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Cycloheptatrienyl-Bridged Heterodimetallic Complexes: Synthesis, Fluxional Behavior, and X-ray Crystal Structure of $[Fe(CO)_3(\mu\text{-}\eta^3\text{:}\eta^2\text{-}C_7H_7)Pd(\eta^5\text{-}C_5H_5)]$

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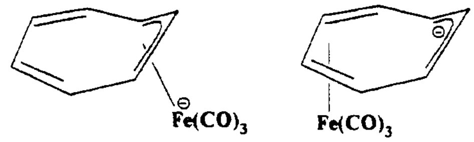
The reaction of $[(\eta^3\text{-}C_7H_7)Fe(CO)_3]^-$ with $[(\eta^4\text{-}C_8H_{12})PdL]^+$ leads to the formation of $[Fe(CO)_3(\mu\text{-}C_7H_7)PdL]$. When $L = C_3H_5$, the known complex $[Fe(CO)_3(\mu\text{-}\eta^3\text{:}\eta^4\text{-}C_7H_7)Pd(\eta^3\text{-}C_3H_5)]$ is obtained. When $L = C_5H_5$, the reaction gives the title compound. In solution the molecule is fluxional in the ^{1}H- and ^{13}C-NMR time scale and exhibits both metal migration and carbonyl group scrambling processes. The spectroscopic data and X-ray crystal structure show that this is the first case of a bridging cycloheptatrienyl metal–metal bonded complex having an uncoordinated double bond in the ring and detectable low-temperature limiting ^{1}H- and ^{13}C-NMR spectra. Crystal data for $[Fe(CO)_3(\mu\text{-}\eta^3\text{:}\eta^2\text{-}C_7H_7)Pd(\eta^5\text{-}C_5H_5)]$: monoclinic, space group $P2_1/n$, $a = 8.772(2)$ Å, $b = 10.308(6)$ Å, $c = 16.078(3)$ Å, $\beta = 93.38(4)°$, $V = 1451(1)$ Å^3, $Z = 4$, $R = 0.019$, $R_w = 0.024$ based on 1929 reflections with $I > 3\sigma(I)$.

A large number of mononuclear transition metal complexes of cycloheptatriene (C_7H_8) and the cycloheptatrienyl anion ($C_7H_7^-$) are known.[1] Dinuclear metal–metal bonded complexes of the above ligands are still relatively rare, but recently some cycloheptatrienyl complexes containing different metals have been reported.[2–6]

The anionic complex $[(C_7H_7)Fe(CO)_3]^-$ [7] (1) is a likely precursor for the synthesis of heterodimetallic cycloheptatrienyl complexes. The actual structure of 1 determined by single-crystal X-ray crystallography is **1a**[8] (Chart I). Molecular orbital calculations[9] predict form **1a** is slightly more stable (14.2 kJ mol^{-1}) than form **1b**. Although the structure of 1 in solution is not known owing to its high fluxionality,[10] there are many evidences which prove the ambident nucleophilicity of 1. The formation of $[(\eta^4\text{-}C_7H_7R)Fe(CO)_3]$ complexes with an *exo* configuration of the R substituent in the reaction of 1 with C,[11–18] Si,[10] and Ge[10] electrophiles is consistent with the presence of form **1b**. However, as noted by Takats *et al.*,[19] since the MO calculations[9] show a higher negative charge on the ring in **1a** than in **1b**, the formation of $[(\eta^4\text{-}C_7H_7R)Fe(CO)_3]$ complexes does not need the presence of form **1b**. Direct attack to iron of the form **1a** appears to be the pathway which affords $[\eta^3\text{-}C_7H_7Fe(CO)_3EPh_3]$[20] (E = Sn, Pb) in the reaction of 1 with triphenyltin and -lead halides. The reaction of 1 with transition metal electrophiles gives, as mentioned, iron–metal bonded cycloheptatrienyl complexes.[2–6]

Chart I



1a 1b

Common characteristics of these complexes are the linkage of the dimetal unit to all the seven carbon atoms of the ring and the high fluxionality of the C_7H_7 ring.[21] Indeed, attempts to reach the slow-exchange limiting NMR spectrum of the cycloheptatrienyl unit have failed except for a complex having the two metal groups linked by a bridging hydride.[22]

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Table I. Summary of Crystal Data, Collection and Reduction of X-ray Data, and Refinement of the Structure of $[Fe(CO)_3(\mu\text{-}\eta^3{:}\eta^2\text{-}C_7H_7)Pd(\eta^5\text{-}C_5H_5)]$

A. Crystal Data	
formula	$C_{15}H_{12}FeO_3Pd$
fw	402.5
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a, Å	8.772(2)
b, Å	10.308(6)
c, Å	16.078(3)
β, deg	93.38(2)
cell vol, Å^3	1451(1)
Z; d_{calc}, g cm^{-3}	4; 1.842
$F(000)$	792
cryst size, mm	0.12 × 0.07 × 0.04
B. Collection and Reduction of X-ray Data	
diffractometer	Enraf-Nonius CAD4
radiation	Mo Kα (λ = 0.710 73 Å)
temp, °C	23 ± 2
scan method	ω
scan range, deg	$0.8 + 0.347 \tan(\theta)$
max scan time, s	45
collected octants	$\pm h, +k, +l$
2θ limits, deg	$6 \le 2\theta \le 50$
no. of collcd data	2667
no. of reflns for Ψ-scan	3
μ (Mo Kα), cm^{-1}	22.25
min transm factor	0.75
cryst decay, %	2
C. Refinement of the Structure	
no. of data used (with $I > 3\sigma(I)$)	1929
no. of refined params	229
fudge p factor	0.035
R^a	0.019
$R_w{}^{b,d}$	0.024
GOF^{c,d}	0.980
max shift (Δ/σ)	1.86
max peak final diff map, e Å^{-3}	0.24

[a] $R = \sum(\|F_o| - k|F_c\|)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - k|F_c|)^2/\sum w|F_o|^2]^{1/2}$. [c] GOF $= [\sum w(|F_o| - k|F_c|)^2/(N_{obs} - N_{var})]^{1/2}$. [d] $w = 4|F_o|^2/\sigma^2(|F_o|^2)$ where $\sigma(|F_o|^2) = [\sigma^2(I) + (pI)^2]^{1/2}/LP$.

Table II. Fractional Atomic Coordinates for $[Fe(CO)_3(\mu\text{-}\eta^3{:}\eta^2\text{-}C_7H_7)Pd(\eta^5\text{-}C_5H_5)]^a$

atom	x/a	y/b	z/c
Pd	0.20940(2)	0.29425(2)	−0.36286(1)
Fe	0.21461(5)	0.22675(4)	−0.52190(2)
O1	−0.0913(3)	0.3442(3)	−0.5328(2)
O2	0.1482(4)	0.1014(3)	−0.6823(2)
O3	0.1.792(3)	−0.0136(2)	−0.4279(2)
C1	0.0293(4)	0.3011(3)	−0.5268(2)
C2	0.1751(4)	0.1529(4)	−0.6202(2)
C3	0.1935(3)	0.0853(3)	−0.4586(2)
C4	0.5423(3)	0.2514(3)	−0.3799(2)
C5	0.4422(3)	0.3591(3)	−0.3671(2)
C6	0.3506(3)	0.4266(3)	−0.4273(2)
C7	0.3381(3)	0.4095(3)	−0.5165(2)
C8	0.4078(4)	0.3141(3)	−0.5625(2)
C9	0.4613(3)	0.1957(3)	−0.5271(2)
C10	0.5484(3)	0.1791(3)	−0.4482(2)
C11	0.0951(5)	0.1747(4)	−0.2650(2)
C12	−0.0190(4)	0.2232(4)	−0.3208(2)
C13	−0.0304(4)	0.3565(5)	−0.3062(2)
C14	0.0803(4)	0.3904(4)	−0.2480(2)
C15	0.1605(4)	0.2791(5)	−0.2229(2)
H1	0.603(3)	0.225(3)	−0.338(2)
H2	0.460(3)	0.403(3)	−0.318(2)
H3	0.312(3)	0.507(3)	−0.408(2)
H4	0.295(3)	0.474(3)	−0.545(2)
H5	0.403(4)	0.320(3)	−0.622(2)
H6	0.483(3)	0.136(3)	−0.564(2)
H7	0.614(3)	0.107(3)	−0.446(2)
H8	0.116(4)	0.097(3)	−0.264(2)
H9	−0.078(4)	0.174(4)	−0.355(2)
H10	−0.082(3)	0.405(3)	−0.333(2)
H11	0.099(4)	0.465(3)	−0.227(2)
H12	0.216(4)	0.289(3)	−0.193(2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table III

Bond Lengths (Å)					
Pd–Fe	2.653(1)	Fe–C3	1.794(4)	C6–C7	1.443(5)
Pd–C5	2.153(3)	Fe–C7	2.172(3)	C7–C8	1.393(5)
Pd–C6	2.150(3)	Fe–C8	2.058(3)	C8–C9	1.415(5)
Pd–C11	2.277(4)	Fe–C9	2.194(3)	C9–C10	1.452(5)
Pd–C12	2.274(4)	O1–C1	1.146(4)	C11–C12	1.397(7)
Pd–C13	2.427(4)	O2–C2	1.143(4)	C11–C15	1.378(8)
Pd–C14	2.434(4)	O3–C3	1.142(4)	C12–C13	1.398(7)
Pd–C15	2.320(4)	C4–C5	1.438(5)	C13–C14	1.355(7)
Fe–C1	1.795(4)	C4–C10	1.331(5)	C14–C15	1.393(7)
Fe–C2	1.770(4)	C5–C6	1.406(5)		

Bond Angles (deg)^a			
Fe–Pd–Et*	79.0(2)	Fe–C1–O1	176.7(4)
Fe–Pd–Cp*	136.5(2)	Fe–C2–O2	177.6(4)
Et*–Pd–Cp*	142.4(2)	Fe–C3–O3	171.0(3)
C5–Pd–C12	164.4(2)	C5–C4–C10	127.2(4)
C6–Pd–C11	165.1(2)	C4–C5–C6	127.8(3)
Pd–Fe–C1	82.2(1)	C5–C6–C7	129.1(3)
Pd–Fe–C2	163.7(1)	C6–C7–C8	127.2(4)
Pd–Fe–C3	70.0(1)	C7–C8–C9	122.8(3)
Pd–Fe–Al*	93.6(2)	C8–C9–C10	126.7(4)
C1–Fe–C2	90.9(2)	C4–C10–C9	127.6(4)
C1–Fe–C3	104.4(2)	C12–C11–C15	107.3(5)
C1–Fe–Al*	127.6(2)	C11–C12–C13	107.4(5)
C2–Fe–C3	97.8(2)	C12–C13–C14	108.3(5)
C2–Fe–Al*	102.3(2)	C13–C14–C15	108.4(5)
C3–Fe–Al*	123.0(2)	C11–C15–C14	108.2(5)

[a] Et*, Al*, and Cp* are the center of mass of the ethylene, allyl, and cyclopentadienyl moieties, respectively.

Here we wish to report on the reaction of 1 with cationic $[(1,5\text{-}\eta^4\text{-}C_8H_{12})PdL]^+$ (L = $\eta^3\text{-}C_3H_5$, $\eta^5\text{-}C_5H_5$) complexes and on the spectroscopic and structural characterization of a metal–metal bonded bridging C_7H_7 complex which represents an interesting new coordination mode of the cycloheptatrienyl ligand. A preliminary account of this work has been published.[23]

Experimental Section

IR spectra were recorded on a Perkin-Elmer 983G spectrophotometer in CaF_2 cells. ^1H- and ^{13}C-NMR spectra were obtained on a Bruker WP 80 SY or AM 200; temperature measurements and calibration were made with a Bruker BVT 1000 control unit.

Mass spectra were recorded on a JEOL SG-2S operating at 70 eV, using the direct inlet technique for the introduction of the sample.

All experimental procedures were performed in standard Schlenk glassware under an atmosphere of purified dinitrogen. Solvents were refluxed in dinitrogen with the appropriate drying agent and distilled before use.

Iron pentacarbonyl (Ventron Corp.) was filtered before use. Cycloheptatriene (Aldrich) and 1,5-cyclooctadiene (Aldrich) were freshly distilled. Cyclopentadiene was obtained by cracking of bicyclopentadiene (Aldrich). Potassium *tert*-butoxide (Aldrich) was sublimed before use. Other reagents were used as received. $[(\eta^4\text{-}C_7H_8)Fe(CO)_3]$,[24] $[(\eta^3\text{-}C_7H_7)Fe(CO)_3]K$,[14] $[(\eta^4\text{-}1,5\text{-}C_8H_{12})PdCl_2]$,[25] $[(\eta^4\text{-}1,5\text{-}C_8H_{12})Pd(\eta^5\text{-}C_5H_5)]BF_4$,[25] $[(\eta^3\text{-}C_3H_5)PdCl]_2$,[26]

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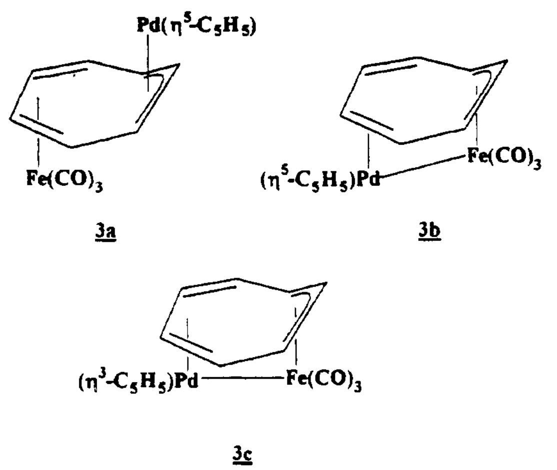
Chart II



3a 3b 3c

Table IV. Mass Spectroscopic Data for $[Fe(CO)_3(\mu\text{-}\eta^3{:}\eta^2\text{-}C_7H_7)Pd(\eta^5\text{-}C_5H_5)]^a$

assignment	*m/e*	rel abund, %
$[Fe(CO)_3(C_7H_7)Pd(C_5H_5)]^+$ (P$^+$)		
$[Fe(CO)_2(C_7H_7)Pd(C_5H_5)]^+$ (P$^+$ − CO)	373.9	5.9
P$^+$ − 2CO	345.8	1.4
P$^+$ − 3CO	317.9	17.1
$(C_7H_7)(C_5H_5)Fe^+$	211.9	68.3
$C_7H_7Pd^+$	196.9	3.1
$FePd^+$	161.8	12.5
$C_7H_7Fe^+$	147.0	34.8
$C_6H_6Fe^+$	133.9	8.1
$C_5H_5Fe^+$	121.0	29.4
$C_7H_7^+$	91.1	100
$C_5H_5^+$	65.0	31.9

[a] The nominal mass corresponding to the most abundant *m/e* value within each cluster is reported; this corresponds to ^{56}Fe (91.68% relative abundance) and/or ^{106}Pd (27.3%) isotopes in the iron and/or palladium containing clusters.

and $[(\eta^4\text{-}1,5\text{-}C_8H_{12})Pd(\eta^3\text{-}C_3H_5)]BF_4$[25] were obtained by published procedures.

Preparation of the Complexes. (μ-η^3:η^2-Cycloheptatrienyl)tricarbonyliron (η^5-Cyclopentadienyl)palladium(*Fe-Pd*) (2), $[Fe(CO)_3(\mu\text{-}\eta^3{:}\eta^2\text{-}C_7H_7)Pd(\eta^5\text{-}C_5H_5)]$. A solution of $[(\eta^3\text{-}C_7H_7)Fe(CO)_3]K$ (5.5 mmol) in 20 mL of dry and deoxygenated THF was added dropwise to a cooled (−78 °C) and magnetically stirred solution of $[(\eta^4\text{-}1,5\text{-}C_8H_{12})Pd(\eta^5\text{-}C_5H_5)]BF_4$ (2 g, 5.5 mmol) in 10 mL of THF. After the addition was completed, the reaction mixture was stirred for an additional 2 h. Solvent was removed from the solution under vacuum, and the reddish-brown residue was extracted with pentane (3 × 15 mL). The filtered extracts were concentrated. Complex **2** as dark red crystals (0.66 g, 30%) was obtained by cooling the solution to −20 °C for 2 days. Anal. Calcd for $C_{15}H_{12}O_3PdFe$: C, 44.76; H, 3.00; Fe, 13.88. Found: C, 44.61; H, 3.12; Fe, 13.79. Infrared spectrum (pentane, room temperature, cm^{-1}): ν_{CO} 2012 (vs), 1955 (vs). ^{1}H-NMR spectrum (acetone-d_6, room temperature, ppm): C_7H_7, δ 4.72; C_5H_5, δ 5.90. ^{13}C-NMR spectrum ($CD_2Cl_2/CDCl_3$, room temperature, ppm): CO, resonance not obtained; C_7H_7, δ 82.2; C_5H_5, δ 101.6.

(μ-η^3:η^4-Cycloheptatrienyl)tricarbonyliron (η^3-Allyl)palladium(*Fe-Pd*) (3) $[Fe(CO)_3(\mu\text{-}\eta^3{:}\eta^4\text{-}C_7H_7)Pd(\eta^3\text{-}C_3H_5)]$. A solution of $[(\eta^3\text{-}C_7H_7)Fe(CO)_3]K$ (2 mmol) in 10 mL of dry and deoxygenated THF was added dropwise to a magnetically stirred solution of $[(\eta^4\text{-}1,5\text{-}C_8H_{12})Pd(\eta^3\text{-}C_3H_5)]BF_4$ (0.69 g, 2 mmol) in 10 mL of THF. After the addition was completed, the reaction mixture was stirred for 1 h. Solvent was removed from the solution under vacuum, and the reddish-brown residue was extracted with boiling hexane. The filtered extract was concentrated. Complex **3** as dark red crystals (0.380 g, 50%) was obtained by cooling the solution to −20 °C for 2 days. Anal. Calcd for $C_{13}H_{12}O_3PdFe$: C, 41.25; H, 3.19; Fe, 14.76. Found: C, 41.11; H, 3.25; Fe, 14.65. Infrared spectrum (pentane, room temperature, cm^{-1}): ν_{CO} 2004 (vs), 1941 (s), 1930 (s). ^{13}C-NMR spectrum (acetone-d_6, room temperature, ppm): CO, resonance not obtained; C_7H_7, δ 84.3; allyl, δ 113.1 (CH) and δ 69.6 (CH$_2$).

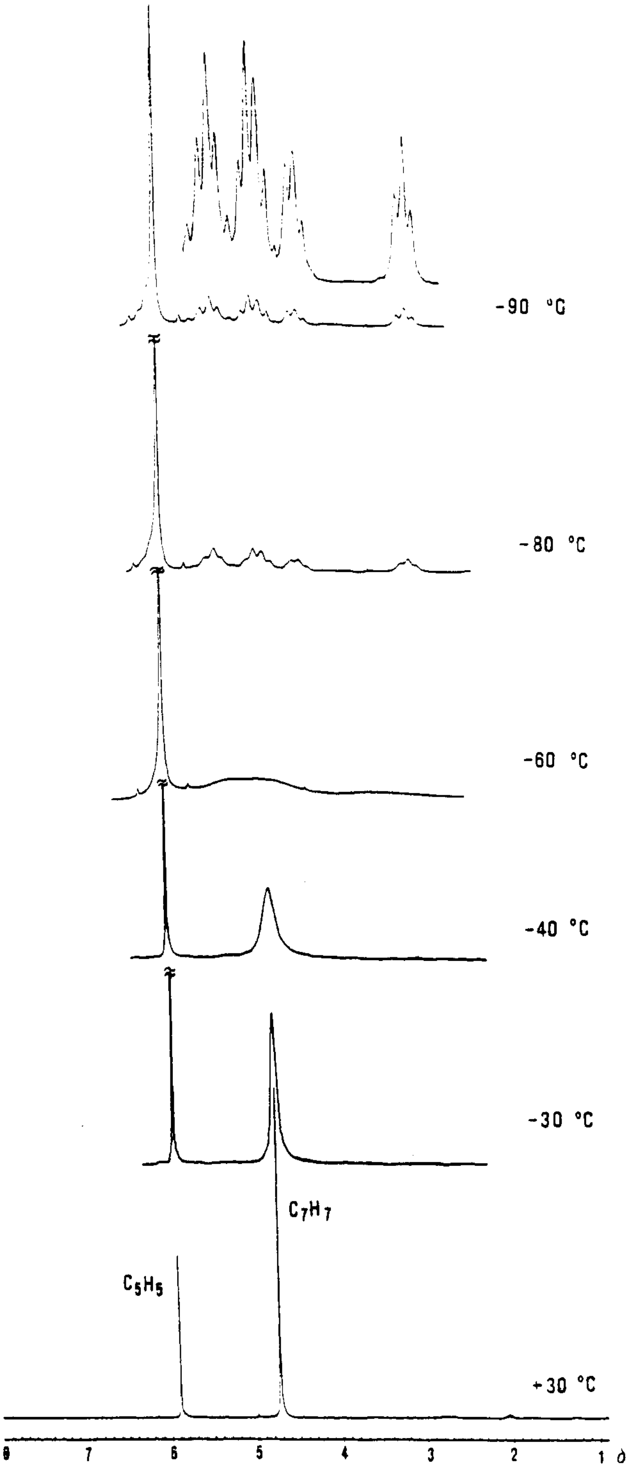


Figure 1. Variable-temperature ^{1}H-NMR spectra of $[Fe(CO)_3(\mu\text{-}\eta^3{:}\eta^2\text{-}C_7H_7)Pd(\eta^5\text{-}C_5H_5)]$ (2) in acetone-d_6 (80.13 MHz).

X-ray Data Collection, Strucure Solution, and Refinement for $[Fe(CO)_3(\mu\text{-}\eta^3{:}\eta^2\text{-}C_7H_7)Pd(\eta^5\text{-}C_5H_5)]$. A red-brown crystal of dimensions 0.12 × 0.07 × 0.04 mm was mounted on an Enraf-Nonius CAD-4 diffractometer, and 25 intense reflections having a θ value in the range 10.0–14.0° were centered using graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). A least squares refinement of their setting angles resulted in the unit-cell parameters reported in Table I, together with an

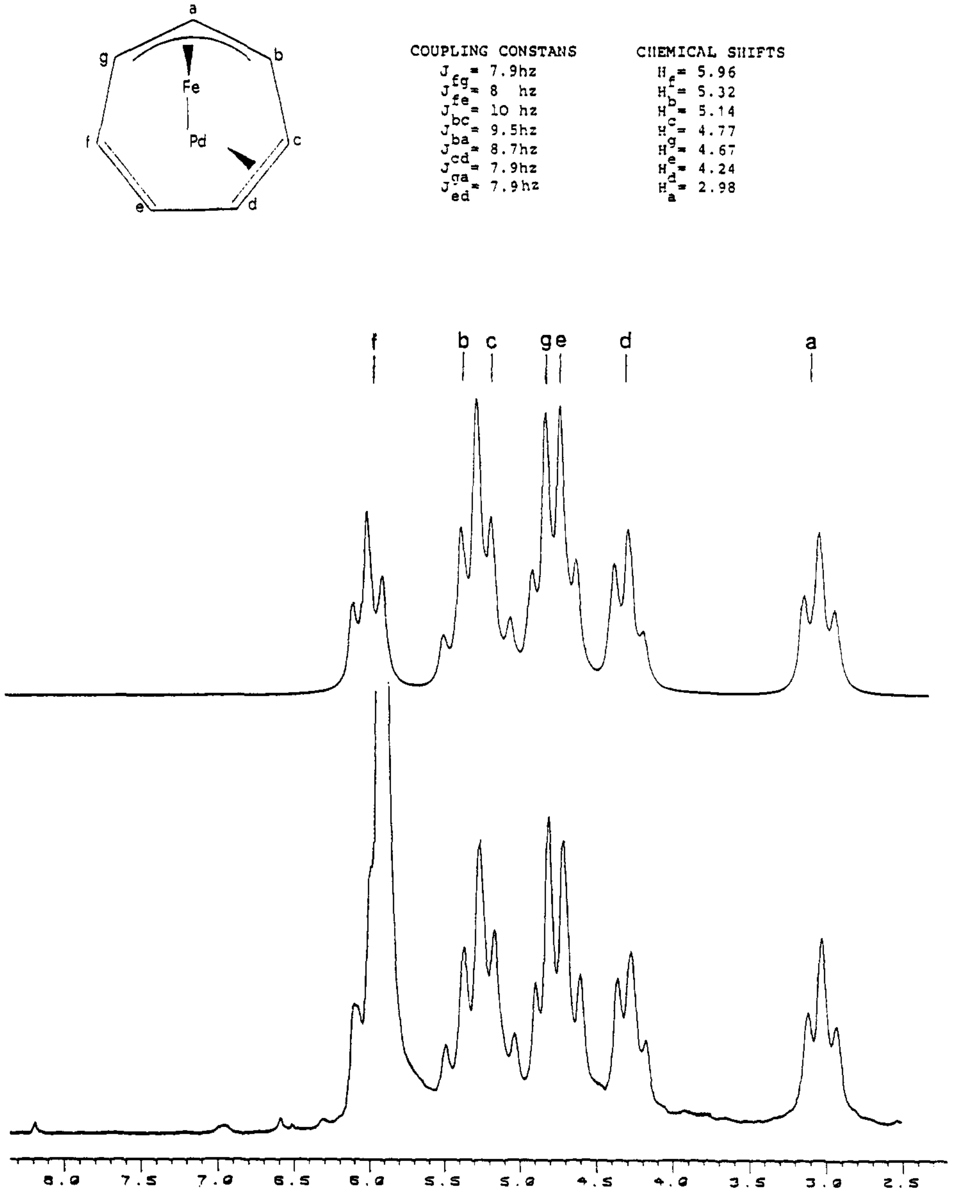


Figure 2. Simulated (upper) and experimental (lower) ^{1}H-NMR spectra of [Fe(CO)$_3$(μ-η^3:η^2-C$_7$H$_7$)Pd(η^5-C$_5$H$_5$)] (−90 °C, acetone-d_6, 80.13 MHz). In the simulated spectrum the C$_5$H$_5$ signal was not considered.

orientation matrix relating the crystal axes to the diffractometer axes. A total of 2667 diffracted intensities [1929 with $I > 3\sigma(I)$] were collected at room temperature with variable scan speed (maximum scan time for each reflection 45 s), by exploring the octant of the reciprocal lattice with $-10 < h < 10$, $0 < k < 12$ and $0 < l < 19$, out to a maximum 2θ angle of 50°. The intensity was checked by monitoring three standard reflections every 180 min; no long range fluctuations of the primary beam intensity were observed. A crystal decay was observed and final drift corrections were between 1.00 and 1.02. The diffracted intensities were also corrected for Lorentz–polarization and background effects. An empirical absorption correction was applied by performing a ψ-scan correction.[27] Scattering factors for neutral atoms and anomalous dispersion corrections were taken from refs 28 and 29, respectively.

The structure was solved by Patterson methods and refined by full-matrix least squares, minimizing the function $\Sigma w(F_o - k|F_c|)^2$. Weights assigned to individual observations were $1/\sigma^2(F_o)$, where $\sigma(F_o) = [\sigma^2(I) + (pI)^2]^{1/2}/2F_oLP$, $\sigma(I)$ is the standard deviation for each reflection as derived from counting statistics, p (=0.035) is a coefficient for improving the goodness of fit, and LP is the Lorentz–polarization factor. All non-hydrogen atoms were given anisotropic thermal parameters. Hydrogen atoms were located from a Fourier difference map, and their positions were refined. The final R value was 0.019 (R_w = 0.024). All the calculations were performed on a PDP11/73 computer using the SDP-Plus Structure Determination Package.[30] The maximum residual in the final difference Fourier synthesis was 0.24 e/Å^3.

The final positional parameters are given in Table II, together with their associated standard deviations. Selected bond distances and angles are to be found in Table III.

Results and Discussion

Slow addition of a THF solution of [(η^3-C$_7$H$_7$)Fe(CO)$_3$]$^-$ to [(η^4-C$_8$H$_{12}$)PdL]$^+$ (L = η^5-C$_5$H$_5$, η^3-C$_3$H$_5$) in THF gives, after workup, moderate yields of crystalline red-brown solids:

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[27] North, A. C. T.; Phillips, D. C.; Scott Mathews, F. *Acta Crystallogr.* **1968**, *A24*, 351.

[28] Cromer, D. T. *International Tables for X-Ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. 4, Table 2.3.1 (present distributor: Kluwer Academic Publishers, Dordrecht).

[29] Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. 4, Table 2.2.b (present distributor: Kluwer Academic Publishers, Dordrecht).

$$[(\eta^3\text{-}C_7H_7)Fe(CO)_3]K + [(\eta^4\text{-}C_8H_{12})PdL]BF_4 \rightarrow \underset{\mathbf{2,3}}{[Fe(CO)_3(C_7H_7)PdL]}$$

$$\mathbf{2}\text{: } L = C_5H_5\text{, yield }30\%\text{; }\mathbf{3}\text{: } L = C_3H_5\text{, yield }50\%$$

when L = η^3-C_3H_5 the identification of the product as $[Fe(CO)_3(\mu\text{-}\eta^3{:}\eta^4\text{-}C_7H_7)Pd(\eta^3\text{-}C_3H_5)]$(*Fe–Pd*) follows by comparison of spectroscopic characteristics (IR and ^{13}C NMR) with the same complex[3] obtained by reaction of $[(\eta^3\text{-}C_7H_7)Fe(CO)_3]Li$ with $[\eta^3\text{-}C_3H_5PdCl]_2$.

Several configurations satisfying the 18 electrons rule can be considered for the complex with L = C_5H_5 (Chart II).

A configuration of type **2a** which has been found in $[Fe(CO)_3(\mu\text{-}\eta^4{:}\eta^3\text{-}C_7H_7)Mo(CO)_2(\eta^5\text{-}C_5H_5)]$,[31] can be ruled out on the basis of the mass spectrum of **2**. The presence of a peak corresponding to the fragment $FePd^+$ (Table IV) with the characteristic isotopic multiplet, is indicative of a configuration with a Fe–Pd bond. The absence in the mass spectrum of P^+ is not unusual in carbonyl complexes.[32,33]

The IR spectrum in the carbonyl stretching region is also not consistent with a configuration **2a**. Indeed, an $Fe(CO)_3$ linked to two conjugated double bonds like in **2a** should show the highest ν(CO) stretching at *circa* 2040 cm^{-1}.[31] Complex **2** presents IR bands at 2012 and 1955 cm^{-1}, similar to other bridging cycloheptatrienyl Fe–M bonded complexes.[3,4]

Actually, the definitive arguments supporting configuration **2b** are the X-ray crystal structure analysis of **2** (*vide infra*) and the rationalization of the ^1H- and ^{13}C-NMR spectra at variable temperatures which confirms that the limiting spectra in solution are consistent with the solid state structure.

NMR Results. At room temperature the ^1H-NMR spectrum presents two singlets at δ = 5.90 (5H) and at δ = 4.72 (7H), easily attributable to the C_5H_5 and C_7H_7 units. A single signal for the seven protons of the cycloheptatrienyl ligand is clearly indicative that the C_7H_7 unit undergoes fluxional movement. Also the room-temperature ^{13}C-NMR spectrum shows two sharp singlets at 101.6 (C_5H_5) and 82.2 ppm (C_7H_7). The other fluxional cycloheptatrienyl bridged Fe–Pd complexes, namely $[Fe(CO)_3(\mu\text{-}\eta^3{:}\eta^4\text{-}C_7H_7)Pd(\eta^3\text{-allyl})]$[3] (allyl = C_3H_5, C_4H_7), show the ^{13}C resonance for the C_7H_7 units at 84.3 and 84.5 ppm, respectively. In addition the absence of carbonyl peaks in the room-temperature ^{13}C-NMR spectrum is due to the local carbonyl scrambling on Fe, an occurrence quite common in $M(CO)_3$ groups.[34–36] Attempts to find at higher temperatures the expected single time-averaged carbonyl signal were frustrated by decomposition of the compound.

The fluxional behavior of **2** is confirmed by variable-temperature ^1H- and ^{13}C-NMR spectra. When the temperature is lowered, the sharp singlet at δ = 4.72 (Figure 1, ^1H NMR) broadens, collapses, and finally reemerges as five apparent multiplets with a 1:2:2:1:1 integration ratio. The low field peak is partially hidden by the C_5H_5 signal. The process is reversible. Since the spin–spin coupling resolution is quite good, we are confident that the low-temperature limiting spectrum is practically reached at 183 K. A four signal spectrum with a 2:2:2:1 ratio would be expected for configuration **2c**, while seven signals should be present for the seven different protons of configuration **2b**. The high field signal is assigned to the central proton of the η^3-enyl mojety of the C_7H_7 ring, in analogy to all the other η^3-C_7H_7 complexes so far reported.[20] Accurate ^1H–^1H homonuclear decoupling experiments which allow assignments and coupling constant determinations show that actually the two signals with integration 2 are attributable each to two different protons. In Figure 2 the correspondence of the simulated spectrum with the experimental one secures the correct assignments. The variable-temperature ^{13}C NMR (Figure 3) confirms the two independent fluxional movements: the local scram-

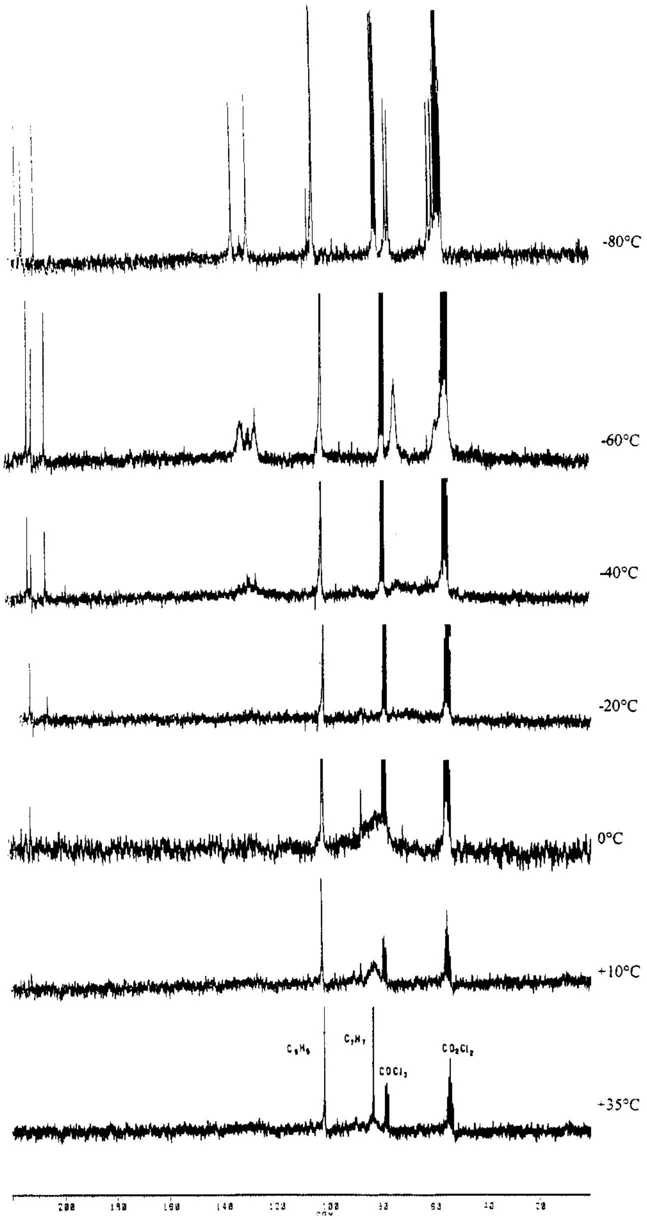

Figure 3. Variable-temperature ^{13}C-NMR spectra of $[Fe(CO)_3(\mu\text{-}\eta^3{:}\eta^2\text{-}C_7H_7)Pd(\eta^5\text{-}C_5H_5)]$ ($CD_2Cl_2/CDCl_3$ 2:1) (200 MHz).

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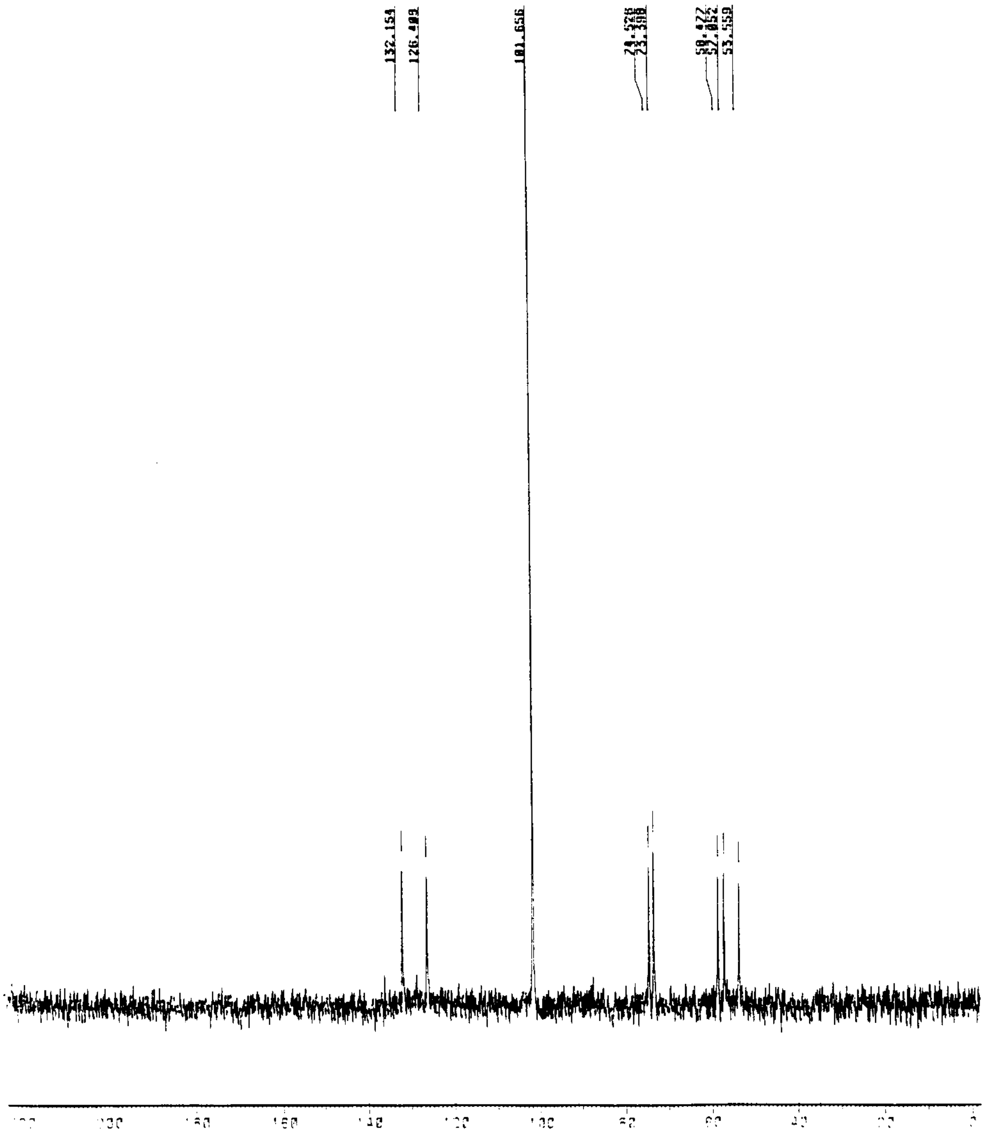

Figure 4. DEPT ^{13}C-NMR spectrum of [Fe(CO)$_3$(μ-η^3:η^2-C$_7$H$_7$)Pd(η^5-C$_5$H$_5$)] at 193 K for the selective detection of CH resonances (200 MHz).

bling of the carbonyl groups on iron and the C$_7$H$_7$ ring whizzing motion. The two processes reach the slow-exchange limiting spectrum at ≈203 K (212.8, 210.6, 206.1 ppm) and 193 K, respectively. At 193 K six lines are clearly attributable to the carbons of the C$_7$H$_7$ ring (132.2, 126.4, 74.5, 73.4, 58.5, and 57.1 ppm) while the seventh line is partially overlapped by the solvent. A DEPT experiment[37,38] which eliminates all the carbon signals but CH (Figure 4) confirms the seven lines of the seven different carbons of the cycloheptatrienyl unit and the single line for C$_5$H$_5$, expected for configuration **2b**. Complex **2** therefore represents the first case among the bridging cycloheptatrienyl heterodimetallic complexes having an uncoordinated double bond in the C$_7$H$_7$ ring. At variance with the other metal–metal bonded bridging cycloheptatrienyl complexes the slow-exchange limiting NMR spectrum of **2** can be reached. At present, our data are not sufficient, by line-shape analysis, to discriminate among the 1 − *n* shift mechanisms responsible for the rotation of the dimetal unit around the cycloheptatrienyl ring. It is evident however that the presence of the uncoordinated double bond must play an important role in increasing the activation energy of the fluxional process.

Molecular Structure of [Fe(CO)$_3$(μ-η^3:η^2-C$_7$H$_7$)Pd(η^5-C$_5$H$_5$)]. Two perspective views of the [Fe(CO)$_3$(μ-η^3:η^2-C$_7$H$_7$)Pd(η^5-C$_5$H$_5$)] molecule, with the appropriate numbering scheme, are shown in Figure 5. The molecule consists of a Fe–Pd heterodimetallic dimer bridged by a cycloheptatrienyl group in the *unique* (μ-η^3:η^2) coordination mode. The coordination sphere around Fe and Pd is completed by three carbonyls and one cyclopentadienyl ligand, respectively, in order to achieve the 18 Ve at each metal center.

The Fe–Pd bond distance (2.653(1) Å) is slightly longer than those found in [Fe$_4$Pd(CO)$_{16}$]$^{2-}$ (average 2.599 Å),[39] where Pd has an essentially square planar stereochemistry, and slightly shorter than, but closer to, those found in [Fe$_6$Pd$_6$(CO)$_{24}$H]$^{3-}$ (average 2.668 Å),[39] where the Pd coordination is less anisotropic.

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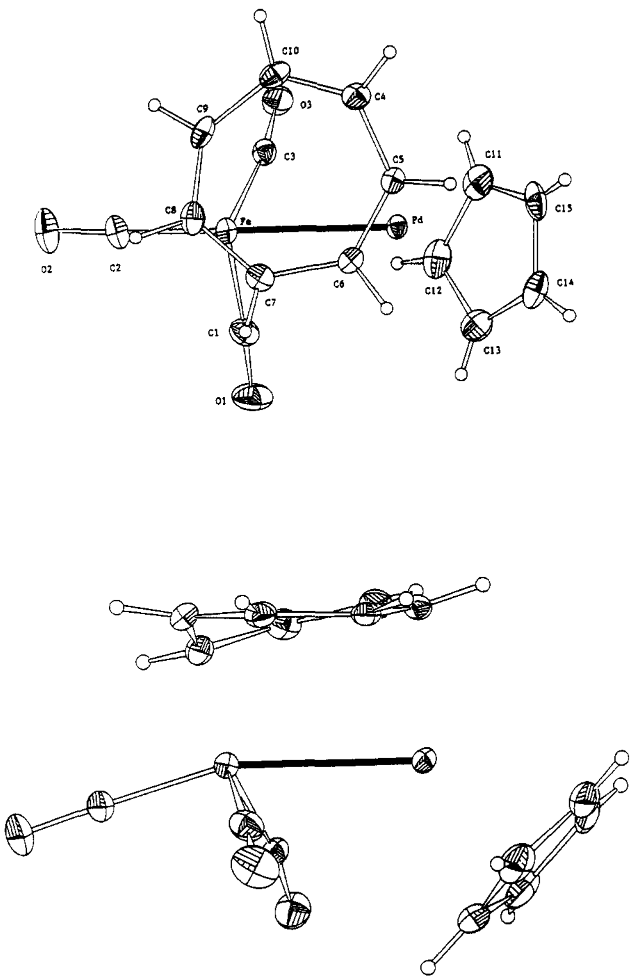

Figure 5. ORTEP drawings (30% probability ellipsoids) of $[Fe(CO)_3(\mu\text{-}\eta^3\text{:}\eta^2\text{-}C_7H_7)Pd(\eta^5\text{-}C_5H_5)]$ showing the molecule (a) along the perpendicular of the C_7H_7 least squares plane and (b) by rotating the previous view of 90° about the Fe–Pd bond.

The π electrons of the C_7H_7 ring are partially localized into one "allylic" (average C–C 1.404 Å) and two "ethylene" moieties (1.331(5) and 1.406(5) Å) separated by long C–C bonds (average C–C 1.444 Å); as a result C_7H_7 is nonplanar and the angles between the ethylene and allylic planes are 13° (inter-ethylene), 24°, and 35°, respectively. Noteworthy, one out of the two double bonds is uncoordinated and, as a consequence, has a shorter C–C bond distance than the coordinated one (1.331(5) vs 1.406(5) Å).

The Fe environment is close to that found in $[(\mu\text{-}\eta^3\text{:}\eta^4\text{-}C_7H_7)Fe(CO)_3Rh(CO)_2]$,[2] the average Fe–C(carbonyl) (1.786 vs 1.771 Å) bond length and the pattern of the Fe–C(ring) interactions (long–short–long) being similar even if, in the present case, we can envisage a slightly semibridging character for one of the carbonyl ligands (Fe–C3–O3 171.0(3)°, Pd···C3 2.653(4) Å) which was not present in $[(\mu\text{-}\eta^3\text{:}\eta^4\text{-}C_7H_7)Fe(CO)_3Rh(CO)_2]$.

The Pd coordination geometry is somewhat related to that of the $[Pd(\eta^5\text{-}C_5H_5)(PEt_3)(styrene)]^+$ cation[40] which also presents a "three-coordinated" Pd atom and a "similar" ligand sphere. Noteworthy, the Pd–C_5H_5 interactions (approximately) trans to the η^2-bonded C_7H_7 atoms are significantly shorter than the others (2.275 vs 2.394 Å); the corresponding distances in the $[Pd(\eta^5\text{-}C_5H_5)(PEt_3)(styrene)]^+$ cation have a similar, even if less marked, behavior (2.254 vs 2.317 Å).

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Supplementary Material Available: Tables of anisotropic thermal parameters and all bond distances and angles (3 pages). Ordering information is given on any current masthead page.

OM930163E

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