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X-ray Crystal Structures of Two (Ethylidyne)tricobalt Clusters: Thermolysis of $Cp^*Co(H_2C{=}CH_2)_2$ Produces $Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}H)$, Not $Cp^*_3Co_3(\mu_3\text{-}CCH_3)_2$

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*Summary: The structures of the μ_3-ethylidyne tricobalt clusters $Cp^*_3Co_3(\mu_3\text{-}CCH_3)_2$ (**2**) and $Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}H)$ (**3**) were determined by X-ray crystallography. The 48-electron cluster **2** consists of an equilateral triangle of cobalt atoms (Co–Co = 2.437(1) Å) symmetrically capped on each face by a μ_3-CCH_3 ligand. Cluster **3** was necessarily disordered by the crystallographic site symmetry (3/m) and was therefore refined by employing a mirror-disordered model (**3a**) which assigned half-weight to the disordered μ_3-CCH_3 ligand. The 46-electron cluster **3a** consists of an equilateral triangle of cobalt atoms (Co–Co = 2.378(1) Å) symmetrically capped on a single face by a μ_3-CCH_3 ligand.*

Introduction

The unusual tricobalt tetrahydride cluster $Cp^*_3Co_3(\mu\text{-}H)_4$ (**1**) is highly reactive due to its paramagnetic, 46 electron configuration and lack of bridging ligands other than hydrogen.[2–4] **1** reacts with acetylene to ultimately form the diamagnetic bis(ethylidyne) cluster $Cp^*_3Co_3(\mu_3\text{-}CCH_3)_2$ (**2**).[5] Both the mono(ethylidyne) monohydride cluster $Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}H)$ (**3**) and the mono(ethylidyne) trihydride cluster $Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_2\text{-}H)_3$ (**4**) were isolated as intermediates in this transformation (Scheme 1).

Our X-ray crystal structure of the bis(ethylidyne) cluster **2** was somewhat different than Pardy's crystal structure of the pyrolysis product of $Cp^*Co(H_2C{=}CH_2)_2$ which was also formulated as **2**.[6] Although the cell constants were similar, Pardy's Co—Co distance was 0.07 Å shorter and the μ_3-C—CH_3 distance was 0.05 Å longer than the values we observed for **2**. The physical and spectroscopic properties of the two materials were also different. Pardy's cluster was air sensitive, while our material was air-stable even in solution. The ^1H NMR spectrum of Pardy's cluster in benzene-d_6 showed only broad, unresolved signals, while the spectrum of **2** displayed sharp peaks at δ 4.48 (6 H) and 1.57 (45 H). In the mass spectrum of our material, the parent ion peak (m/z 636) was the most intense peak in the spectrum; for Pardy's material, no parent ion was observed and the two highest mass peaks were at m/z 628 (low intensity) and 610 (high intensity). These discrepancies caused us to question whether Pardy's cluster was in fact **2**, although we had no alternative formulation for Pardy's cluster.

We have since determined the X-ray crystal structure of the mono(ethylidyne) cluster **3**, which was complicated by a mirror disorder of the ethylidyne and hydride ligands. An ordered model (**3b**) which assigned full weight to the ethylidyne ligand was nearly identical with the structure Pardy reported for his tricobalt cluster. In addition, the physical and spectroscopic properties of **3** were similar to those reported for Pardy's cluster. These observations strongly suggested that Pardy had actually synthesized the mono(ethylidyne) cluster **3** and had failed to detect the mirror disorder of the μ_3 ligands in the subsequent X-ray diffraction study. Here we report the X-ray crystal structures for clusters **2** and **3** along with a reanalysis of the synthesis and original X-ray data for Pardy's cluster.

Results and Discussion

X-ray Crystal Structure of $Cp^*_3Co_3(\mu_3\text{-}CCH_3)_2$ (2). The structure of **2** obtained from the reaction of **1** with acetylene consists of an equilateral triangle of three cobalt atoms symmetrically capped on each face by a μ_3-CCH_3 ligand (Figure 1; Tables 1 and 2). The bond lengths and angles of **2** are similar to those of other tricobalt clusters possessing μ_3-alkylidyne ligands.[7–11] The Co–Co distance in the 48-electron cluster **2** (2.437(1) Å) is similar to that of other 48-electron $Cp^*_3Co_3$ clusters but is 0.06 Å longer than the Co—Co distance in the 48-electron Cp cluster $Cp_3Co_3(\mu_3\text{-}CCH_3)_2$ (2.371 Å).[7] Dahl has previously noted that substitution of bulky Cp* ligands for the sterically less demanding Cp ligands in a tricobalt cluster increases the Co–Co distance due to Cp*–Cp* repulsion.[12] The Cp* ligands are arranged head to tail about the cobalt triangle. The three equivalent C(7) Cp* methyl groups on one cluster face form a plane 2.556 Å above the tricobalt plane, and the ethylidyne methyl carbon (C(2)) projects 0.25 Å above the C(7) plane.

X-ray Crystal Structure of $Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}H)$ (3). Preliminary analysis of **3**, obtained as an inter-

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Scheme 1

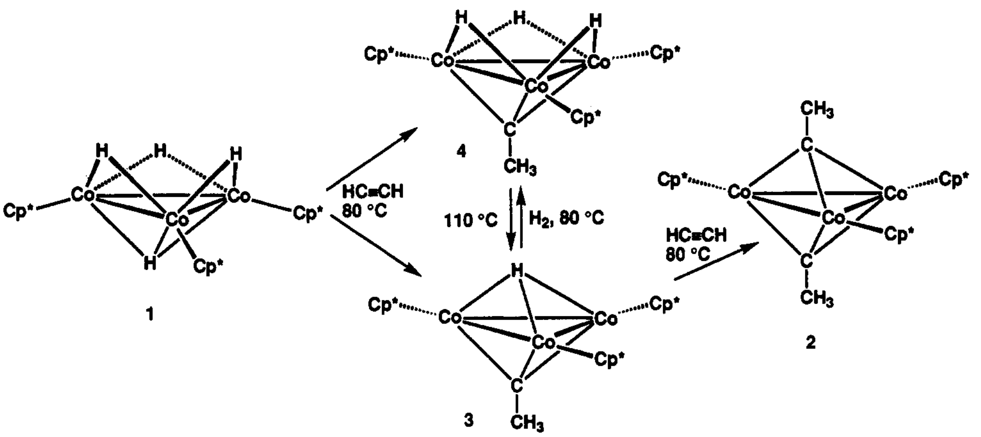


Table 1. Crystal Structure Data for $Cp^*_3Co_3(\mu_3\text{-}CCH_3)_2$ (2), $Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}H)$ (3), and Pardy's Cluster

compd	2	3	Pardy's cluster[a]
empirical formula	$C_{34}H_{51}Co_3$	$C_{32}H_{49}Co_3$	$C_{34}H_{51}Co_3$
color; habit	black; prisms	black; plate	black; hexagon
cryst size (mm)	0.5 × 0.3 × 0.3	0.7 × 0.4 × 0.2	0.3 × 0.3 × 0.2
cryst syst	hexagonal	hexagonal	hexagonal
space group	$P6_3/m$	$P6_3/m$	$P6_3/m$
unit cell dimens (Å)			
a	10.716(2)	10.700(1)	10.678(3)
c	15.485(3)	15.482(2)	15.440(4)
V (Å³)	1539.8(7)	1535.0(3)	1524.5(7)
no. of peaks to determine cell	18	25	
2θ range of cell peaks (deg)	25.0–30.0	25.0–30.0	
Z	2	2	2

[a] Reference 6.

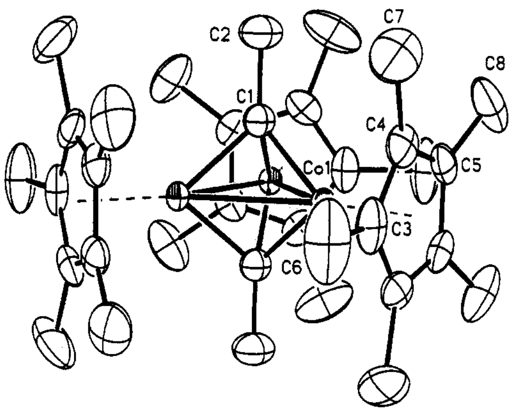


Figure 1. X-ray crystal structure of $Cp^*_3Co_3(\mu_3\text{-}CCH_3)_2$ (2) with thermal ellipsoids shown at the 35% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Cp^*_3Co_3(\mu_3\text{-}CCH_3)_2$ (2)

Co(1)–Co(1a)	2.437(1)	Co(1)–C(3)	2.120(3)
Co(1)–C(1)	1.873(3)	Co(1)–C(4)	2.115(3)
C(1)–C(2)	1.477(7)	Co(1)–C(5)	2.090(3)
Co(1)–C(1)–C(2)	131.3(1)	Co(1)–Co(1a)–C(1)	49.4(1)
Co(1)–C(1)–Co(1a)	81.1(1)	C(1)–Co(1)–C(1a)	82.6(2)

mediate in the reaction of 1 with acetylene, revealed that the ethylidyne and hydride ligands were necessarily disordered under the crystallographic site symmetry (3/m). Because of the disorder, 3 was refined according to two independent models: a mirror-disordered model (**3a**) (Figure 2; Tables 1 and 3) assigned half-weight (7.5 electrons) to the atoms of the independent ethylidyne ligand and an ordered model (**3b**) assigned full weight (15 electrons) to the ethylidyne ligand. Comparison of the parameters for each refinement (Table 4) revealed that **3a** was the more reliable model. For example, (1) the discrepancy factor for **3a** ($R(F)$ = 2.77%, $wR(F)$ = 4.03%) was lower than for **3b** ($R(F)$ = 3.57%, $wR(F)$ = 6.23%), (2) the goodness-of-fit parameter for **3a** (1.56) was superior to that for **3b** (2.08), (3) the bond distances and bond angles for **3a** were more precise than in **3b**, and (4) the thermal ellipsoids for the ethylidyne carbon atoms of **3a** were substantially smaller than those observed in **3b**.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}H)$ (3a)

Co(1)–Co(1a)	2.378(1)	Co(1)–C(3)	2.137(3)
Co(1)–C(1)	1.916(4)	Co(1)–C(4)	2.115(3)
C(1)–C(3)	1.448(9)	Co(1)–C(5)	2.101(3)
Co(1)–C(1)–C(2)	134.2(1)	Co(1)–Co(1a)–C(1)	51.6(1)
Co(1)–C(1)–Co(1a)	76.7(2)	C(1)–Co(1)–C(1a)	88.5(3)

Table 4. Refinement parameters for 2, 3a, 3b, and Pardy's Cluster

compd	2	3a	3b	Pardy's cluster[a]
empirical formula	$C_{34}H_{51}Co_3$	$C_{32}H_{49}Co_3$	$C_{34}H_{51}Co_3$	$C_{34}H_{51}Co_3$
fw	636.5	610.5	636.5	636.5
$R(F)$ (%)	2.54	2.77	3.57	6.2
$wR(F)$ (%)	4.49	4.03	6.23	
goodness of fit	1.58	1.56	2.08	
D_c (g cm⁻³)	1.373	1.321	1.377	1.391
$F(000)$	672	644	672	

[a] Reference 6.

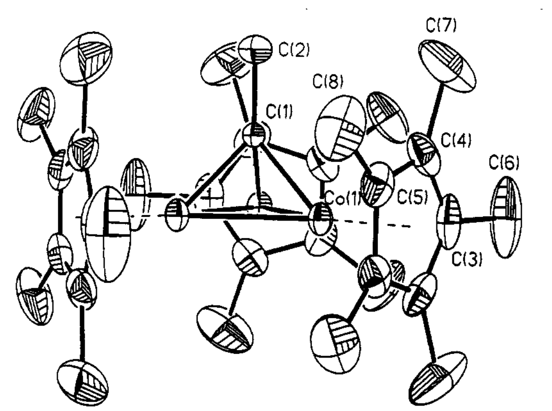


Figure 2. X-ray crystal structure of $Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}H)$ (3a) with thermal ellipsoids shown at the 35% probability level. One ethylidyne ligand has been removed for clarity.

Although the refinement parameters obtained for **3a** were consistently superior to those obtained for **3b**, these values varied only slightly between the two refinements and the $R(F)$ values for **3a** and **3b** differed by less than 1%. Because the ethylidyne atoms are in identical positions in both model **3a** and model **3b**, the two models differ only in the predicted scattering from the ethylidyne ligand. The excess electron density predicted by model **3b** therefore generates abnormally large temperature factors on the ethylidyne carbon atoms but has a minimal effect on the R value. In fact, the large thermal ellipsoids on the ethylidyne carbon atoms were the only crystallographic anomalies in **3b** directly indicative of the mirror disorder. As a result, it appears unlikely that the mirror disorder in **3** could have been unambiguously assigned by crystallographic methods without the aid of additional spectroscopic and physical data.

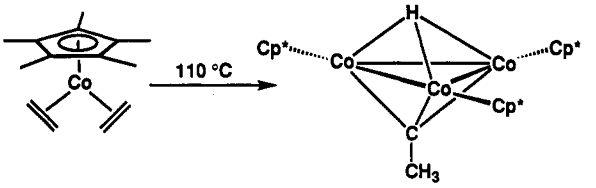
In light of these results, we suggested that Pardy and co-workers reexamine their X-ray structure. G.W.S. reanalyzed the original data set with **3a** as the model. A better fit for mono(ethylidyne) **3** than for bis(ethylidyne) **2** was found, in complete agreement with the results reported here.

Structure **3a** consists of an equilateral triangle of cobalt atoms symmetrically capped on one face by a μ_3-CCH_3 ligand. The μ_3-H ligand which presumably caps the opposite cluster face was not observed crystallographically. The substitution of the μ_3-H ligand in **3** for the μ_3-CCH_3 ligand of **2** does not appear to significantly alter the geometry of the ethylidyne ligand or the arrangement of the Cp* ligands.

The spatial relationship between the Cp* ligands and the ethylidyne ligand in **3a** is nearly identical with that observed for **2** and appears to contribute directly to the mirror disorder in **3**. Because the ethylidyne methyl group projects only 0.22 Å above the surrounding Cp* ligands, the contour of the cluster face is determined primarily by the Cp* ligands and is affected only slightly by the ethylidyne ligand. The dominant steric influence and high symmetry ($3/m$) of the $Cp^*_3Co_3$ core in **3** combined with the lack of a significant dipole allow the cluster to crystallize with the ethylidyne ligand positioned randomly above and below the Co_3 plane. The influence of the $Cp^*_3Co_3$ core on the crystal geometry is also demonstrated by the similarity in the cell parameters observed for both **2** and **3a** and also for the dicarbonyl cluster $Cp^*_3Co_3(\mu_3\text{-}CO)_2$ ($P6_3/m$, a = 10.636(3) Å, c = 15.294(7) Å, V = 1498(1) Å^3, Z = 2)[10b] and the carbonyl ethylidyne cluster $Cp^*_3Co_3(\mu_3\text{-}CO)(\mu_3\text{-}CCH_3)(\mu_2\text{-}H)$ ($P6_3$/m, a = 10.6493(6) Å, c = 15.431(4) Å, V = 1528.4(4) Å^3, Z = 2).[13] The disorder of small ligands in molecules possessing sterically demanding ancillary ligands such as tertiary phosphines or porphyrins has been observed.[14]

The Co–Co distance of **3a** (2.378(1) Å) is only slightly longer than the value observed for the 46-electron cluster $Cp^*_3Co_3(\mu_3\text{-}CO)_2$ (2.370 Å) and is consistent with a 46-electron $(Cp^*Co)_3$ cluster with apical carbon atoms.[10b,12] However, the Co–Co distance in the 46 electron cluster **3a** is considerably shorter (0.059 Å) than in the 48-electron cluster **2**, in accord with theoretical predictions.[15] The 0.059-Å lengthening of the Co–Co distances between 46-electron **3a** and 48-electron **2** is consistent with a 0.03 Å/electron lengthening of the M–M distances in the 48/49/50-electron series of trimetallic clusters $Cp_3CoNi_2(\mu_3\text{-}CO)_2$ (2.356 Å),[16] $Cp_3Ni_3(\mu_3\text{-}CO)_2$ (2.389 Å),[16] and $[K(2,2,2\text{-}crypt)]^+ [Cp_3Ni_3(\mu_3\text{-}CO)_2]^-$ (2.421 Å).[17]

Scheme 2



3

Thermolysis of $Cp^*Co(H_2C{=}CH_2)_2$. Pardy's original report claimed that thermolysis of $Cp^*Co(H_2C{=}CH_2)_2$ in n-octane for 24 h formed $Cp^*_3Co_3(\mu_3\text{-}CCH_3)_2$ in 60% isolated yield. However, in our hands, thermolysis of $Cp^*Co(CH_2{=}CH_2)_2$ gave only the mono(ethylidyne) cluster $Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}H)$ (**3**), which was isolated in a 48% yield as dark brown microcrystals (Scheme 2).[6] Cluster **3** obtained in this reaction was >95% pure, contained no trace of **2** by ^{1}H NMR analysis, and displayed a ^{1}H NMR spectrum (δ 53.6) and mass spectrum (m/z 610) identical with that of an authentic sample.[5]

Experimental Section

Synthesis of $Cp^*Co(H_2C{=}CH_2)_2$. When a 75-mL thick-walled sealed tube containing a purple solution of $Cp^*_2Co_2(\mu\text{-}H)_3$[2] (400 mg, 1.0 mmol) and ethylene (9.6 mmol) in 30 mL of benzene was heated at 90 °C for 12 h, the solution turned brown. Evaporation of the solvent and vacuum sublimation of the residue at 60 °C gave $Cp^*Co(H_2C{=}CH_2)_2$ (350 mg, 68%) as orange crystals. The ^{1}H NMR spectrum was identical with that of an authentic sample.[18]

Thermolysis of $Cp^*Co(H_2C{=}CH_2)_2$. An orange solution of $Cp^*Co(H_2C{=}CH_2)_2$ (220 mg, 0.88 mmol) in 4 mL of n-octane[19] was heated at 110 °C for 24 h. The resulting dark brown precipitate was filtered, washed with 2 mL of pentane, and dried to give $Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}H)$ (**3**) (85 mg, 48%) as dark brown microcrystals which were >95% pure by ^{1}H NMR analysis. ^{1}H NMR (200 MHz, C_6D_6): δ 53.6 (br s, C_5Me_5). HRMS (EI) calcd (found) for $C_{32}H_{49}Co_3$: 610.1827 (610.1830).

X-ray Crystallographic Determinations and Refinements. Each crystal was coated in epoxy and mounted on the tip of a thin glass fiber. Diffraction data were obtained with graphite-monochromated Mo Kα radiation on a Siemens P4RA diffractometer at 295 K in the range $4 < 2\theta < 50°$ by the θ–2θ scan technique. Automatic indexing of 18–20 well-centered reflections determined the unit cell; precise unit cell dimensions were determined by the least-squares refinement of 25 well centered, high angle reflections ($25° < 2\theta < 30°$). Systematic absences and statistical analyses of each data set were consistent with the space group $P6_3/m$. Standard reflections showed no significant decrease in intensity throughout data

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(19) n-Octane (Aldrich 99+%) was dried over sodium and distilled immediately prior to use.

Table 5. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (×10^3) for $Cp^*_3Co_3(\mu_3\text{-}CCH_3)_2$ (2)

	x	*y*	*z*	*U*(eq) (Å^2)[a]
Co(1)	5239(1)	3061(1)	2500	27(1)
C(1)	6667	3333	1701(3)	44(1)
C(2)	6667	3333	747(3)	70(2)
C(3)	3009(3)	1513(4)	2500	59(2)
C(4)	3347(3)	2386(3)	1761(2)	53(1)
C(5)	3907(2)	3816(3)	2034(2)	50(1)
C(6)	2176(4)	−123(5)	2500	112(3)
C(7)	3021(4)	1845(5)	843(3)	112(3)
C(8)	4272(4)	5079(4)	1462(3)	93(2)

[a] Equivalent isotropic *U*, defined as one-third of the trace of the orthogonalized U_{ij} tensor.

acquisition. Initial positions for Co atoms were found by direct methods, and all non-hydrogen atoms were located from successive difference Fourier maps. All non-hydrogen atoms were refined anisotropically; carbon-bound hydrogen atoms were fixed at idealized positions with isotropic thermal parameters of $U = 0.08$ Å^2. Crystallographic computations were performed employing SHELXTL-PLUS[20] software on VAX computers.

X-ray Crystallography of $Cp^*_3Co_3(\mu_3\text{-}CCH_3)_2$ (2). Slow evaporation of a toluene solution gave black crystals of 2[5] suitable for X-ray analysis. The 2136 reflections collected produced 881 independent, observed reflections ($|F| > 4.0\sigma(F)$). The highest peak and deepest hole on the final difference map were +0.22 and −0.32 e Å^{-3}, respectively. Crystallographic data (Table 1), atomic coordinates (Table 5), and selected bond lengths and bond angles (Table 2) are presented.

X-ray Crystallography of $Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}H)$ (3). Slow evaporation of a 1:1 benzene/hexane solution gave black crystals of 3[5] suitable for X-ray analysis. The 2118 reflections collected produced 873 independent, observed reflections ($|F| > 4.0\sigma(F)$); an empirical absorption correction was applied to the data.[21] Crystallographic $3/m$ site symmetry required disorder of the bridging ligands; **3** was therefore refined by employing two independent models: (1) a mirror-disordered mono(ethylidyne) model (**3a**) which assigned half-weight (7.5 electrons) to the apical carbon atom and the methyl group of the independent ethylidyne ligand and (2) an ordered bis(ethylidyne) model (**3b**) assigned full weight (15 electrons) to the atoms of the ethylidyne ligand. In both models, the hydrogen atoms of the ethylidyne methyl group were fixed at calculated positions and the hydride ligand was deleted. The atoms of the ethylidyne ligand were refined without restriction along the crystallographic 3-fold axis. Attempts to remove the crystallographic mirror plane and refine the data in the noncentrosymmetric space group $P6_3$ led to an unstable refinement, anomalous atomic parameters and poor convergence of the data.[22]

Table 6. Atomic Coordinates (×10^5) and Equivalent Isotropic Displacement Coefficients (×10^4) for $Cp^*_3Co_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}H)$ (3a)

	x	*y*	*z*	*U*(eq) (Å^2)[a]
Co(1)	52 706(4)	30 643(4)	25 000	322(2)
C(1)	66 667	33 333	33 633(39)	229(15)
C(2)	66 667	33 333	42 988(46)	438(21)
C(3)	30 191(34)	15 070(38)	25 000	655(17)
C(4)	33 696(25)	23 780(29)	32 333(18)	592(12)
C(5)	39 124(22)	38 101(25)	29 602(17)	527(10)
C(6)	21 654(48)	−1 243(48)	25 000	1 357(39)
C(7)	30 755(51)	18 578(52)	41 542(27)	1 292(30)
C(8)	42 856(38)	50 878(39)	35 353(27)	1 009(20)

[a] Equivalent isotropic *U*, defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Refinement of 3a and 3b. Anisotropic refinement of all non-hydrogen atoms in model **3a** converged at $R(F)$ = 2.77% ($wR(F)$ = 4.03%). The highest peak and deepest hole on the final difference map were +0.27 and −0.27 e Å^{-3}, respectively. The temperature factors on the ethylidyne carbon atoms C(1) (U_{eq} = 0.0023(2) Å^2) and C(2) (U_{eq} = 0.0044(2) Å^2) were of typical size (see below). Crystallographic data (Table 1), atomic coordinates (Table 6), selected bond lengths and bond angles (Table 3) are presented. Anisotropic refinement of all non-hydrogen atoms in model **3b** converged at $R(F)$ = 3.57% ($wR(F)$ = 6.23 %). The largest residual on the final difference map was −0.48 e Å^{-3}. The refinement produced unusually large temperature factors on the ethylidyne carbon atoms C(1) (U_{eq} = 0.0072(2) Å^2) and C(2) (U_{eq} = 0.0121(2) Å^2). No additional anomalies were observed.

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Supplementary Material Available: Tables of structure determination data, anisotropic thermal parameters for non-hydrogen atoms, selected interatomic distances and angles, and idealized atomic parameters for hydrogen atoms as well as figures giving stereoviews of the unit cells of compounds **2** and **3** (16 pages). Ordering information is given on any current masthead page.

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(20) SHELXTL-PLUS, Siemens Analytical X-Ray Instruments, Inc.

(21) Empirical absorption corrections were based on ψ-scan measurements at different azimuthal angles.

(22) See also: (a) Marsh, R. E.; Schomaker, V. *Acta Crystallogr.* **1979**, *B35*, 1933. (b) Marsh, R. E. *Acta Crystallogr.* **1981**, *B37*, 1985. (c) Marsh, R. E.; Herbstein, F. H. *Acta Crystallogr.* **1983**, *B39*, 280. (d) Marsh, R. E. *Acta Crystallogr.* **1986**, *B42*, 193. (e) Marsh, R. E.; Herbstein, F. H. *Acta Crystallogr.* **1988**, *B44*, 77. (f) Marsh, R. E.; Schomaker, V. *Inorg. Chem.* **1979**, *18*, 2331.