Inorg. Chem. **1996,** *35,* 5393−5395

Notes

A Hexanuclear Ruthenium Carbonyl Cluster Containing both μ_3-Nitrene and μ_5-Nitrido Ligands

Kenneth Ka Hong Lee and Wing Tak Wong*

Department of Chemistry, The University of Hong Kong,
Pokfulam Road, Hong Kong

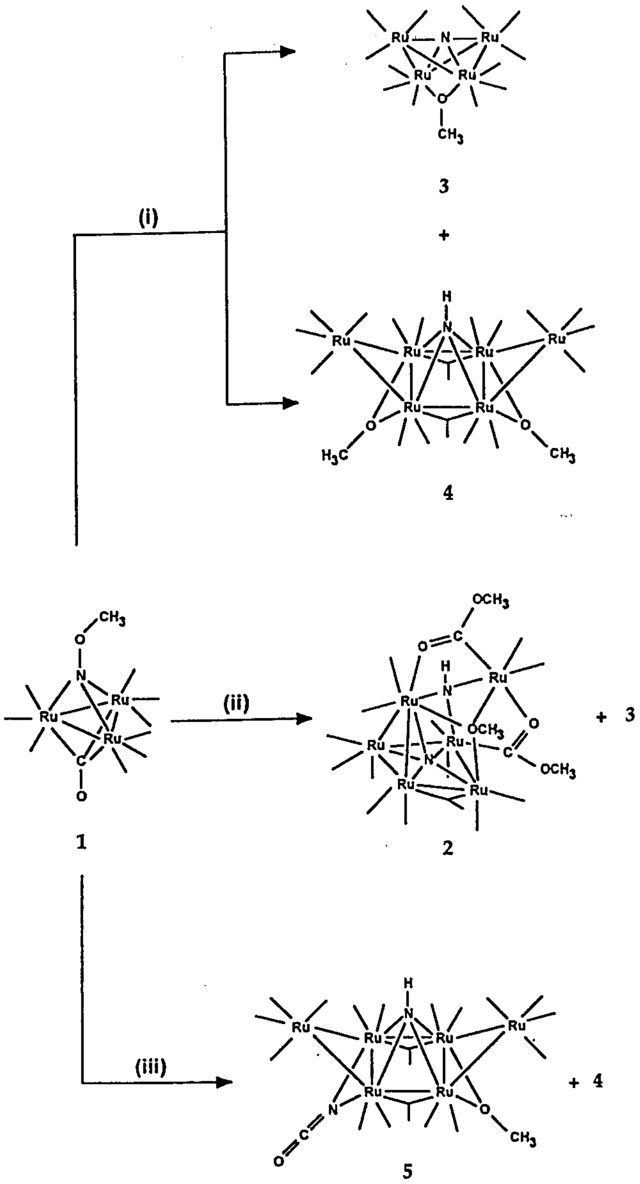
Received February 14, 1996

Introduction

Trinuclear metal carbonyl clusters containing a μ_3-phenylimido ligand, $[M_3(CO)_{10}NPh]$ (M = Fe,[1] Ru,[2] and Os[3]), have been extensively investigated over the past decade. However, triruthenium clusters possessing triply bridging O-alkylated nitrosyl moieties (μ_3-NOMe) are relatively unexplored.

Metal clusters containing either nitrene[4] or nitrido[5] ligand have been known for a long time and these species are believed to be the key intermediates in several chemical processes such as reduction of nitrogen oxides and the Haber process.[6] In previous papers,[7,8] we have reported the N−O bond cleavage of $[Ru_3(CO)_{10}NOMe]$ **1** to give a series of polynuclear carbonyl clusters containing either quadruply bridging nitrene[9] (μ_4-NH) or nitrido ligands. However, clusters containing both nitrene and nitrido moieties are very rare. The only example we are aware of is $[(\eta^5\text{-}C_5Me_5)_3Mo_3Co_2(CO)_8(\mu_3\text{-}NH)(\mu_4\text{-}N)]$ reported by Dahl[10] from photolysis of a mixture of $[Co(CO)_3NO]$ and $[Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_2]$. We present, in this paper, the structural characterization of an unprecedented hexaruthenium carbonyl cluster possessing both a μ_3-nitrene and a μ_5-nitrido ligand from thermolysis of **1**.

Scheme 1



(i) Toluene, 90°C, 3h; (ii) n-octane, reflux, 0.5h; (iii) vacuum pyrolysis, 150°C, 10 min

Results and Discussion

When a *n*-octane solution of compound **1** was heated under reflux, the compound $[Ru_6(CO)_{13}(\mu\text{-}CO)(\mu_3\text{-}NH)(\mu_5\text{-}N)(\mu_3\text{-}$

---

(1) Song, J.-S.; Han, S.-H,; Nguyen, S. T.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1990**, *9*, 2386.

(2) (a) Smieja, J. A.; Gladfelter, W. L. *Inorg. Chem.* **1986**, *25*, 2667. (b) Bhaduri, S.; Gopalkrishnan, K. S.; Sheldrick, G. M.; Clegg, W.; Stalke, D. *J. Chem. Soc., Dalton Trans.* **1983**, 2339. (c) Bhaduri, S.; Gopalkrishnan, K. S.; Clegg, W.; Jones, P. G.; Sheldrick, G. M.; Stalke, D. *J. Chem. Soc., Dalton Trans.* **1984**, 1765. (d) Bhaduri, S.; Khwaja, H.; Jones, P. G. *J. Chem. Soc., Chem. Commun.* **1988**, 194. (e) Bhaduri, S.; Khwaja, H.; Sapre, N.; Sharma, K.; Basu, A.; Jones, P. G.; Carpenter, G. *J. Chem. Soc., Dalton Trans.* **1990**, 1313. (f) Han, S.-H.; Geoffroy, G. L.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 3426. (g) Han, S.-H.; Song, J.-S.; Macklin, P. D.; Nguyen, S. T.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1989**, *8*, 2127. (h) Pizzotti, M.; Porta, F.; Cenini, S.; Demartin, F. *J. Organomet. Chem.* **1988**, *356*, 105. (i) Smieja, J. A.; Gozum, J. E.; Gladfelter, W. L. *Organometallics* **1987**, *6*, 1311. (j) Han, S.-H.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1986**, *5*, 2561. (k) Han, S.-H.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1987**, *6*, 2380. (l) Chi, Y.; Hsu, H.-F.; Liu, L.-K.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1992**, *11*, 1763. (m) Chi, Y.; Hwang, D.-K.; Chen, S.-F.; Liu, L.-K. *J. Chem. Soc., Chem. Commun.* **1989**, 1540. (n) Han, S.-H.; Nguyen, S. T.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1988**, *7*, 2034.

(3) Ramage, D. L.; Geoffroy, G. L.; Rheingold, A. L.; Haggerty, B. S. *Organometallics* **1992**, *11*, 1242.

(4) (a) Fjare, D. E.; Keyes, D. G.; Gladfelter, W. L. *J. Organomet. Chem.* **1983**, *250*, 383. (b) Legzdins, P.; Nurse, C. R.; Rettig, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 3727. (c) Gourdon, A.; Jeannin, Y. *Organometallics* **1986**, 5, 2406. (d) Bedard, R. L.; Rae, A. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1986**, *108*, 5924. (e) Sun, W.; Yang, S.; Wang, H.; Yin, Y.; Yu, K. *Polyhedron* **1992**, *11*, 1143.

(5) (a) Tachikawa, M.; Stein, J.; Muetterties, E. L.; Teller, R. G.; Beno, M. A.; Gebert, E.; Williams, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 6648. (b) Fjare, D. E.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 1572. (c) Fjare, D. E.; Gladfelter, W. L. *Inorg. Chem.* **1981**, *20*, 3533. (d) Braga, D.; Johnson, B. F. G.; Lewis, J.; Mace, J. M.; McPartlin, M.; Puga, J.; Nelson, W. J. H.; Raithby, P. R.; Whitmire, K. H. *J. Chem. Soc., Chem. Commun.* **1982**, 1081. (e) Blohm, M. L.; Fjare, D. E.; Gladfelter, W. L. *Inorg. Chem.* **1983**, *22*, 1004. (f) Blohm, M. L.; Gladfelter, W. L. *Organometallics* **1985**, *4*, 45. (g) Gourdon, A.; Jeannin, Y. *J. Organomet. Chem.* **1985**, *290*, 199. (h) Blohm, M. L.; Fjare, D. E.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1986**, *108*, 2301. (i) Harris, S.; Blohm, M. L.; Gladfelter, W. L. *Inorg. Chem.* **1989**, *28*, 2290. (j) Hourihane, R.; Spalding, T. R.; Ferguson, G.; Deeney, T.; Zanello, P. *J. Chem. Soc., Dalton Trans.* **1993**, 43.

(6) Gladfelter, W. L. *Adv. Organomet. Chem.* **1985**, *24*, 41.

(7) Lee, K. K. H.; Wong, W. T. *J. Organomet. Chem.* **1995**, *503*, C43.

(8) Lee, K. K. H.; Wong, W. T. *J. Chem. Soc., Dalton Trans.* **1996**, 1707.

(9) Blohm, M. L.; Gladfelter, W. L. *Organometallics* **1986**, *5*, 1049.

(10) Gibson, C. P.; Dahl, L. F. *Organometallics* **1988**, *7*, 543.

S0020-1669(96)00161-9 CCC: $12.00

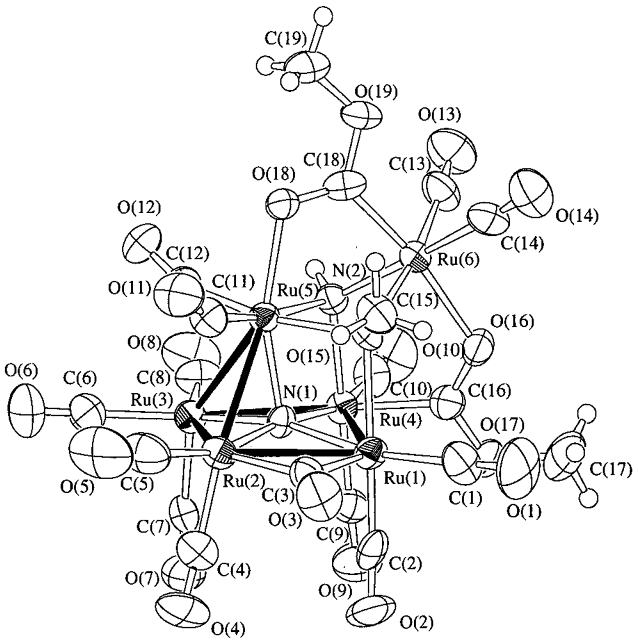


Figure 1. ORTEP plot (50% probability) showing the molecular structure of $[Ru_6(CO)_{13}(\mu\text{-}CO)(\mu_3\text{-}NH)(\mu_5\text{-}N)(\mu_3\text{-}OMe)\{\mu_2\text{-}\eta^2\text{-}C(O)OMe\}_2]$, **2**, and the atom-numbering scheme.

Table 1. Crystallographic Data for $[Ru_6(CO)_{13}(\mu\text{-}CO)(\mu_3\text{-}NH)(\mu_5\text{-}N)(\mu_3\text{-}OMe)\{\mu_2\text{-}\eta^2\text{-}C(O)OMe\}_2]$, **2**

formula: $C_{19}H_{10}N_2O_{19}Ru_6$
fw = 1176.7
space group: $P2_1/n$ (No.14, nonstandard setting)
$a = 9.338(6)$ Å
$b = 33.415(7)$ Å
$c = 10.516(7)$ Å
$\beta = 100.30(6)°$
$V = 3228(3)$
Z = 4
$D_{calc} = 2.421$ g cm^{-3}
μ(Mo Kα) = 28.16 cm^{-1}
$T = 298$ K
$\lambda = 0.710\,73$ Å
$R^a = 0.034$
$R_w{}^b = 0.037$

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$ where $w = [\sigma^2(F_o)]^{-1}$.

OMe)$\{\mu_2\text{-}\eta^2\text{-}C(O)OMe\}_2]$, **2**, was isolated together with $[Ru_4(CO)_{12}(\mu_4\text{-}N)(\mu\text{-}OMe)]$, **3**, as a minor product. Compound **3** was prepared previously by thermolysis of **1** at 90 °C in toluene and was accompanied by $[Ru_6(CO)_{16}(\mu\text{-}CO)_2(\mu_4\text{-}NH)(\mu\text{-}OMe)_2]$, **4**.[8] On the other hand, vacuum pyrolysis of **1** in the solid state at 150 °C afforded **4** and $[Ru_6(CO)_{16}(\mu\text{-}CO)_2(\mu_4\text{-}NH)(\mu\text{-}OMe)(\mu\text{-}NCO)]$, **5**, in moderate yields (Scheme 1).

The molecular structure of **2** as revealed by X-ray crystallographic analysis is depicted in Figure 1. All solution spectroscopic data are consistent with the solid state structure. The geometry of **2** consists of a distorted square-pyramidal of $Ru_5(\mu_5\text{-}N)$ metal core with an additional Ru atom capped on one of the triruthenium planes by means of some bridging organic moieties. The basal tetraruthenium plane, Ru(1)−Ru(2)−Ru(3)−Ru(4) adopts a trapezoidal geometry with a maximum deviation of 0.032 Å from the least square plane. The Ru-Ru bond distances within the basal plane span a wide range [2.787(2)−3.027(2) Å] with an apical Ru atom capped asymmetrically such that only two Ru(basal)−Ru(apex) bonds [Ru(3)−Ru(5) 2.787(1) Å and Ru(2)−Ru(5) 2.812(2) Å] are formed while the opposite edges [Ru(1)···Ru(5) 3.243(2) Å and Ru(4)···Ru(5) 3.181(2) Å] are significantly longer than the Ru−Ru metal bond found in $[Ru_3(CO)_{12}]$, indicating that there is no significant metal−metal bond between them. It is interesting to note that thermolysis of a related sulfur containing ruthenium cluster, $[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}PhNCSNHPh)]$ gives a μ_5-sulfido complex $[Ru_6(CO)_{16}(\mu\text{-}H)(\mu_5\text{-}S)(\mu_3\text{-}\eta^2\text{-}PhNCSNHPh)]$.[11] The dihedral angle between the planes Ru(2)−Ru(3)−Ru(5) and Ru(1)−Ru(2)−Ru(3)−Ru(4) is found to be 63.4°. The nitrido ligand occupies an interstitial position 0.200 Å above the base of the square-pyramid and is almost equidistant apart from the five Ru vertices with an average Ru−N distance of 2.05(9) Å which is similar to that observed in $PPN[Ru_5N(CO)_{14}]$[5e,f] [average Ru−N distance of 2.05(2) Å].

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

Bond Distances

Ru(1)−Ru(2)	2.879(2)	Ru(3)−N(1)	2.000(9)
Ru(2)−Ru(3)	2.787(2)	Ru(4)−N(1)	2.104(9)
Ru(3)−Ru(4)	2.918(1)	Ru(5)−N(1)	2.005(9)
Ru(1)−Ru(4)	3.027(2)	Ru(4)−N(2)	2.105(9)
Ru(2)−Ru(5)	2.812(2)	Ru(5)−N(2)	2.071(9)
Ru(3)−Ru(5)	2.787(1)	Ru(6)−N(2)	2.045(9)
Ru(1)−O(15)	2.203(7)	Ru(1)···Ru(5)	3.243(2)
Ru(5)−O(15)	2.151(7)	Ru(4)···Ru(5)	3.181(2)
Ru(6)−O(15)	2.210(7)	Ru(5)···Ru(6)	3.092(2)
Ru(5)−O(18)	2.148(8)	Ru(1)···Ru(6)	3.842(2)
Ru(6)−C(18)	1.99(1)	Ru(4)···Ru(6)	3.544(2)
Ru(4)−C(16)	2.04(1)	Ru(2)···C(11)	2.55(1)
Ru(6)−O(16)	2.174(8)	Ru(3)···C(12)	2.50(1)
Ru(1)−N(1)	2.096(8)	N(2)−H	0.88
Ru(2)−N(1)	2.047(9)		

Bond Angles

Ru(1)−Ru(4)−Ru(3)	86.34(4)	Ru(5)−N(2)−Ru(6)	97.2(4)
Ru(2)−Ru(3)−Ru(4)	92.92(4)	Ru(1)−O(15)−Ru(5)	96.0(3)
Ru(1)−Ru(2)−Ru(3)	91.77(4)	Ru(1)−O(15)−Ru(6)	121.1(3)
Ru(2)−Ru(1)−Ru(4)	88.88(4)	Ru(5)−O(15)−Ru(6)	90.1(3)
Ru(2)−Ru(3)−Ru(5)	60.60(4)	Ru(6)−C(18)−O(18)	121.6(9)
Ru(2)−Ru(5)−Ru(3)	59.70(4)	Ru(6)−C(18)−O(19)	121.3(10)
Ru(3)−Ru(2)−Ru(5)	59.70(5)	Ru(4)−C(16)−O(17)	115.3(9)
Ru(1)−Ru(2)−Ru(5)	69.28(4)	Ru(4)−C(16)−O(16)	124.8(9)
Ru(4)−Ru(3)−Ru(5)	67.67(4)	Ru(5)−C(11)−O(11)	158(1)
Ru(2)−N(1)−Ru(5)	87.9(3)	Ru(5)−C(12)−O(12)	157(1)
Ru(3)−N(1)−Ru(5)	88.2(3)	O(18)−C(18)−O(19)	117(1)
Ru(4)−N(2)−Ru(5)	99.1(4)	O(16)−C(16)−O(17)	119(1)
Ru(4)−N(2)−Ru(6)	117.3(4)		

Moreover, the Ru(1)−Ru(4)−Ru(5) triruthenium face is "capped" by the sixth ruthenium carbonyl fragment in a similar way to that observed in $[PtRu_5(CO)_{13}(\mu\text{-}PhC_2Ph)(\mu_3\text{-}PhC_2Ph)(\mu_5\text{-}C)]$[12] but with μ_3-nitrene, μ_3-methoxy, and two $\mu_2\text{-}\eta^2$-C(O)OMe ligands as bridging groups. These triply bridging nitrene and methoxy group which act as a 4e and 5e donors respectively are bridged over the triruthenium groupings Ru(4)−Ru(5)−Ru(6) and Ru(1)−Ru(5)−Ru(6). The coordination geometry of Ru(6) can be described as a distorted octahedron with two carbonyls, nitrene, and methoxy fragments occupying an equatorial plane accompanied by O-bound and C-bound $\mu_2\text{-}\eta^2$-C(O)OMe groups coordinated in a *trans* manner. The coordination sphere is completed by terminal and bridging carbonyls to give a CVE count of 96. Six metal−metal bonds in **2** would be expected by the EAN rule, and this is observed.

Experimental Section

General Procedures. All operations were carried out under argon using standard Schlenk techniques.[13] Solvents were dried according to standard procedures and distilled prior to use. All chemicals, unless otherwise stated, were purchased from commercial sources and used

---

(11) Bodensieck, U.; Hoferkamp, L.; Stoeckli-Evans, H.; Süss-Fink, G. *J. Chem. Soc., Dalton Trans.* **1993**, 127.

(12) Adams, R. D.; Wu, W. *Organometallics* **1993**, *12*, 1238.

(13) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: Oxford, UK., 1980.

as received. Thin layer chromatography (TLC) was prepared in air with plates coated with Silica (Merck Kieselgel 60 GF_{254}). Compound **1** was prepared by literature procedures.[14,15] Elemental analyses were performed by Butterworth Laboratories Ltd., U.K. Infrared spectra were recorded on a Bio-Rad FTS-7 IR spectrometer using 0.5 mm CaF_2 solution cells. ^{1}H NMR spectra were taken on a Bruker DPX-300 NMR spectrometer using deuteriated solvents as lock and TMS as reference. Fast-atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT 95 mass spectrometer.

Thermolysis of [$Ru_3(CO)_{10}NOMe$], 1. [$Ru_3(CO)_{10}NOMe$], **1** (126 mg, 0.2 mmol), was dissolved in 60 mL of *n*-octane. The yellow solution was then heated under reflux for 30 min to give a dark brown suspension. The solvent was removed *in vacuo* and the residue was chromatographed on TLC plates using *n*-hexane/dichloromethane (75:25) as eluent. The first few yellow bands were identified, in order of elution, as [$Ru_3(CO)_{12}$], [$Ru_4(CO)_{12}(\mu_4\text{-N})(\mu\text{-OMe})$] (**3**), [$Ru_3(\mu\text{-H})(CO)_{10}NH_2$],[16] and a trace of **1**. A dark green band with $R_f \sim 0.5$ was isolated, which was characterized as **2** (15mg, 0.013 mmol). Anal. Calcd for $C_{19}H_{10}N_2O_{19}Ru_6$: C, 19.37; H, 0.85; N, 2.38. Found: C, 19.41; H, 0.84; N, 2.39. IR (*n*-hexane), ν(CO): 2078 (m), 2058 (vs), 2037 (sh), 2032 (vs), 2019 (s), 2010 (m), 2000 (s), 1989 (w), 1981 (sh), 1963 (w), 1950 (w), 1831 cm^{-1} (m). ^{1}H NMR ($CDCl_3$, 295 K, 300 MHz): 4.31 (s, 3H), 3.72 (s, 3H), 3.17 (s, 3H) and −0.33 (br, 1H). FAB−MS: *m/z* 1177 M^+ (calcd 1177).

X-ray Crystal Structure Determination. Dark green crystals of **2** were obtained by slow evaporation of a *n*-hexane/dichloromethane solution at −20 °C. Crystals suitable for X-ray diffraction study were glued on top of a glass fiber by means of epoxy resin and mounted on a Rigaku-AFC7R diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) for unit-cell determination and data collection. A summary of the crystallographic data, structure, solution and refinement is given in Table 1. Lorentz-polarization and Ψ-scan absorption corrections[17] were applied to all intensity data. The positions of ruthenium atoms were determined by direct methods (SIR88).[18] The molecular structure was determined by subsequent Fourier and difference Fourier techniques.

Atomic coordinates and thermal parameters were refined by full-matrix least-squares analysis with the ruthenium atoms and non-hydrogen atoms refined anisotropically. The hydrogen atom of the nitrene moiety was located by difference Fourier synthesis while hydrogen atoms of the organic moieties were generated in their ideal positions (C−H, 0.95 Å). All calculations were performed on a Silicon-Graphics computer using the program package TEXSAN.[19] Selected bond parameters are given in Table 2.

Acknowledgment. We thank the Hong Kong Research Grants Council and the University of Hong Kong for financial support.

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

IC960161X

---

(14) Stevens, R. E.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1982**, *104*, 6454.
(15) Stevens, R. E.; Guettler, R. D.; Gladfelter, W. L. *Inorg. Chem.* **1990**, *29*, 451.
(16) Johnson, B. F. G.; Lewis, J.; Mace, J. M. *J. Chem. Soc., Chem. Commun.* **1984**, 186. (b) Smieja, J. A.; Stevens, R. E.; Fjare, D. E.; Gladfelter, W. L. *Inorg. Chem.* **1985**, *24*, 3206.
(17) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *24*, 351.
(18) Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Polidori, G.; Spagna, R.; Viterbo, D. *J. Appl. Crystallogr.* **1989**, *22*, 389.
(19) TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, 1985 and 1992.