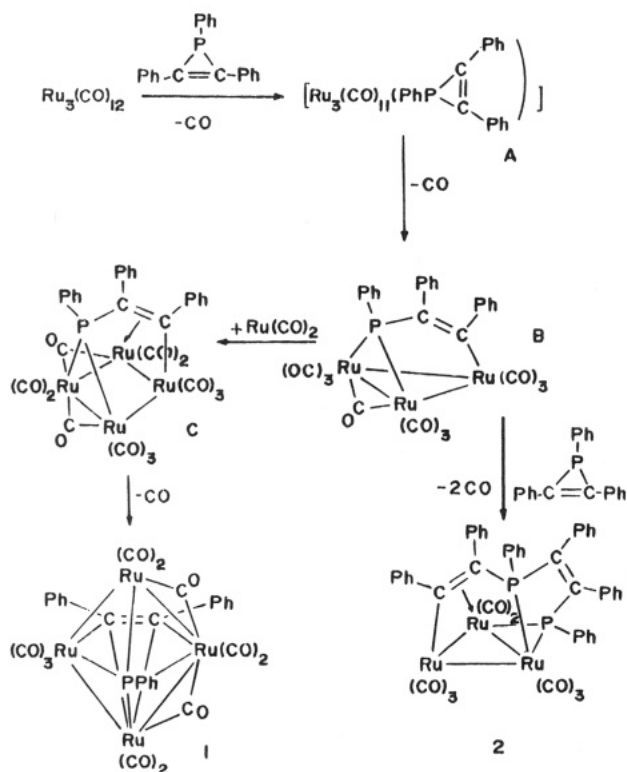


Figure 1. Molecular structure of compound **2** with displacement ellipsoids drawn at 30% probability. In the CO groups both atoms are identically numbered; only O atoms are labeled.

Scheme 1



confirm the stoichiometry $[\text{Ru}_3(\text{CO})_8(\text{C}_4\text{Ph}_6\text{P}_2)]$, while a single-crystal X-ray structure determination has established the mode of bonding of the organic ligand. Both phosphiridene ligands have opened by P–C bond cleavage, and these fragments have coupled head-to-tail through a P–C bond to give the ligand chain, $\text{PhPCPh-CPhPPhCPhCPh}$, bonded as an eight-electron donor. With three Ru–Ru bonds, the 48-electron cluster would be electron precise. The molecular structure of cluster **2** is shown in Figure 1.

There are three distinct types of linkage of the ligand to the metal atoms: a three-electron donating phosphido

Table 1. Crystal Data, Intensity Data Collection Parameters, and Final Refinement Results for Compound 2

Crystal Data	
formula	$\text{C}_{48}\text{H}_{30}\text{O}_8\text{P}_2\text{Ru}_3$
fw	1099.02
color	dark red
morphology	prisms
specimen size (mm^3)	$0.44 \times 0.25 \times 0.17$
T (K)	295(1)
a (Å)	15.439(3)
b (Å)	12.654(2)
c (Å)	23.313(3)
β (deg)	105.833(9)
V (Å ³)	4382(1)
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
Z	4
D_{calc} (g cm^{-3})	1.667
$F(000)$	2176
$\mu(\text{Mo K}\alpha)$ (mm^{-1})	1.148
2θ range for cell (deg)	24.5–31.9
no. of reflns for cell	25
Data Collection	
scan type	$\omega-2\theta$
scan width (deg)	$1.42 + 0.35 \tan \theta$
ω scan speed (deg min^{-1})	8.0
2θ range (deg)	4.0–45.0
hkl range	0–14, 0–13, –24–24
no. of reflns measd	5165
no. of reflns unique	4899
R_{int}	0.046
Refinement (Last Cycle)	
absorption corr	empirical (ΔF)
transmissn factor	0.962–1.141
no. of params refined	550
no. of reflns obsd	3939 [$I > 2\sigma(I)$]
weighting scheme	$w = \sigma(F)^{-2}$
R	0.0217
R_w	0.0257
S (g.o.f.)	1.647
$\Delta\sigma$ max	0.0005
$\Delta\rho$, min, max (e Å^{-3})	–0.27, 0.22

bridge [P(1) bridging Ru(1) and Ru(2)], a two-electron donating tertiary phosphine, P(2), and a three-electron donating μ_2, η^1, η^2 -vinyl bridge [atoms C(3) and C(4)

Table 2. Selected Geometric Parameters (Å, deg) for Compound 2

Bond Lengths			
Ru(1)–Ru(2)	2.8700(5)	Ru(3)–C(31)	1.888(5)
Ru(1)–Ru(3)	3.0482(6)	Ru(3)–C(32)	1.871(5)
Ru(1)–P(1)	2.397(1)	Ru(3)–C(33)	1.950(5)
Ru(1)–P(2)	2.337(1)	P(1)–C(1)	1.858(4)
Ru(1)–C(11)	1.947(5)	P(1)–C(41)	1.814(4)
Ru(1)–C(12)	1.925(5)	P(2)–C(2)	1.850(4)
Ru(1)–C(13)	1.942(5)	P(2)–C(3)	1.820(4)
Ru(2)–Ru(3)	2.6634(6)	P(2)–C(71)	1.813(4)
Ru(2)–P(1)	2.261(1)	C(1)–C(2)	1.348(5)
Ru(2)–C(3)	2.316(4)	C(1)–C(51)	1.474(5)
Ru(2)–C(4)	2.217(4)	C(2)–C(61)	1.493(6)
Ru(2)–C(21)	1.861(5)	C(3)–C(4)	1.429(5)
Ru(2)–C(22)	1.886(5)	C(3)–C(81)	1.516(5)
Ru(3)–C(4)	2.093(4)	C(4)–C(91)	1.496(5)
Bond Angles			
Ru(2)–Ru(1)–Ru(3)	53.39(1)	Ru(1)–Ru(3)–Ru(2)	59.88(1)
Ru(2)–Ru(1)–P(1)	49.87(3)	Ru(1)–Ru(3)–C(4)	88.1(1)
Ru(2)–Ru(1)–P(2)	70.35(3)	Ru(2)–Ru(3)–C(4)	54.0(1)
Ru(3)–Ru(1)–P(1)	103.25(3)	Ru(1)–P(1)–Ru(2)	76.01(3)
Ru(3)–Ru(1)–P(2)	82.02(3)	Ru(1)–P(1)–C(1)	105.1(1)
P(1)–Ru(1)–P(2)	74.90(4)	Ru(2)–P(1)–C(1)	119.1(1)
Ru(1)–Ru(2)–Ru(3)	66.73(1)	Ru(1)–P(2)–C(2)	106.1(1)
Ru(1)–Ru(2)–P(1)	54.12(3)	Ru(1)–P(2)–C(3)	109.4(1)
Ru(1)–Ru(2)–C(3)	81.32(9)	C(2)–P(2)–C(3)	105.2(2)
Ru(1)–Ru(2)–C(4)	90.4(1)	P(1)–C(1)–C(2)	114.6(3)
Ru(3)–Ru(2)–P(1)	120.84(3)	P(2)–C(2)–C(1)	114.1(3)
Ru(3)–Ru(2)–C(3)	78.13(9)	Ru(2)–C(3)–P(2)	93.5(2)
Ru(3)–Ru(2)–C(4)	49.8(1)	Ru(2)–C(3)–C(4)	67.9(2)
P(1)–Ru(2)–C(3)	93.3(1)	P(2)–C(3)–C(4)	118.6(3)
P(1)–Ru(2)–C(4)	126.0(1)	Ru(2)–C(4)–Ru(3)	76.3(1)
C(3)–Ru(2)–C(4)	36.7(1)	Ru(2)–C(4)–C(3)	75.4(2)
Ru(3)–C(4)–C(3)	125.8(3)		

bridging Ru(2) and Ru(3)]. The coordinated C(3)–C(4) bond is 1.429(5) Å, whereas the noncoordinated bond C(1)–C(2) is shorter, 1.348(5) Å (see Tables 1 and 2).

It is worth noting that the P(1)–C(1) bond lengths of 1.858(4) Å and P(2)–C(2) of 1.850(4) Å are elongated presumably due to the fact that the C(1)–C(2) double bond is not coordinated to the metal framework and also to the strain created by fitting the six-atom ligand chain around the three metal centers; this could also justify the notorious variation of metal–metal distances (Ru(1)–Ru(2), 2.8700(5) Å; Ru(1)–Ru(3), 3.0482(6) Å; and Ru(2)–Ru(3), 2.6634(6) Å) even though they must be considered as normal Ru–Ru single bonds as were found in a series of polyphosphido ruthenium clusters.⁷ The unsymmetrical nature of the electron distribution in the compound is also indicated by the very unsymmetrical phosphido bridge: Ru(1)–P(1), 2.307(1) Å, and Ru(2)–P(1), 2.261(1) Å (see Table 3).

Experimental Section

[Ru₃(CO)₁₂] was purchased from Strem Chemicals Inc. 1,2,3-Triphenylphosphine was synthesized by the published method.⁸ All solvents were dried by conventional techniques and distilled under nitrogen prior to use. NMR spectra were obtained on a Bruker AM-300 instrument, and IR spectra (cyclohexane solutions) were recorded on a Nicolet 5DXC FTIR spectrometer.

Preparation of Complex 2. To a refluxing solution of 200 mg of [Ru₃(CO)₁₂] (0.31 mmol) in dried THF (50 mL) under nitrogen was added 84 mg (0.31 mmol) of 1,2,3-triphenylphosphine. After 24 h, the IR spectrum showed that no [Ru₃(CO)₁₂] remained and the reaction was stopped. Removal of

Table 3. Fractional Coordinates and Equivalent Isotropic Displacement Parameters^a (Å²)

atom	x	y	z	B _{eq}
Ru(1)	0.18309(2)	-0.14244(3)	-0.18093(2)	2.68(2)
Ru(2)	0.32969(2)	-0.11395(3)	-0.07574(1)	2.27(1)
Ru(3)	0.20466(2)	0.03622(3)	-0.09042(2)	2.62(2)
P(1)	0.31664(7)	-0.24569(8)	-0.14310(5)	2.54(5)
P(2)	0.15656(7)	-0.24045(8)	-0.10247(5)	2.39(5)
O(11)	0.2707(3)	-0.0042(3)	-0.2583(1)	5.5(2)
O(12)	0.1104(3)	-0.3118(3)	-0.2745(2)	6.4(2)
O(13)	0.0004(3)	-0.0296(3)	-0.2101(2)	7.0(2)
O(21)	0.5085(2)	-0.1484(3)	0.0134(2)	4.8(2)
O(22)	0.4234(2)	0.0422(3)	-0.1373(1)	4.8(2)
O(31)	0.0152(2)	0.0813(3)	-0.0834(2)	5.7(2)
O(32)	0.2772(2)	0.2130(3)	-0.0042(2)	5.5(2)
O(33)	0.2154(3)	0.1883(3)	-0.1912(2)	6.6(2)
C(1)	0.2761(3)	-0.3774(3)	-0.1264(2)	2.6(2)
C(2)	0.1993(3)	-0.3751(3)	-0.1094(2)	2.6(2)
C(3)	0.2270(2)	-0.1901(3)	-0.0320(2)	2.2(2)
C(4)	0.2334(2)	-0.0783(3)	-0.0231(2)	2.2(2)
C(11)	0.2373(3)	-0.0536(4)	-0.2299(2)	3.6(2)
C(12)	0.1366(3)	-0.2488(4)	-0.2404(2)	3.7(2)
C(13)	0.0707(4)	-0.0644(4)	-0.1967(2)	4.1(2)
C(21)	0.4384(3)	-0.1374(3)	-0.0185(2)	3.0(2)
C(22)	0.3864(3)	-0.0140(4)	-0.1134(2)	3.2(2)
C(31)	0.0855(3)	0.0647(3)	-0.0885(2)	3.7(2)
C(32)	0.2501(3)	0.1446(4)	-0.0360(2)	3.5(2)
C(33)	0.2114(3)	0.1307(4)	-0.1551(2)	4.1(2)
C(41)	0.3980(3)	-0.2701(3)	-0.1849(2)	3.1(2)
C(42)	0.4858(4)	-0.2896(4)	-0.1535(2)	4.9(3)
C(43)	0.5501(4)	-0.3149(5)	-0.1838(3)	6.6(3)
C(44)	0.5246(5)	-0.3207(5)	-0.2445(4)	6.9(4)
C(45)	0.4383(5)	-0.2999(5)	-0.2764(3)	6.3(3)
C(46)	0.3751(3)	-0.2740(4)	-0.2463(2)	4.6(2)
C(51)	0.3286(3)	-0.4748(3)	-0.1258(2)	2.7(2)
C(52)	0.3493(3)	-0.5130(4)	-0.1763(2)	4.0(2)
C(53)	0.3957(4)	-0.6070(4)	-0.1745(2)	4.7(2)
C(54)	0.4209(3)	-0.6645(4)	-0.1235(2)	4.6(2)
C(55)	0.4026(3)	-0.6275(4)	-0.0725(2)	4.2(2)
C(56)	0.3567(3)	-0.5338(3)	-0.0740(2)	3.6(2)
C(61)	0.1482(3)	-0.4711(3)	-0.1006(2)	2.9(2)
C(62)	0.1249(3)	-0.5444(4)	-0.1464(2)	4.0(2)
C(63)	0.0732(3)	-0.6316(4)	-0.1412(3)	5.3(3)
C(64)	0.0440(4)	-0.6450(4)	-0.0915(3)	5.9(3)
C(65)	0.0673(4)	-0.5741(4)	-0.0461(3)	5.6(3)
C(66)	0.1195(3)	-0.4868(4)	-0.0503(2)	4.4(2)
C(71)	0.0402(3)	-0.2558(3)	-0.1016(2)	2.9(2)
C(72)	0.0054(3)	-0.2071(4)	-0.0600(2)	3.6(2)
C(73)	-0.0840(3)	-0.2194(4)	-0.0614(2)	5.1(3)
C(74)	-0.1395(3)	-0.2781(5)	-0.1049(3)	6.2(3)
C(75)	-0.1080(4)	-0.3244(5)	-0.1478(3)	6.0(3)
C(76)	-0.0183(3)	-0.3142(4)	-0.1471(2)	4.4(2)
C(81)	0.2526(3)	-0.2690(3)	0.0188(2)	2.5(2)
C(82)	0.3292(3)	-0.3293(3)	0.0291(2)	3.2(2)
C(83)	0.3506(3)	-0.4037(4)	0.0743(2)	4.2(2)
C(84)	0.2949(4)	-0.4183(4)	0.1107(2)	4.7(2)
C(85)	0.2187(4)	-0.3573(4)	0.1021(2)	4.6(2)
C(86)	0.1971(3)	-0.2829(4)	0.0562(2)	3.6(2)
C(91)	0.2565(3)	-0.0398(3)	0.0399(2)	2.5(2)
C(92)	0.1889(3)	-0.0307(4)	0.0684(2)	4.1(2)
C(93)	0.2047(4)	0.0094(4)	0.1251(2)	4.8(3)
C(94)	0.2888(4)	0.0407(4)	0.1552(2)	5.0(3)
C(95)	0.3570(3)	0.0339(4)	0.1286(2)	5.2(3)
C(96)	0.3403(3)	-0.0065(4)	0.0709(2)	4.1(2)

^a Equivalent isotropic displacement parameters are as follows: $B_{eq} = \frac{1}{3} \pi^2 [(aa^*)^2 U_{11} + (bb^*)^2 U_{22} + (cc^*)^2 U_{33} + 2aa^*bb \cos \gamma U_{12} + 2aa^*cc \cos \beta U_{13} + 2bb^*cc \cos \alpha U_{23}]$.

the solvent under reduced pressure and TLC of the orange-red residue (SiO₂, hexane/CH₂Cl₂ eluant, 1:1) gave a red-orange band characterized as [Ru₄(CO)₁₁(PPh)(PhC₂Ph)], **1**, (17 mg, 12%), as dark-red crystals, and a deep-orange band characterized as [Ru₃(CO)₈(C₄Ph₆P₂)], **2**, (62 mg, 44%) as dark-red crystals from hexane. **1**: IR (ν (CO), cm⁻¹) 2087 s, 2056 vs, 2045 vs, 2034 vs, 2021 s, 2008 m, 1987 m, 1975 w. ³¹P-{¹H} NMR (δ , ppm, C₇D₈) +350. Anal. Calcd (found) for C₃₁H₁₅O₁₁PRu₄: C, 37.27 (37.61); H, 1.52 (1.61). **2**: IR (ν (CO), cm⁻¹) 2073 vs, 2046 s, 2013 s, 1997 m, 1991 m, 1964 m, 1935

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m. $^{31}\text{P}\{^1\text{H}\}$ NMR (δ , ppm, CDCl_3) +249.3 (d, $J = 10.5$ Hz), +79.9 (d, $J = 10.5$ Hz). Anal. Calcd (found) for $\text{C}_{48}\text{H}_{30}\text{O}_8\text{P}_2\text{Ru}_3$: C, 52.45 (52.87); H, 2.75 (2.88).

Crystallography. Crystal data, intensity data collection parameters and final refinement results are summarized in Table 1. Selected geometric parameters are given in Table 2.

All measurements were carried out on a Rigaku AFC-7S diffractometer, using graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å). Unit-cell parameters were obtained from the least-squares fit of the setting angles of 25 automatically centered reflections. Intensities were recorded using fixed ω scan speed. Weak reflections [$I < 15\sigma(I)$] were rescanned up to four times, with accumulated counts. The check reflections, monitored every 150 measurements, showed an average decay of 8.9%. The data were scaled using the check reflections and corrected for Lorentz and polarization effects. In the latter stages of refinement an empirical absorption correction⁹ was applied.

The space group was uniquely determined by the systematic absences. The structure was solved by direct methods¹⁰ and refined on F by full-matrix least-squares. Non-hydrogen atoms were refined anisotropically, while H atoms were placed in calculated positions (C–H, 0.96 Å) and assigned fixed coordinates and fixed isotropic displacement parameters [$B_{\text{iso}} = 1.2B_{\text{eq}}(\text{C})$].

Data collection and cell refinement were carried out using the MSC/AFC Diffractometer Control program.¹¹ All other

calculations and drawings were made using the teXsan software package.¹² Neutral-atom scattering factors were taken from ref 13, anomalous scattering corrections from ref 14, and mass absorption coefficients from ref 15.

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Supporting Information Available: Tables of positional and displacement parameters for the hydrogen atoms, anisotropic displacement parameters, bond lengths and angles, and least-squares mean planes (10 pages). Ordering information is given in any current masthead page.

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