

the fact that for sulfur-33  $I = 3/2$ , then we obtain

$$\pi v^{1/2} = R_1 = 1/T_1 = 0.1(eqQ/\hbar)^2\tau_c \quad (2)$$

where  $eq$  is the electric field gradient at the sulfur nucleus and  $eQ$ , a fixed constant, is the nuclear quadrupole moment.  $\tau_c$  is the molecular correlation time and is a measure of how rapidly the molecule moves from one orientation to an appreciably different one in its environment. For nonviscous liquids at room temperature  $\tau_c$  is usually about  $10^{-12}$  s. The value of the sulfur-33 quadrupole coupling constant ( $e^2qQ/\hbar$ ) ranges from about 2 Hz to about 5 MHz. Thus for highly symmetric environments such as exist in sulfones, we expect relaxation times of 100–900 ms or line widths of a few hertz. For highly unsymmetric environments we expect  $T_1$  values of 100  $\mu$ s or less and line widths of several kilohertz or more (see ref 10, Chapter 4 for more details).

Since  $\tau_c$  is temperature dependent ( $\tau_c = \tau_0 \exp(v/(RT))$ ), we can obtain sharper sulfur-33 resonance lines by working at elevated temperatures and, wherever possible, by using low-viscosity solvents. For example,  $\text{Me}_2\text{SO}$  is a poor solvent because it has a high viscosity, which leads to broader lines.

In the NMR measurements presented here we have used relatively high temperatures (30–45 °C) and low-viscosity solvents. The spectra were obtained at 15.339 MHz on a JEOL FX-200 spectrometer using 15-mm-diameter sample tubes or at 20.710 MHz on an IBM-WP-270 spectrometer using 10-mm-diameter sample tubes. In most cases, for the 10-mm sample tubes, about 1 g of sample was dissolved in about 1.5 mL of solvent. One-half hour or less of signal averaging was usually enough to give a signal-to-noise ratio,  $S/N$ , of 20/1 or better. In all cases proton decoupling was used to remove residual, long-range proton-sulfur spin-spin coupling.

The chemical-shift and line-width values that we obtained are summarized in Table I. For comparison, we have also listed in Table I the chemical-shift and line-width values obtained in ref 4 and 5. The agreement between the chemical shift values is reasonably good, especially considering the rather broad lines observed in the two earlier references.

We have recorded sulfur-33 spectra for  $(\text{CH}_3)_2\text{SO}_2$  both with and without proton coupling. The proton-decoupled spectrum at 40 °C has a line width of 6.8 Hz. The proton-coupled sulfur-33 spectrum has a line width of about 15 Hz. Since the protons are all equivalent, one might expect the sulfur-33 spectrum to be a heptet with a splitting of  $J_{\text{S-H}}$  Hz between each of the lines in the multiplet. Due to the width of the individual lines the fine structure is not observed. Based on the width of the observed line at half-height one expects a value of  $J_{\text{S-H}}$  of about 3 Hz for dimethyl sulfone.

On the basis of the present work and that in the literature<sup>3-6</sup> it is clear that four-coordinate sulfur, such as in sulfones and sulfonic acid derivatives, has both line widths and chemical shifts that are quite different from those in sulfoxides, sulfides, and thiophenes. Consequently it is quite clear that the structure of 1 must be that depicted and not 2.

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**Registry No.**  $\text{CS}_2$ , 75-15-0;  $\text{PhN}=\text{S}(\text{O})(\text{CH}_3)_2$ , 56157-97-2;  $\text{CH}_3\text{CH}=\text{CHS}(\text{O})_2\text{Ph}$ , 28975-80-6;  $\text{Ph}_2\text{S}(\text{O})_2$ , 127-63-9;  $\text{CH}_2\text{CH}_2\text{O}-\text{CH}_2\text{CH}_2\text{S}(\text{O})_2$ , 107-61-9;  $\text{CH}_3-p-\text{C}_6\text{H}_4\text{S}(\text{O})_2\text{CO}_2\text{CH}_3$ , 60279-10-9;  $\text{CH}_3-p-\text{C}_6\text{H}_4\text{S}(\text{O})\text{OCO}_2\text{CH}_3$ , 93714-76-2;  $(\text{PhS}(\text{O})_2)_2\text{CH}_2$ , 3406-02-8;  $\text{CH}_3-p-\text{C}_6\text{H}_4\text{S}(\text{O})_2\text{CH}_3$ , 3185-99-7;  $\text{PhS}(\text{O})_2\text{CH}_3$ , 3112-85-4;  $\text{CH}_3\text{S}(\text{O})_2\text{CH}_2\text{CO}_2\text{CH}_3$ , 62020-09-1;  $(\text{CH}_3)_2\text{S}(\text{O})_2$ , 67-71-0;  $\text{H}_2\text{C}=\text{CHCH}_2\text{S}(\text{O})_2\text{Ph}$ , 16212-05-8;  $\text{PhCH}_2\text{S}(\text{O})_2\text{CO}_2\text{CH}_3$ , 93714-77-3;  $\text{Na}_2\text{SO}_4$ , 7757-82-6;  $\text{CH}_3\text{SCH}_2\text{S}(\text{O})_2\text{Ph}$ , 59431-14-0;  $\text{CH}_2\text{CH}=\text{CHCH}_2-\text{S}(\text{O})_2$ , 77-79-2;  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{S}(\text{O})_2$ , 126-33-0;  $\text{CH}_3-p-\text{C}_6\text{H}_4\text{S}(\text{O})_2\text{NH}(\text{NH}_2)$ , 1576-35-8;  $\text{CH}_3-p-\text{C}_6\text{H}_4\text{S}(\text{O})_2\text{N}(\text{CH}_3)(\text{NO})$ , 80-11-5;  $\text{CH}_3-p-\text{C}_6\text{H}_4\text{S}(\text{O})_2\text{CN}$ , 19158-51-1;  $(\text{CH}_3)_2\text{SO}$ , 67-68-5;  $\text{CH}=\text{CHC}-\text{H}=\text{CHS}$ , 110-02-1;  $^{33}\text{S}$ , 14257-58-0.

## Raman Spectroscopic Study of Acetylene on Supported Rhodium Catalysts

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There exists a relatively large body of experimental observation concerning the interaction of small hydrocarbon molecules with group 8 metals.<sup>1,2</sup> Synthetic chemists have amassed a wealth of data concerning the distribution of reaction products for hydrogenation reactions on these metals which indicate that cis addition to unsaturated adsorbates is predominant.<sup>3,4</sup> This information is to be contrasted with the microscopic information obtained by using conventional surface science experimental techniques which have detected surface intermediates not having obvious preference for cis vs. trans products.<sup>1</sup> Surface hydrocarbon chemistry has been probed by a wide variety of methods including electron energy loss spectroscopy (EELS),<sup>5</sup> low-energy electron diffraction (LEED),<sup>6</sup> secondary ion mass spectrometry (SIMS),<sup>7</sup> ultraviolet photoelectron spectroscopy (UPS),<sup>8</sup> and near edge X-ray fine structure spectroscopy (NEXAFS).<sup>9</sup> All of these experimental techniques require ultrahigh vacuum conditions and consequently are not necessarily sensitive to the species of importance under catalytically relevant conditions. Surface-sensitive probes that can operate under higher pressures and coverages are clearly desirable. Optical spectroscopies, such as Raman spectroscopy, provide such a probe since photons rather than charged particles interact with the surface, and they are not scattered efficiently by the gas phase. Surface-enhanced Raman spectra of organic adsorbates on catalytically important group 8 metals have recently been described.<sup>10</sup> This paper reports enhanced Raman spectra of acetylene on a supported rhodium catalyst and the identification of  $\sigma_2\pi-\text{C}_2\text{H}_2(\text{ads})$  on this surface under conditions in which it has

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(11) Rhodium supported on high-purity alumina was prepared by the hydrogen reduction of rhodium trichloride<sup>11</sup> by utilizing a high-vacuum combination reactor and Raman cell<sup>10</sup> developed in this laboratory. Reduction occurred at 150 °C under 100 torr of  $\text{H}_2$ ; after reduction the sample temperature was maintained at 150 °C with continuous pumping so that a final base pressure of  $5 \times 10^{-7}$  torr was achieved. After cooling to room temperature, acetylene was admitted to the cell and Raman spectra were obtained with the 488.0-nm line of an  $\text{Ar}^+$  ion laser. The size distribution of metal crystallites on supported rhodium prepared in this manner has been investigated by electron microscopy. At 10% (wt %) Rh loading the average particle is present as a two-dimensional raft with a diameter of approximately 2.6 nm.<sup>12</sup> Transmission infrared spectroscopy of CO adsorbed on this kind of surface (10% Rh/ $\text{Al}_2\text{O}_3$ ) yields spectra that greatly resemble those obtained on a Rh(111) surface,<sup>13</sup> indicating that the distribution of adsorption sites, at least for CO, is the same on these two surfaces.

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Table I. Comparison of Group Frequencies

$C_2H_2$		$C_2H_2$ on Pt(111) (EELS) (140 K)	$[Os_3(CO)_9-(CCH_2)]^b$	$Co_2(CO)_6^-C_2H_2^d$	$CH_3C-Co_3(CO)_9^e$	$C_2H_2$ on 10%	Rh
$\Sigma_g^+$	$^1A_u$						
3374	<i>a</i>	3000	2986	3116	2888	<i>a</i>	$\nu_{CH}(s)$
1974	1380	1424	1331	1402	1161	1476	$\nu_{CC}$
3289	3020	<i>a</i>	3047	3086	2930	<i>a</i>	$\nu_{CH}(as)$
612	1049	760	1470	894	1420	1098	$\delta_{CH}(s)$
					1356		
730	<i>a</i>	<i>a</i>	1051	768	1004	981	$\delta_{CH}(as)$
			963				
			811				
2701	<i>a</i>	2224	2180	2359	<i>a</i>	<i>a</i>	$\nu_{CD}(s)$
1762	1310	1248	1282	1346	1161	1408 (1451)	$\nu_{CC}$
2439	2215	<i>a</i>	2140	2297	2192	<i>a</i>	$\nu_{CD}(as)$
537	844	568	760	751.4	828	849.2 (1081)	$\delta_{CD}(s)$
					1031		
505	<i>a</i>	<i>a</i>	742	602	1002	717 (982)	$\delta_{CD}(as)$

<sup>a</sup>  $\sigma_2$ ,  $\pi$ .<sup>23</sup> <sup>b</sup> Vinylidene.<sup>15</sup> <sup>c</sup> Ethylidyne.<sup>19</sup> <sup>d</sup>  $\sigma_2$ ,  $\pi$ .<sup>18</sup> values in parentheses are for  $^{13}C$ .

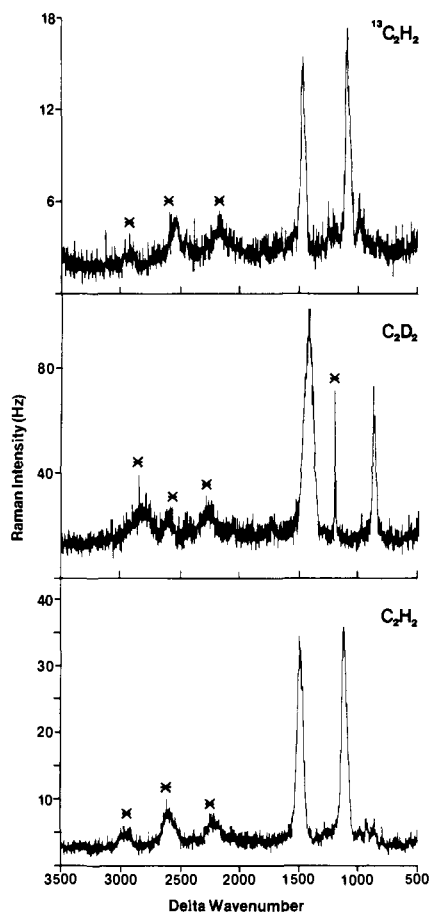


Figure 1. Raman spectra of acetylenes on supported rhodium, pressure 47 torr, laser line 4880 Å, laser power 200mW; the peaks marked with asterisks correspond to combinations of the intense peaks.

been surmised that  $C_2H_2$  is present as an alkylidyne species on single-crystal rhodium surfaces.<sup>1</sup>

Raman spectra of  $C_2H_2$ ,  $C_2D_2$ , and  $^{13}C_2H_2$  have been measured at room temperature and saturation coverage (47 torr) on alumina-supported rhodium. These spectra are presented in Figure 1. Isotope labeling enables us to assign the most intense bands at 1476 and 1098  $cm^{-1}$  to CC stretching and CH bending motions, respectively. Of these the correct assignment of the  $\nu_{CC}$  vibration is of paramount importance since it provides information about the bond order and orientation of the CC unit.<sup>15</sup> In the lower frequency region, there is a very small peak at 981  $cm^{-1}$  which exhibits an isotopic shift characteristic of a C-H motion.<sup>16</sup> This

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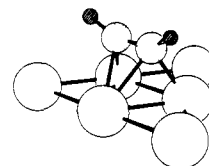


Figure 2. Representation of acetylene bound to a 3-fold site.

is tentatively assigned to the antisymmetric bending mode,  $\delta_{CH}(as)$ . Vibrations in chemisorbed adsorbates are traditionally assigned by analogy to structurally characterized metal clusters. Table I shows the vibrational assignments in several model cluster compounds as well as the observed vibrations of  $C_2H_2$  on a single-crystal Pt surface and our data on supported rhodium. The vibrational data for  $C_2H_2$  chemisorbed is consistent with orientation of the C-C bond parallel to the metal surface and either perpendicular to  $Rh_2$  unit, i.e., a 2-fold site, for which the cluster analogue is  $\sigma_2\pi-(C_2H_2)Co_2(CO)_6$  or interacting with a  $Rh_3$  3-fold site as exemplified by  $Os_3(CO)_{10}(PhC_2Ph)$ .<sup>20</sup> Closer matching of our Raman data with the group frequencies in  $(C_2H_2)Co_2(CO)_6$  provides a basis for a slight preference for the location of  $C_2H_2$  adsorbed on a 2-fold surface site. The chemically important conclusions, however, are that, on alumina-supported rhodium, the C-C bond is essentially parallel to the metal surface, that the C-C bond angle is decreased from the 180° in free acetylene, and that the CC bond order is approximately 1.9 (see Figure 2). The low C-C stretching frequency, smaller than that of ethylene, is taken as evidence that the actual bond order is less than 2. This argues for a tilted arrangement to maximize the  $\pi$  "back-bonding" to a third surface atom. The surface hydrocarbon species observed by Raman spectroscopy is tightly bound since no significant changes in signal intensity or peak position occur on evacuating the cell to  $5 \times 10^{-7}$  torr. It is also chemically active as the intensity of the spectrum is diminished upon addition of 100 torr of hydrogen at 150 °C.

Stability of the  $\sigma_2\pi-C_2H_2$  on supported Rh at 300 K is in striking contrast to the facile rearrangement from  $\sigma_2\pi-C_2H_2$  to a surface alkylidyne at 270 K on bulk, single-crystal Rh(111).<sup>1</sup> The persistence of this surface species at higher temperatures provides a straightforward and logical pathway to the observed cis-1,2 addition of hydrogen or deuterium to the C-C triple bond in alkynes on supported metal catalysts. It is considerably more difficult to accommodate the established stereo- and regiospecificity of supported metal catalysts in terms of a surface alkylidyne species. The ability of the Raman technique to characterize

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various adsorbates on supported catalysts is indicated by spectra of  $\text{CH}_3\text{C}\equiv\text{CCH}_3$ ,  $\text{CF}_3\text{C}\equiv\text{CCF}_3$ , and  $\text{CF}_3\text{C}\equiv\text{CH}$ <sup>21</sup> in which  $\nu_{\text{CC}}$  modes in analogous  $\sigma_2\pi$  surface species are assigned to bands at 1576, 1540, and 1572  $\text{cm}^{-1}$ , respectively.<sup>22</sup> At least three mechanisms may account for the difference in surface species on the single crystal and the supported metal: (1) metal-support interactions change the nature of the binding of the adsorbate to the metal; (2) rearrangement and hydrogen transfer in the adsorbate require the cooperation of several neighboring sites and these sites are blocked at saturation coverage; (3) the finite size of the metal crystallite leads to changes in the electronic structure of the metal so that the adsorbate binding is fundamentally different.

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**Registry No.** Acetylene, 74-86-2; rhodium, 7440-16-6.

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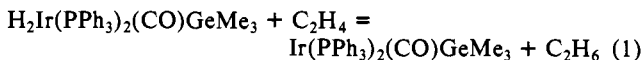
### Phosphinoalkylsilyl Complexes. 6.<sup>1</sup> Isolation of a Silyl Complex of Iridium(I). Crystal and Molecular Structure of Dicarbonyl(triphenylphosphine)-[(diphenylphosphino)ethyl]dimethylsilyl]iridium

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Hydrometalation of dicobalt octacarbonyl with triorganosilanes, -germanes, or -stannanes gives access<sup>2</sup> to thermally stable products  $\text{R}_3\text{MCo}(\text{CO})_4$  which may be regarded as heavy-element congeners of the extremely reactive<sup>3</sup> tetracarbonylcobalt alkyls  $\text{RCo}(\text{CO})_4$  ( $\text{R} = \text{Me, Et, etc.}$ ). By contrast, although alkyl- $\text{M}^{\text{I}}$ (I) derivatives are known<sup>4,5</sup> for both rhodium and iridium, the extensive family of silyl, germyl, or stannyl compounds formed by these two metals are almost exclusively  $\text{M}^{\text{III}}$  species.<sup>6</sup> Exceptions appear to be provided only by a series of complexes  $\text{R}_3\text{M}^{\text{I}}\text{Ir}(\text{CO})_3(\text{PPh}_3)$  ( $\text{M} = \text{Ge, R} = \text{Ph; M} = \text{Sn, R} = \text{Me or Ph}$ ) and  $\text{Me}_3\text{SnRh}(\text{CO})_2(\text{PPh}_3)_2$  (**1**), synthesized from anionic  $\text{M}^{\text{I}}$  precursors by Collman et al.,<sup>7</sup> and by  $\text{Me}_3\text{GeIr}(\text{CO})(\text{PPh}_3)_2$  (**2**), a compound isolated by Glockling and Wilbey<sup>8</sup> through reaction of ethylene with a dihydrido-iridium(III) complex, eq 1. We have recently em-



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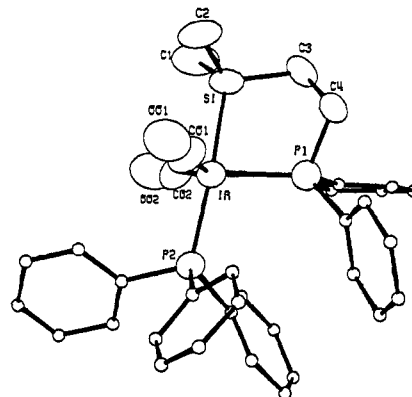
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**Figure 1.** ORTEP drawing of molecule 4. Selected bond distances and angles: Ir-Si, 2.454 (6); Ir-P(1), 2.342 (5); Ir-P(2), 2.371 (5); Ir-CO(1), 1.873 (19); Ir-CO(2), 1.795 (24) Å. Si-Ir-P(1), 81.9 (2)°; Si-Ir-P(2), 175.7 (2)°; P(1)-Ir-P(2), 101.7 (2)°; Si-Ir-CO(1), 87.5 (8)°; Si-Ir-CO(2), 84.1 (8)°; P(1)-Ir-CO(1), 108.2 (7)°; P(1)-Ir-CO(2), 119.6 (6)°; P(2)-Ir-CO(1), 93.5 (8)°; P(2)-Ir-CO(2), 92.0 (8)°.

phasized<sup>1</sup> that corresponding silyl- $\text{M}^{\text{I}}$ (I) compounds have remained unknown although such species are of potential significance in relation to silyl coupling reactions<sup>9</sup> and in spite of the fact that routes to silyl complexes of the platinum-group elements have been extensively researched<sup>10</sup> in relation to metal-catalyzed olefin hydrosilylation. Against this background we wish to describe the formation of a chelate-stabilized silyl-iridium(I) complex via reductive elimination from Ir(III): the stereochemistry of the product has also been established by an X-ray structure determination.

We concluded on the basis of preliminary experiments<sup>11</sup> that UV irradiation was without effect on the *cis*-dihydrido-iridium(III) complex  $[\text{Ir}(\text{PPh}_2\text{CH}_2\text{CH}_2\text{SiMe}_2)(\text{PPh}_3)(\text{CO})_2]$  (**3**). In fact prolonged photolysis (250 h, 450-W medium-pressure Hg lamp) in an evacuated quartz tube of a THF solution of compound **3**, which results in extensive decomposition, is accompanied by conversion in low yield (<30%) to a product for which IR and <sup>31</sup>P NMR data<sup>12</sup> were compatible with formulation as an iridium(I) species  $[\text{Ir}(\text{PPh}_2\text{CH}_2\text{CH}_2\text{SiMe}_2)(\text{PPh}_3)(\text{CO})_2]$  (**4**). Accordingly a similar reaction performed under an atmosphere of CO gas afforded compound **4** in over 80% yield in only 8 h. The same complex is recovered in ca. 80% yield after filtration and extraction into hexane following treatment of the precursor<sup>8</sup>

$[\text{Ir}(\text{PPh}_2\text{CH}_2\text{CH}_2\text{SiMe}_2)(\text{PPh}_3)(\text{CO})(\text{H})(\text{Cl})]$  (**5**) in THF solution with  $\text{MeMgCl}$  then CO gas. Careful recrystallization (ether/hexane mixture) provided colorless needles of compound **4** suitable for X-ray diffraction.<sup>12</sup> The crystal structure determination confirms the geometry proposed on the basis of the spectral data (ORTEP drawing, Figure 1). The molecule possesses no symmetry (centrosymmetric space group), adopting a five-coordinate arrangement in which Si is axial, trans to the triphenylphosphine P atom with the two CO ligands in the equatorial plane; bond angles are close to those in an idealized trigonal bipyramid. The Ir-Si bond length at 2.454 (6) Å is rather longer

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(12) Data for compound **4**. Anal. Calcd for  $\text{C}_{36}\text{H}_{35}\text{IrO}_2\text{P}_2\text{Si}$ : C, 55.20; H, 4.51. Found: C 54.52; H, 4.40. IR (KBr pellet)  $\nu_{\text{CO}}$  1960, 1912  $\text{cm}^{-1}$ . NMR: <sup>1</sup>H ( $\text{C}_6\text{D}_6$ , 250 MHz)  $\delta$  0.999 (s, 3 H), 0.992 (s, 3 H, SiCH<sub>3</sub>), 0.64 (m, 2 H, SiCH<sub>2</sub>), 2.28 (m, 2 H, PCH<sub>2</sub>), 6.80-7.31 (m, 25 H, PH<sub>2</sub>- and PPh<sub>3</sub> hydrogens); <sup>31</sup>P (THF, 24.3 MHz)  $\delta$  -114.0 (PPh<sub>2</sub>-), -140.0 (PPh<sub>3</sub>), <sup>2</sup>J<sub>P-P</sub> = 24 Hz. Crystal data:  $\text{IrP}_2\text{SiO}_2\text{C}_{36}\text{H}_{35}$ ; *M* 781.9; monoclinic; space group *P2<sub>1</sub>/c*; *a* = 13.376 (5) Å, *b* = 28.804 (8) Å, *c* = 10.023 (5) Å;  $\beta$  = 109.50 (4)°; *V* = 3640 Å<sup>3</sup>; *Z* = 4; *D*<sub>calc</sub> = 1.43 g cm<sup>-3</sup>; Picker four circle diffractometer, Mo K $\alpha$  ( $\lambda$  = 0.71069 Å) radiation,  $\mu$  = 3.6 cm<sup>-1</sup>; 2743 observed reflections refined to a conventional *R* = 0.066 (*R*<sub>w</sub> = 0.073).