Isolation of Intermediates in the $Co_2(CO)_8$-Catalyzed Cyclotrimerization of Cyclooctyne. Crystal and Molecular Structure of a Cobaltacyclopentadiene Complex

M. A. BENNETT* and P. B. DONALDSON

Dicobalt octacarbonyl reacts with cyclooctyne at room temperature to give an orange air-stable complex $Co_2(CO)_5(C_8H_{12})_2$ as the major organocobalt product together with the μ-cyclooctyne complex $Co_2(CO)_6(C_8H_{12})$ and the aromatic cyclotrimer tris(hexamethylene)benzene. The crystal and molecular structure of $Co_2(CO)_5(C_8H_{12})_2$ has been determined by three-dimensional X-ray structural analysis using 4682 reflections, with $F^2 > 3\sigma(F^2)$, collected on a four-circle diffractometer. Crystals of $Co_2(CO)_5(C_8H_{12})_2$ are triclinic, space group $P\bar{1}$, with $a = 13.529$ (3) Å, $b = 8.587$ (2) Å, $c = 9.848$ (2) Å, $\alpha = 103.92$ (1)°, $\beta = 100.44$ (1)°, $\gamma = 102.16$ (1)°, and $Z = 2$. The structure was solved by conventional heavy-atom methods and was refined to final weighted and unweighted R factors of 0.031 and 0.044. In its general features the structure resembles those of the well-known ferracyclopentadiene complexes $Fe_2(CO)_6(alkyne)_2$. Two cyclooctyne units are joined in a metallacyclopentadiene unit containing one cobalt atom carrying three carbon monoxide groups, and the ring is π bonded to the second cobalt atom which carries two carbon monoxide groups. The Co–Co distance of 2.4738 (7) Å is in the range expected for a metal–metal bond. The cobaltacyclopentadiene ring is approximately planar and the near equality of C–C bond lengths [1.423 Å average] indicates extensive electron delocalization Both $Co_2(CO)_6(C_8H_{12})$ and $Co_2(C-O)_5(C_8H_{12})_2$ catalyze cyclotrimerization of cyclooctyne at room temperature, apparently independently of each other.

Introduction

Dicobalt octacarbonyl, $Co_2(CO)_8$, reacts with acetylenes (ac) to give a wide variety of organometallic and organic products.[1-3] The first complex formed under mild conditions is $Co_2(CO)_6(ac)$ (I), which contains a bridging acetylene


I
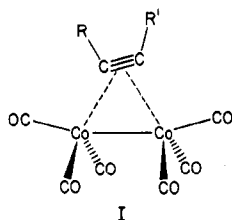
ligand, but on heating with an excess of acetylene organo-metallic complexes of formulas $Co_2(CO)_6(ac)_4$ or Co_2-$(CO)_4(ac)_3$ are produced, in addition to cyclopentadienones, quinones, benzenes, and polymers.[4] The relative amounts of these products depend on reaction conditions and on the alkyne substituents. Cobalt carbonyl complexes such as $Co_2(CO)_8$, $Hg[Co(CO)_4]_2$, and $Co_2(CO)_6(ac)$ also catalyze the cyclo-trimerization of acetylenes to benzenes. It has been suggested[5,6] that the $Co_2(CO)_6(ac)_4$ complexes are cyclo-pentadienone cobalt carbonyls (II), and the $Co_2(CO)_4(ac)_3$

II
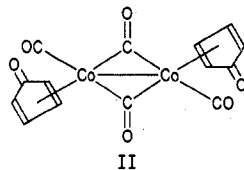
(substituents on cyclopentadienone omitted for clarity)

complexes are known from X-ray studies to contain a bridging unit of three linked alkyne units in a so-called "fly-over" arrangement (III).[7,8] Although the latter compounds do give

III
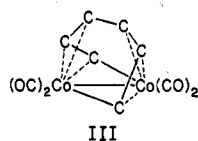
(substituents on carbon chain omitted for clarity)

aromatic trimers on chemical or thermal degradation, they do not catalyze alkyne cyclotrimerization. The mechanism of the catalytic process is unknown, although a study of the $Co_2(CO)_8$-catalyzed cyclotrimerization of $CH_3C_2CD_3$ has

eliminated the possibility that an intermediate cyclobutadiene metal complex is involved.[9] Cyclooligomerization of the simplest unsubstituted isolable cyclic alkyne, cyclooctyne (C_8H_{12}), is catalyzed by a number of transition metal com-pounds, e.g., $NiBr_2$,[10] $Ni(CN)_2$,[10] $Ni(CH_2=CHCN)_2$,[11] Pt-$(PPh_3)_2(C_8H_{12})$,[11] $TiCl_4$,[12] and $Fe(CO)_5$[13] under very mild conditions, and we have therefore investigated the reaction of cyclooctyne with $Co_2(CO)_8$ to see if intermediates in cyclo-oligomerization could be isolated.

Experimental Section

Starting Materials. Hydrocarbon solvents were stored over sodium wire and degassed before use. Chromatographic separations were carried out on columns (100 cm × 4 cm) containing degassed Florisil (60–100 mesh) using degassed n-pentane or benzene as eluent. Samples were collected under nitrogen.

Dicobalt octacarbonyl (Strem) was used as received, and cyclooctyne was prepared by heating cycloocteno-1,2,3-selenadiazole in vacuo.[14,15]

Physical Measurements. The following instruments were used: a PE457 grating instrument calibrated in the $\nu(CO)$ region with DCl (IR), an AEI MS902 operating at 70 eV (mass spectra), a Varian HA100 (^1H NMR), and a Jeol FX-60 FT spectrometer operating at 15.02 MHz (^{13}C NMR). Microanalyses were carried out by the Microanalytical Unit of this University. Melting points were measured on a Gallenkamp hot-stage apparatus in capillaries sealed under nitrogen and are uncorrected.

Reaction of Dicobalt Octacarbonyl with Cyclooctyne. A solution of $Co_2(CO)_8$ (0.401 g, 1.17 mmol) in n-pentane (150 mL) contained in a 250-mL Schlenk flask at room temperature (22 °C) was treated under nitrogen with cyclooctyne (0.752 g, sixfold molar excess) from a syringe. On stirring the mixture, carbon monoxide was rapidly evolved. The reaction gradually subsided but gas evolution continued over a 2-h period. Nitrogen was then bubbled through the solution until the volume was ca. 50 mL and the brownish yellow mixture was chromatographed in n-pentane on Florisil; other adsorbents caused complete decomposition. The faster running brown band contained a mixture of $Co_2(CO)_6(C_8H_{12})$ and colorless tris(hexamethylene)-benzene, $C_{24}H_{36}$, while the slower moving orange band contained $Co_2(CO)_5(C_8H_{12})_2$ and $C_{24}H_{36}$. The organocobalt complexes were separated from the aromatic compound by repeated chromatography.

The first band gave μ-**cyclooctyne-hexacarbonyldicobalt**, Co_2-$(CO)_6(C_8H_{12})$ (0.11 g, 22%), as moderately air-sensitive, red-brown waxy crystals, mp 36–38 °C, from n-pentane at −10 °C: IR (cm^{-1}) (thin film) 2086 (m), 2045 (s), 2024 (vs), 2010 (s) [$\nu(CO)$], 1625 (m) [$\nu(C\equiv C)$]; (C_6H_{14}) 2087 (m), 2045 (s), 2025 (vs), 2012 (s) [$\nu(CO)$]; mass spectrum m/e (relative intensity) 394 (6), 366 (28), 338 (14), 310 (34), 282 (30), 254 (28), 226 (14), 117 (34), 115 (28), 105 (40), 103 (42), 101 (36), 91 (60), 89 (54), 87 (40), 77 (100), 75 (69); ^1H NMR (CD_2Cl_2) δ 1.64, 3.00 (br, m, CH_2) ^{13}C NMR (CD_2Cl_2) δ 27.0, 27.4, 36.5 (s, CH_2), 99.9 (s, $C\equiv C$), (overlapping, br, s, CO). Anal. Calcd for $C_{14}H_{12}O_6Co_2$: C, 42.64; H, 3.04; Co,

29.95; mol wt 393.9299. Found: C, 42.54; H, 3.25; Co, 29.66; mol wt 393.9296 (P⁺, mass spectrometry).

Evaporation of the more slowly moving orange band gave air-stable, orange crystals of **dicarbonyl[2–5-η-2,3:4,5-bis(hexamethylene)(tricarbonylcobalta)cyclopentadiene]cobalt**(*Co–Co*), Co₂(CO)₅(C₈H₁₂)₂: mp 101–103 °C (0.36 g, 66%); IR (cm⁻¹) (C₆H₁₄) 2070 (m), 2014 (vs), 2006 (m), 1966 (vs); mass spectrum *m/e* (relative intensity) 474 (6), 446 (8), 418 (10), 390 (8), 388 (15), 362 (6), 360 (14), 332 (18), 244 (42), 216 (100), 201 (20), 173 (55), 159 (65), 145 (87), 131 (95), 117 (off scale), 105 (off scale), 91 (off scale), 79 (96), 77 (95); ¹H NMR (C₆D₆) δ 1.0–3.05 (overlapping multiplets, CH₂; main peaks at δ 1.50, 2.55, and 2.95); ¹³C NMR (CD₂Cl₂, –90 °C) δ 25.06, 26.75, 29.61, 32.34, 41.04 (s, CH₂), 138.43, 180.89 (s, C=C), 201.94, 204.79 (s, CO). Anal. Calcd for C₂₁H₂₄O₅Co₂: C, 53.16; H, 5.06; Co, 24.89; mol wt 474.0287. Found: C, 53.38; H, 5.10; Co, 24.35; mol wt 474.0286 (P⁺, mass spectrometry). Other accurate mass measurements were as follow. P – CO⁺: calcd, 446.0037; found, 446.0038. P – 2CO⁺: calcd, 418.0388; found, 418.0386. P – 3CO⁺: calcd, 390.0439; found, 390.0439. (C₈H₁₂)₂⁺: calcd, 216.1877; found, 216.1877.

The most slowly moving band eluted with *n*-pentane gave on evaporation and recrystallization from *n*-pentane colorless needles of **Tris(hexamethylene)benzene, C₂₄H₃₆** (0.45 g, 59% or ca. 90% of available excess of cyclooctyne): mp 199–200 °C (lit.[16] mp 197–198 °C); mass spectrum *m/e* (relative intensity) 324 (100), 281 (98), 253 (23), 241 (15), 239 (18), 211 (34), 199 (21), 185 (37), 171 (28), 157 (24), 155 (26), 143 (31), 141 (27), 129 (26), 128 (25), 91 (26), 79 (16), 77 (19). Anal. Calcd for C₂₄H₃₆: C, 88.81; H, 11.19. Found: C, 88.95; H, 11.08.

Elution with benzene gave two bands, the faster moving of which afforded yellow plates identified as **bis(hexamethylene)-1,4-benzoquinone, [C₈H₁₂CO]₂** (0.045 g, 5%): mp 148–149 °C (lit.[13] mp 148 °C); IR (Nujol) 1640 cm⁻¹ [ν(C=O)] (lit.[13] 1640 cm⁻¹); mass spectrum *m/e* (relative intensity) 274 (67), 272 (100), 244 (10), 229 (14), 216 (9), 215 (10), 203 (12), 201 (9), 189 (12), 187 (14), 175 (13), 173 (11), 161 (14), 159 (10), 147 (9), 145 (10), 131 (11), 117 (12), 105 (18), 91 (59), 79 (30), 77 (34). Anal. Calcd for C₁₈H₂₄O₂: C, 79.41; H, 8.82; mol wt 272.1774. Found: C, 79.38; H, 8.79; mol wt 272.1775 (P⁺, mass spectrometry).

The more slowly moving orange band eluted with benzene gave a 3–5% yield of a red organocobalt complex of empirical formula Co₂(CO)₆(C₈H₁₂)₄ which is still being studied.

Catalysis of Cyclooctyne Trimerization. (i) A solution of Co₂(CO)₆(C₈H₁₂) (0.04 g, 0.1 mmol) in *n*-hexane (100 mL) was stirred under nitrogen with cyclooctyne (1.22 g, 3.77 mmol) at room temperature. No gas was evolved and after 8 h, needles of tris-(hexamethylene)benzene (1.16 g, 94%) had deposited. The IR spectrum of the solution in the ν(CO) region showed that Co₂(CO)₆(C₈H₁₂) was still present, and there was no evidence for the formation of Co₂(CO)₅(C₈H₁₂)₂ or any other cobalt carbonyl complexes.

(ii) A solution of Co₂(CO)₅(C₈H₁₂)₂ (0.025 g, 0.05 mmol) was treated with cyclooctyne (0.98 g, 3.02 mmol) as in (i). After 8 h, 0.941 g (96%) of tris(hexamethylene)benzene was isolated and the IR spectrum of the solution in the ν(CO) region showed that unchanged Co₂(CO)₅(C₈H₁₂)₂ was the only organocobalt carbonyl complex present.

Collection and Reduction of X-ray Intensity Data

Chunky orange crystals of Co₂(CO)₅(C₈H₁₂)₂ suitable for X-ray diffraction studies were grown from *n*-hexane by slow evaporation at 4 °C. The crystal selected for the experiment was an eight-sided prism with faces (100), (1̄00), (010), (01̄0), (001), (001̄), (101̄), and (1̄01). Preliminary photographs indicated that the complex crystallizes in the triclinic crystal system; there was no evidence of diffraction symmetry higher than $C_i(\bar{1})$. The choice of the centrosymmetric triclinic space group P1̄ (C_i^1, No. 2) was confirmed by the successful solution and refinement of the structure. The crystal was mounted on a Picker FACS-1 automated diffractometer with the crystal *b* axis approximately coincident with the diffractometer ϕ axis. Unit cell dimensions and the crystal orientation matrix were obtained from the least-squares refinement[17] of the setting angles obtained for 12 carefully centered high-angle reflections (2θ > 45°). Full crystal data are listed in Table I. The experimental conditions and data collection methods used are described in Table II. No crystal decomposition was observed and the reflection intensities were reduced to |F_o| values, each reflection being assigned an individual estimated standard deviation. Formulas

Table I. Crystal Data for Co₂(CO)₅(C₈H₁₂)₂

a = 13.529 (3) Å ^{a,b,c}	α = 103.92 (1)°
b = 8.587 (2) Å	β = 100.44 (1)°
c = 9.848 (2) Å	γ = 102.16 (1)°
Temp 22.5 ± 1 °C	Cell vol 1052.6 Å³
Formula C₂₁H₂₄O₅Co₂	Mol wt 474.03
d_{obsd} = 1.492 g cm⁻³	d_{calcd} = 1.495 g cm⁻³
Space group P1̄ (C_i^1, No. 2)	Z = 2
Cryst dimensions 0.029 × 0.014 × 0.019 cm^d	μ(Mo Kα) = 16.67 cm⁻¹

^{a} Estimated standard deviations (in parentheses) in this and the following tables, and also in the text, refer to the least significant digit(s). ^{b} The "reduced" cell obtained from a Delaunay reduction [B. Delaunay, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.,* **84**, 109 (1933)] agreed with these cell parameters. ^{c} No significant variation in cell dimensions was evident after data collection. ^{d} Crystal dimensions are parallel to a^*, b^*, and c^*, respectively.

Table II. Details of X-ray Data Collection

Radiation	Mo Kα
Wavelength	0.7093 Å
Monochromator	Graphite cryst (002 reflecting plane)
Tube takeoff angle	3.0°
Cryst–counter dist	28.5 cm
Scan technique	Coupled ω/2θ scans
Scan speed	2° min⁻¹
Scan width	From 0.88° below the Mo Kα₁ max to 0.88° above the Mo Kα₂ max of each peak
Scan range limits	3° ≤ 2θ ≤ 60°
Total bkgd counting time^a	20 s
"Standard" reflctn indices	(006), (350), (800), measd after every 100 reflctns
Form of data collected	*hkl, h̄kl, h̄kl̄, hkl̄*
Total data collected	6760
Data with $I/\sigma(I) \geq 3.0$	4682
Data with $I/\sigma(I) \geq 6.0$	3970

^{a} 10-s stationary background counts were taken at the limits of the scan and the background was assumed to be linear between these two points.

used in the data reduction programs have been described elsewhere.[18] The instrumental uncertainty factor (p)[19] was set at a value of 0.002$^{1/2}$. After sorting of reflection data and averaging of equivalent reflections, data with $I \leq 3\sigma(I)$ were discarded as being unobserved and those reflections for which the individual background measurements differed significantly ($B_1/B_2 > 4.0\sigma$) were also discarded. The statistical R factor for the 4682 reflections of the final data set was 0.020.

Structure Solution and Refinement

The positions of the two cobalt atoms were found from a three-dimensional Patterson map. The remaining carbon and oxygen atoms were located on successive electron density difference maps. The structure was refined by block-diagonal least-squares methods to final unweighted and weighted R factors of R_1 = 0.033 and R_2 = 0.049. Atomic scattering factors for the nonhydrogen atoms[20] were corrected for real and imaginary contributions from anomalous scattering.[21,22] Although most hydrogen positions could be located on a difference Fourier map (R_1 = 0.045), all hydrogen atoms were included at calculated positions assuming a C–H distance of 1.0 Å, and equivalent fixed isotropic temperature factors were set at 10% greater than those of the attached atom. The positional and thermal parameters were not refined but recalculated after each refinement cycle. Scattering factors for hydrogen were obtained from the analytical fit of those of Stewart et al.[23] Full details of the refinement sequence are given in Table III.

Four full-matrix refinement cycles were then done on the model as described (R_1 = 0.031, R_2 = 0.044). No individual parameter shift was greater than 0.1 of the corresponding parameter esd. A final difference Fourier map showed no positive maxima >0.3 e Å⁻³. The standard deviation of an observation of unit weight [$\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$ (where *m* is the number of observations and *n* is the number of parameters varied) is 1.40; cf. 1.0 for ideal weighting. There is no evidence of serious extinction effects and no dependence of the minimized function on either |F_o| or $\lambda^{-1} \sin \theta$. The computer

Table III. Least-Squares Refinement Sequence

Set no.	Conditions	No. of cycles	$R_1{}^a$	$R_2{}^b$
1	Two Co atoms included	1	0.335	0.414
1	All non-H atoms included; temp factors invariant	4	0.183	0.206
1	B's varied; anomalous dispersion	1	0.120	0.139
2	Absorption-corrected data$^{b\ 13}$		0.099	0.112
2	Anisotropic temp factors^{c,d}	3	0.045	0.061
2	H atoms included	2	0.033	0.049
2	Full-matrix refinement	4	0.031	0.044

^{a} $R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$ and $R_2 = \{w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$, where F_o is the observed and F_c is the calculated structure factor and w is the weight. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized. ^{b} The transmission factor applied to $|F_o|^2$ averaged 0.896 and ranged from 0.834 to 0.927. ^{c} Anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ were used. ^{d} Weights of the form $\sigma = \sigma_2$ were also introduced, where $\sigma_2 = [(\sigma_1/Lp)^2 + PF_o{}^4]^{1/2}/2F_o$, and $\sigma_1 = $ [peak count + (peak time/background time)$^2]^{1/2} \times$ total background time. Lp is the Lorentz-polarization factor, and P is the instrumental uncertainty factor.

programs used have been described elsewhere.[18] Calculations were performed on the Univac-1108 computer of the Australian National University Computer Centre. Final atomic positional and thermal parameters are listed in Table IV. A list of observed and calculated structure factor amplitudes ($\times 10$) is available as supplementary material.

Results and Discussion

Although the reaction of cyclooctyne, C_8H_{12}, with dicobalt octacarbonyl, $Co_2(CO)_8$, gives the expected μ-alkyne complex

$Co_2(CO)_6(C_8H_{12})$ in about 20% yield, the main organocobalt complex, formed in 66% yield, is an orange-red crystalline air-stable solid of formula $Co_2(CO)_5(C_8H_{12})_2$. Single-crystal X-ray diffraction analysis shows this to be a metallacyclopentadiene complex, IV, a type which has not been isolated hitherto from cobalt carbonyl–acetylene reactions. However, the structure is similar to that proposed on the basis of ^{19}F NMR spectroscopy for the complexes $Rh_2(PF_3)_5(ac)_2$ isolated from the reaction of $Rh_2(PF_3)_8$ with dimethyl acetylenedicarboxylate or methyl propiolate.[24]

The mass spectra of both organocobalt complexes show parent ions and successive loss of CO groups, a feature which is also observed in the case of the metallacyclopentadiene complexes $M_2(CO)_6(ac)_2$ (M = Fe, Ru, Os);[25] peaks due to CH_2 loss from the eight-membered rings are also observed, the pattern being similar to that for cyclooctyne and tris-(hexamethylene)benzene (see Experimental Section).

The IR spectrum of $Co_2(CO)_6(C_8H_{12})$ shows four strong $\nu(CO)$ bands in the 2000-cm^{-1} region which resemble in position and intensity those of other $Co_2(CO)_6(ac)$ complexes.[26-28] The latter generally show five terminal $\nu(CO)$ bands and we suggest that the lowest frequency $\nu(CO)$ absorption in $Co_2(CO)_6(C_8H_{12})$ at 2010 cm^{-1} consists of two overlapping bands which correspond to those at 2016 and 2005 cm^{-1} in the IR spectrum of $Co_2(CO)_6(CH_3C_2CH_3)$.[28] The $\nu(C\equiv C)$ band at 2210 cm^{-1} in free cyclooctyne[29] is shifted to 1625 cm^{-1} in $Co_2(CO)_6(C_8H_{12})$, the decrease in frequency being similar to that observed in forming the 2-butyne complex $Co_2(CO)_6(CH_3C_2CH_3)$.[30] The ^1H NMR spectrum of $Co_2(CO)_6(C_8H_{12})$ exhibits two broad areas of methylene

Table IV. Atomic Positional and Thermal Parameters

ATOM	X/A	Y/B	Z/C	BETA11	BETA22	BETA33	BETA12	BETA13	BETA23
CO(1)	0.15937(2)	0.00025(3)	-0.32922(3)	0.00475(2)	0.01290(5)	0.00808(3)	0.00203(2)	0.00058(2)	0.00311(3)
CO(2)	0.32093(2)	0.12363(3)	-0.13390(3)	0.00500(2)	0.00960(4)	0.00840(3)	0.00152(2)	0.00055(2)	0.00204(3)
C(1)	0.30004(1)	-0.0251(3)	-0.3341(2)	0.0053(1)	0.0130(3)	0.0080(2)	0.0016(2)	0.0019(1)	0.0030(2)
C(2)	0.3510(2)	-0.0018(4)	-0.4557(3)	0.0077(2)	0.0224(5)	0.0129(3)	0.0040(2)	0.0049(2)	0.0082(3)
C(3)	0.3039(3)	-0.1477(5)	-0.5945(3)	0.0113(3)	0.0350(6)	0.0092(3)	0.0077(4)	0.0046(2)	0.0030(4)
C(4)	0.2983(3)	-0.3218(5)	-0.5777(3)	0.0129(3)	0.0295(7)	0.0135(4)	0.0076(4)	0.0029(3)	-0.0022(4)
C(5)	0.3979(3)	-0.3535(5)	-0.5142(4)	0.0127(3)	0.0309(8)	0.0177(5)	0.0096(4)	0.0053(3)	-0.0005(5)
C(6)	0.4178(2)	-0.3426(4)	-0.3519(3)	0.0092(2)	0.0205(5)	0.0169(4)	0.0046(2)	0.0027(4)	0.0027(4)
C(7)	0.4394(2)	-0.1687(3)	-0.2463(3)	0.0059(1)	0.0187(4)	0.0129(3)	0.0046(2)	0.0023(2)	0.0036(3)
C(8)	0.3425(1)	-0.1099(2)	-0.2400(2)	0.0051(1)	0.0108(3)	0.0086(2)	0.0020(1)	0.0013(1)	0.0016(2)
C(9)	0.2841(1)	-0.1287(2)	-0.1351(2)	0.0056(1)	0.0094(3)	0.0072(2)	0.0017(1)	0.0009(1)	0.0019(2)
C(10)	0.3186(2)	-0.1992(3)	-0.0135(2)	0.0076(2)	0.0146(4)	0.0099(2)	0.0029(2)	0.0014(2)	0.0053(2)
C(11)	0.2664(2)	-0.3846(3)	-0.0406(3)	0.0101(2)	0.0145(4)	0.0174(4)	0.0030(2)	0.0025(2)	0.0081(3)
C(12)	0.1509(3)	-0.4275(3)	-0.0339(3)	0.0126(3)	0.0162(4)	0.0164(4)	0.0009(3)	0.0040(3)	0.0075(4)
C(13)	0.0738(2)	-0.4046(3)	-0.1535(3)	0.0090(2)	0.0166(4)	0.0153(4)	-0.0011(2)	0.0033(2)	0.0026(3)
C(14)	0.0375(2)	-0.2474(3)	-0.1165(3)	0.0070(2)	0.0210(5)	0.0137(3)	0.0010(2)	0.0045(2)	0.0052(3)
C(15)	0.1228(2)	-0.0833(3)	-0.0531(2)	0.0071(1)	0.0158(4)	0.0099(2)	0.0003(1)	0.0039(2)	0.0032(2)
C(16)	0.1966(1)	-0.0623(2)	-0.1509(2)	0.0053(1)	0.0108(3)	0.0069(2)	0.0014(1)	0.0015(1)	0.0018(2)
C(17)	0.1731(2)	0.1424(4)	-0.4368(3)	0.0067(2)	0.0237(6)	0.0186(4)	0.0035(2)	0.0016(2)	0.0121(4)
O(17)	0.1811(2)	0.2343(4)	-0.5003(3)	0.0120(2)	0.0441(7)	0.0388(6)	0.0080(3)	0.0059(3)	0.0334(6)
C(18)	0.0569(2)	0.0792(3)	-0.2695(2)	0.0071(2)	0.0200(5)	0.0106(3)	0.0051(2)	0.0004(2)	0.0036(3)
O(18)	-0.0096(2)	0.1275(3)	-0.2366(2)	0.0103(2)	0.0371(6)	0.0157(3)	0.0130(3)	0.0034(2)	0.0062(3)
C(19)	0.0903(2)	-0.2015(3)	-0.4472(2)	0.0062(1)	0.0168(4)	0.0089(2)	0.0019(2)	0.0008(1)	0.0027(3)
O(19)	0.0457(2)	-0.3293(3)	-0.5188(2)	0.0108(2)	0.0194(4)	0.0147(3)	-0.0005(2)	-0.0003(2)	-0.0009(3)
C(20)	0.3156(2)	0.2327(3)	0.0379(2)	0.0090(2)	0.0124(3)	0.0113(3)	0.0019(2)	0.0011(2)	0.0007(3)
O(20)	0.3097(2)	0.3000(3)	0.1494(2)	0.0155(2)	0.0219(4)	0.0138(3)	0.0034(3)	0.0050(2)	-0.0028(3)
C(21)	0.4198(2)	0.2795(3)	-0.1514(3)	0.0066(1)	0.0138(4)	0.0135(3)	0.0011(2)	0.0005(2)	0.0045(3)
O(21)	0.4842(2)	0.3797(3)	-0.1647(3)	0.0095(2)	0.0214(4)	0.0252(4)	-0.0027(2)	0.0028(2)	0.0097(3)

| ATOM	X/A	Y/B	Z/C	B(A**2)		ATOM	X/A	Y/B	Z/C	B(A**2)
H(21)	0.427	0.010	-0.424	5.2		H(101)	0.302	-0.135	0.075	4.4
H(22)	0.341	0.103	-0.478	5.2		H(102)	0.396	-0.184	0.003	4.4
H(31)	0.347	-0.133	-0.665	7.0		H(111)	0.306	-0.424	0.034	5.8
H(32)	0.231	-0.146	-0.634	7.0		H(112)	0.271	-0.446	-0.138	5.8
H(41)	0.269	-0.402	-0.676	8.0		H(121)	0.146	-0.356	0.059	6.7
H(42)	0.250	-0.340	-0.514	8.0		H(122)	0.130	-0.548	-0.036	6.7
H(51)	0.457	-0.269	-0.527	8.4		H(131)	0.011	-0.502	-0.183	6.0
H(52)	0.398	-0.467	-0.569	8.4		H(132)	0.107	-0.403	-0.236	6.0
H(61)	0.480	-0.385	-0.327	6.1		H(141)	-0.005	-0.257	-0.044	5.4
H(62)	0.355	-0.415	-0.337	6.1		H(142)	-0.007	-0.242	-0.207	5.4
H(71)	0.489	-0.088	-0.276	4.8		H(151)	0.163	-0.062	0.043	4.3
H(72)	0.472	-0.173	-0.148	4.8		H(152)	0.089	0.011	-0.041	4.3
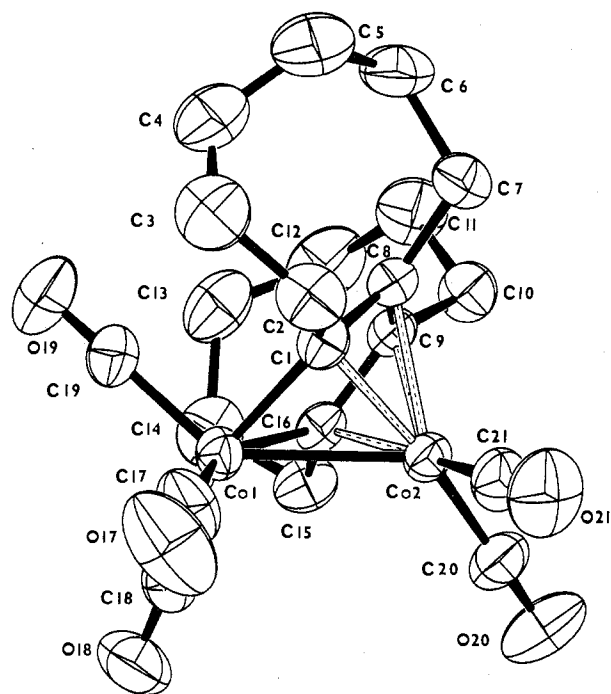
Figure 1. General view of $Co_2(CO)_5(C_8H_{12})_2$.

Table V. Selected Interatomic Distances (Å)

Co(1)–Co(2)	2.4738 (7)	C(5)–C(6)	1.549 (5)
Co(1)–C(1)	1.973 (2)	C(6)–C(7)	1.535 (4)
Co(1)–C(16)	1.968 (2)	C(7)–C(8)	1.507 (3)
Co(1)–C(17)	1.801 (3)	C(8)–C(9)	1.428 (3)
Co(1)–C(18)	1.797 (3)	C(9)–C(10)	1.511 (3)
Co(1)–C(19)	1.783 (2)	C(9)–C(16)	1.419 (3)
Co(2)–C(1)	2.009 (2)	C(10)–C(11)	1.535 (3)
Co(2)–C(8)	2.132 (2)	C(11)–C(12)	1.546 (4)
Co(2)–C(9)	2.116 (2)	C(12)–C(13)	1.505 (4)
Co(2)–C(16)	2.012 (2)	C(13)–C(14)	1.518 (4)
Co(2)–C(20)	1.748 (2)	C(14)–C(15)	1.530 (3)
Co(2)–C(21)	1.747 (3)	C(15)–C(16)	1.520 (3)
C(1)–C(2)	1.516 (3)	C(17)–O(17)	1.120 (3)
C(1)–C(8)	1.422 (3)	C(18)–O(18)	1.133 (3)
C(2)–C(3)	1.540 (4)	C(19)–O(19)	1.123 (3)
C(3)–C(4)	1.531 (5)	C(20)–O(20)	1.137 (3)
C(4)–C(5)	1.487 (5)	C(21)–O(21)	1.138 (3)

absorption both at ambient temperature and at –90 °C, and the ^{13}C NMR spectrum shows, as expected, three methylene carbon singlets in the normal region and a coordinated alkyne carbon singlet at δ 99.9; cf. δ 94.4 for the alkyne carbon atoms in $Co_2(CO)_6(CH_3C_2CH_3)$.[31] A broad resonance at δ ca. 200 due to coordinated ^{13}CO sharpens slightly on cooling to –90 °C but is not resolved into the two peaks in a 2:1 ratio expected for the $Co_2(CO)_6$(ac) structure. The three carbon monoxide groups on each cobalt atom are probably undergoing fast intramolecular exchange similar to that established for the PF$_3$ groups in $Rh_2(PF_3)_6$(ac) complexes which are structurally similar to $Co_2(CO)_6$(ac).[32] Limiting ^{13}CO spectra have only been observed for $Co_2(CO)_6$ complexes of the strongly electron-withdrawing acetylenes $CF_3C_2CF_3$ and CH_3O_2C-$C_2CO_2CH_3$; for the complexes of other acetylenes the process is fast on the NMR time scale at the lowest accessible temperature.[31]

The IR spectrum of $Co_2(CO)_5(C_8H_{12})_2$ shows four strong ν(CO) bands, the intensity pattern or positions of which do not correspond with those of $Co_2(CO)_6$(ac), $Co_2(CO)_4$(ac)$_3$, or any other organocobalt complex in the literature. The structure of $Co_2(CO)_5(C_8H_{12})_2$ as revealed by X-ray diffraction consists of a cobaltacyclopentadiene ring containing a cobalt atom Co(1) and four carbon atoms [C(1), C(8), C(9), and C(16)] derived from two cyclooctyne units (Figure 1).
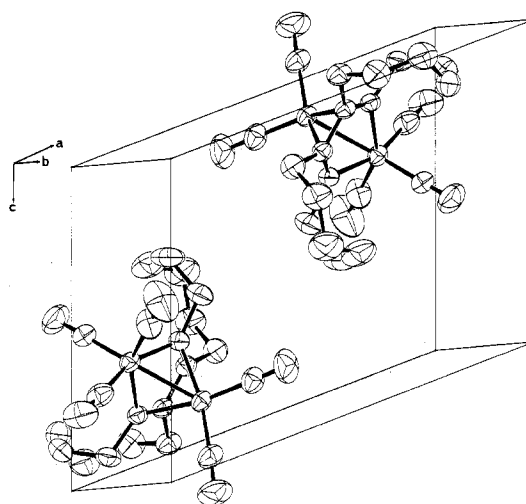

Figure 2. Unit cell contents.

Table VI. Selected Interatomic Angles (deg)

Co(2)–Co(1)–C(1)	52.24 (6)	C(5)–C(6)–C(7)	116.4 (3)
Co(2)–Co(1)–C(16)	52.36 (6)	C(6)–C(7)–C(8)	113.3 (2)
Co(2)–Co(1)–C(17)	101.40 (9)	C(1)–C(8)–C(7)	124.2 (2)
Co(2)–Co(1)–C(18)	108.33 (8)	C(1)–C(8)–C(9)	112.2 (2)
Co(2)–Co(1)–C(19)	136.92 (7)	C(7)–C(8)–C(9)	123.5 (2)
C(1)–Co(1)–C(16)	79.41 (8)	C(8)–C(9)–C(10)	122.6 (2)
C(1)–Co(1)–C(17)	90.2 (1)	C(8)–C(9)–C(16)	112.9 (2)
C(1)–Co(1)–C(18)	160.1 (1)	C(9)–C(10)–C(11)	114.9 (2)
C(1)–Co(1)–C(19)	96.3 (1)	C(10)–C(11)–C(12)	115.7 (2)
C(16)–Co(1)–C(17)	152.6 (1)	C(11)–C(12)–C(13)	116.4 (2)
C(16)–Co(1)–C(18)	91.3 (1)	C(12)–C(13)–C(14)	115.8 (2)
C(16)–Co(1)–C(19)	98.5 (1)	C(13)–C(14)–C(15)	116.4 (2)
C(17)–Co(1)–C(18)	90.2 (1)	C(14)–C(15)–C(16)	111.5 (2)
C(17)–Co(1)–C(19)	108.0 (1)	Co(1)–C(16)–C(9)	116.4 (1)
C(18)–Co(1)–C(19)	102.5 (1)	C(9)–C(16)–C(15)	118.9 (2)
Co(1)–Co(2)–C(1)	50.95 (6)	C(15)–C(16)–Co(1)	122.8 (1)
Co(1)–Co(2)–C(8)	77.59 (5)	Co(1)–C(17)–O(17)	177.8 (3)
Co(1)–Co(2)–C(9)	77.72 (5)	Co(1)–C(18)–O(18)	177.7 (2)
Co(1)–Co(2)–C(16)	50.79 (5)	Co(1)–C(19)–O(19)	178.3 (2)
Co(1)–Co(2)–C(20)	120.03 (8)	Co(2)–C(20)–O(20)	178.0 (2)
Co(1)–Co(2)–C(21)	119.42 (8)	Co(2)–C(21)–O(21)	179.0 (2)
C(1)–Co(2)–C(8)	40.02 (8)	Co(1)–C(1)–Co(2)	76.81 (7)
C(1)–Co(2)–C(9)	69.95 (8)	Co(2)–C(1)–C(2)	131.6 (2)
C(1)–Co(2)–C(16)	77.55 (8)	Co(2)–C(1)–C(8)	74.7 (1)
C(1)–Co(2)–C(20)	169.5 (1)	Co(2)–C(8)–C(1)	65.3 (1)
C(1)–Co(2)–C(21)	94.1 (1)	Co(2)–C(8)–C(7)	131.7 (1)
C(8)–Co(2)–C(9)	39.29 (7)	Co(2)–C(8)–C(9)	69.7 (1)
C(8)–Co(2)–C(16)	69.79 (8)	Co(2)–C(9)–C(8)	71.0 (1)
C(8)–Co(2)–C(20)	138.9 (1)	Co(2)–C(9)–C(10)	127.5 (1)
C(8)–Co(2)–C(21)	107.4 (1)	Co(2)–C(9)–C(16)	66.0 (1)
C(9)–Co(2)–C(16)	40.12 (8)	Co(1)–C(16)–Co(2)	76.85 (7)
C(9)–Co(2)–C(20)	104.3 (1)	Co(2)–C(16)–C(9)	73.9 (1)
C(9)–Co(2)–C(21)	142.0 (1)	Co(2)–C(16)–C(15)	131.7 (1)
C(16)–Co(2)–C(20)	92.4 (1)	C(20)–Co(2)–C(21)	95.6 (1)
C(16)–Co(2)–C(21)	169.9 (1)	Co(1)–C(1)–C(2)	123.1 (2)
C(2)–C(3)–C(4)	116.0 (2)	Co(1)–C(1)–C(8)	116.3 (1)
C(3)–C(4)–C(5)	117.0 (3)	C(2)–C(1)–C(8)	118.6 (2)
C(4)–C(5)–C(6)	115.7 (3)	C(1)–C(2)–C(3)	112.5 (2)

The packing of the two molecules in the unit cell is shown in Figure 2. Selected interatomic distances, interatomic angles, and least-squares planes with associated deviations are given in Tables V–VII. Three carbon monoxide groups are attached to Co(1); one of them, C(17)–O(17), is approximately cis to C(1) and trans to C(16) [C(1)–Co(1)–C(17) = 90.2 (1)°, C(16)–Co(1)–C(17) = 152.6 (1)°], and the other, C(18)–O(18), is approximately trans to C(1) and cis to C(16) [C-(1)–Co(1)–C(18) = 160.1 (1)°, C(16)–Co(1)–Co(18) = 91.3 (1)°]. The other carbonyl group C(19)–O(19) is cis to both C(1) and C(16) [C(1)–Co(1)–C(19) = 96.3 (1)°, C(16)–Co(1)–C(19) = 98.5 (1)°]; hence the ligand arrangement about Co(1) is approximately square pyramidal if we exclude

Table VII. $Co_2(CO)_5(C_8H_{12})_2$ Least-Squares Planes

(i) Best Weighted Least-Squares Planes

Plane	Atoms defining plane	Equation[a]
1	C(1), C(8), C(9), C(16)	$-0.2800X - 0.7289Y - 0.6248Z - 0.0909 = 0$
2	C(1), C(8), C(9), C(16), Co(1)	$-0.1696X - 0.8155Y - 0.5534Z - 0.4658 = 0$
3	C(1), C(2), C(7), C(8), C(9), C(10), C(11), C(15), C(16)	$-0.2566X - 0.7530Y - 0.6059Z - 0.1651 = 0$
4	C(1), C(16), Co(1)	$-0.0982X - 0.8534Y - 0.5119Z - 0.5020 = 0$

(ii) Deviations of Atoms from Best Planes (A)[b]

Atom	Plane 1	Atom	Plane 2	Atom	Plane 3	Atom	Plane 3
C(1)	−0.004 (2)	C(1)	−0.143 (2)	C(1)	−0.044 (2)	C(15)	0.058 (2)
C(8)	0.007 (2)	C(8)	0.076 (2)	C(2)	0.014 (3)	C(16)	−0.023 (2)
C(9)	−0.006 (2)	C(9)	0.067 (2)	C(7)	0.047 (3)	Co(1)	0.2821 (3)
C(16)	0.004 (2)	C(16)	−0.126 (2)	C(8)	0.020 (2)	Co(2)	−1.5958 (3)
Co(1)	0.3722 (3)	Co(1)	0.0023 (3)	C(9)	0.014 (2)		
Co(2)	−1.5659 (3)	Co(2)	−1.6706 (3)	C(10)	−0.063 (2)		

[a] The equations of the planes $LX + MY + NZ + D = 0$ refer to orthogonal coordinates. [b] Dihedral angle between planes 1 and 4 is 14.22°.

the Co(1)–Co(2) bond (see below). The double bonds of the cobaltacyclopentadiene ring are equal within experimental error [C(1)–C(8) = 1.422 (3) Å, C(8)–C(9) = 1.428 (3) Å, C(9)–C(16) = 1.419 (3) Å], implying extensive π-electron delocalization, and the ring is π bonded to the second cobalt atom Co(2) [Co(2)–C(1) = 2.009 (2) Å, Co(2)–C(8) = 2.132 (2) Å, Co(2)–C(9) = 2.116 (2) Å, Co(2)–C(16) = 2.012 (2) Å]. Of the two carbon monoxide groups attached to Co(2), one, C(20)–O(20), is approximately trans to C(1) and cis to C(16) [C(1)–Co(2)–C(20) = 169.5 (1)°, C(1)–Co(2)–C(21) = 94.1 (1)°], while the other, C(21)–O(21), is approximately cis to C(1) and trans to C(16) [C(16)–Co(2)–C(20) = 92.4 (1)°, C(16)–Co(2)–C(21) = 169.9 (1)°]. The distance Co(1)–Co(2) of 2.4738 (7) Å is within the range expected for a metal–metal single bond; this must be present if each metal atom is to have a rare gas configuration. As a consequence, there is a dihedral angle of 14.2° at carbon atoms C(1) and C(16), the bending being toward Co(2). There is a clear resemblance to the published structures of ferracyclopentadiene complexes, $Fe_2(CO)_6(ac)_2$, and related compounds,[33-39] although the Co(1)–Co(2)–CO angles [Co(1)–Co(2)–C(20) = 120.03 (8)°, Co(1)–Co(2)–C(21) = 119.42 (8)°] are approximately 12–14° smaller than in the iron complexes. This bending back of the carbonyl groups toward Co(1) is hardly surprising because the third carbonyl group, which frequently occupies a semibridging position in the ferracyclopentadienes, is absent in the cobalt structure.

The eight-membered carbocycles have a distorted crown configuration. The C–C bond lengths are normal and there is no disorder analogous to that found for the six-membered carbon rings in the structure of the metallocyclopentadiene complex (1,7-cyclododecadiyne)hexacarbonyldiiron.[38] The only close intermolecular contact is that between C(13) and O(19) ($\bar{x}$, $\bar{y}$ − 1, $\bar{z}$ − 1) of 3.355 (3) Å.

The ¹H NMR spectrum of $Co_2(CO)_5(C_8H_{12})_2$ shows complex methylene resonances in the range δ 1.0–3.05 which are unchanged at −90 °C. The ¹³C NMR spectrum at room temperature shows five methylene carbon singlets and a singlet at δ 138.43. On cooling to −90 °C, a second broader singlet appears at δ 180.89 together with a pair of poorly resolved singlets in the region of δ 200. By analogy with the ¹³C NMR spectrum of the ferracyclopentadiene complexes $Fe_2(CO)_6(ac)_2$ (ac = HC_2H, PhC_2H, PhC_2Ph)[39] we assign the peaks at δ 138.43 and δ 180.89 to the carbon atoms of the cobaltacyclopentadiene ring; the broader peak at lower field probably corresponds to the σ-bonded carbon atoms which are likely to be the more strongly affected by the ⁵⁹Co quadrupole.[40] The singlets in the region of δ 200 are clearly due to the carbonyl groups on each cobalt atom, those of the Co(CO)₃ group being apparently equivalent on the NMR time scale. They may be undergoing a tritopal rearrangement similar to that suggested

for the $Rh(PF_3)_3$ unit in the $Rh_2(PF_3)_5(ac)_2$ complexes;[24] studies with ¹³CO-enriched samples are in progress.

The organic products isolated from the reaction of $Co_2(CO)_8$ with cyclooctyne are the aromatic cyclotrimer, tris(hexamethylene)benzene, and ca. 5% of bis(hexamethylene)-1,4-benzoquinone. Cyclotrimerization is catalyzed at room temperature by both $Co_2(CO)_6(C_8H_{12})$ and $Co_2(CO)_5(C_8H_{12})_2$. No other cyclotrimers similar to that formed in the $Pt(PPh_3)_2(C_8H_{12})$-promoted oligomerization of cyclooctyne[11] could be detected. Significantly, reaction of $Co_2(CO)_6(C_8H_{12})$ with cyclooctyne affords the aromatic cyclotrimer without formation of $Co_2(CO)_5(C_8H_{12})_2$ or of a "fly-over" complex (III) containing three cyclooctyne units. Likewise, $Co_2(CO)_5(C_8H_{12})_2$-catalyzed cyclotrimerization of cyclooctyne does not appear to proceed by reversion to $Co_2(CO)_6(C_8H_{12})$, nor can a "fly-over" complex be isolated from the reaction. Thus, there are at least two independent routes for the $Co_2(CO)_8$-catalyzed cyclotrimerization of cyclooctyne.

Since it is isoelectronic with the well-known ferracyclopentadienes $Fe_2(CO)_6(ac)_2$, the stability of $Co_2(CO)_5(C_8H_{12})_2$ is not surprising, but it is not clear why cyclooctyne should be the only alkyne of the many studied to form such a complex. Our results lend support to the idea that cobaltacyclopentadienes, $Co_2(CO)_5(ac)_2$, may be formed as transient intermediates in $Co_2(CO)_8$–alkyne reactions. They may be the precursors of the "fly-over" complexes $Co_2(CO)_4(ac)_3$, since we find that $Co_2(CO)_5(C_8H_{12})_2$ reacts with methyl propiolate to give a pair of isomeric "fly-over" complexes $Co_2(CO)_4\{(C_8H_{12})_2HC_2CO_2CH_3\}$,[41] but it is not obvious why the same reaction does not occur with cyclooctyne itself. At present we can only conclude that the course of $Co_2(CO)_8$–alkyne reactions is very dependent on the alkyne substituents. Further work on the reactions of $Co_2(CO)_6(C_8H_{12})$ and $Co_2(CO)_5(C_8H_{12})_2$ with unsaturated molecules is in progress.

References and Notes

(1) W. Hübel in "Organic Synthesis via Metal Carbonyls", Vol. 1, I. Wender and P. Pino, Ed., Interscience, New York, N.Y., 1968, p 273.
(2) F. L. Bowden and A. B. P. Lever, *Organomet. Chem. Rev., Sect. A*, 3, 227 (1968).
(3) R. S. Dickson and P. J. Fraser, *Adv. Organomet. Chem.*, 12, 323 (1974).
(4) U. Krüerke and W. Hübel, *Chem. Ber.*, 94, 2829 (1961).
(5) W. Hübel and C. Hoogzand, *Chem. Ber.*, 93, 103 (1960).

(6) C. Hoogzand and W. Hübel in "Organic Synthesis via Metal Carbonyls", Vol. 1, I. Wender and P. Pino, Ed., Interscience, New York, N.Y., 1968, p 343.

(7) O. S. Mills and G. Robinson, *Proc. Chem. Soc., London*, 187 (1964).

(8) R. S. Dickson, P. J. Fraser, and B. M. Gatehouse, *J. Chem. Soc., Dalton Trans.*, 2278 (1972).

(9) G. M. Whitesides and W. J. Ehmann, *J. Am. Chem. Soc.*, **91**, 3800 (1969).

(10) G. Wittig and P. Fritze, *Justus Liebigs Ann. Chem.*, **712**, 79 (1968).

(11) G. Wittig and S. Fischer, *Chem. Ber.*, **105**, 3542 (1972).

(12) H. Meier, J. Heiss, H. Suhr, and Eu. Müller, *Tetrahedron*, **24**, 2307 (1968).

(13) H. Kolshorn, H. Meier, and Eu. Müller, *Tetrahedron Lett.*, 1469 (1971).

(14) H. Meier and E. Voigt, *Tetrahedron*, **28**, 187 (1972).

(15) I. Lalezari, A. Shafiee, and M. Yalpani, *J. Heterocycl. Chem.*, 1411 (1972).

(16) G. Wittig and A. Krebs, *Chem. Ber.*, **94**, 3260 (1961).

(17) The Busing and Levy programs [*Acta Crystallogr.*, **22**, 457 (1967)] were used for diffractometer control and data collection.

(18) M. A. Bennett, R. N. Johnson, G. B. Robertson, T. W. Turney, and P. O. Whimp, *Inorg. Chem.*, **15**, 97 (1976).

(19) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1967); P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(20) "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, p 99.

(21) C. T. Prewitt, Ph.D. Thesis, Massachusetts Institute of Technology, 1962, p 163.

(22) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(23) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(24) M. A. Bennett, R. N. Johnson, and T. W. Turney, *Inorg. Chem.*, **15**, 107 (1976).

(25) G. A. Vaglio, O. Gambino, R. P. Ferrari, and G. Cetini, *Org. Mass. Spectrom.*, **5**, 493 (1971).

(26) G. Bor, *Chem. Ber.*, **96**, 2644 (1963).

(27) Y. Iwashita, F. Tamura, and A. Nakamura, *Inorg. Chem.*, **8**, 1179 (1969).

(28) S. F. A. Kettle and P. L. Stanghellini, *Inorg. Chem.*, **16**, 753 (1977).

(29) A. T. Blomquist and L. H. Liu, *J. Am. Chem. Soc.*, **75**, 2153 (1953).

(30) Y. Iwashita, A. Ishikawa, and M. Kainosho, *Spectrochim. Acta, Part A*, **27**, 271 (1971).

(31) S. Aime, L. Milone, R. Rossetti, and P. L. Stanghellini, *Inorg. Chim. Acta*, **22**, 135 (1977).

(32) M. A. Bennett, R. N. Johnson, and T. W. Turney, *Inorg. Chem.*, **15**, 90 (1976).

(33) A. A. Hock and O. S. Mills, *Acta Crystallogr.*, **14**, 139 (1961).

(34) R. P. Dodge and V. Schomaker, *J. Organomet. Chem.*, **3**, 274 (1965).

(35) Y. Degrève, J. Meunier-Piret, M. van Meersche, and P. Piret, *Acta Crystallogr.*, **23**, 119 (1967).

(36) E. F. Epstein and L. F. Dahl, *J. Am. Chem. Soc.*, **92**, 493 (1970).

(37) J. A. D. Jeffreys and C. M. Willis, *J. Chem. Soc., Dalton Trans.*, 2169 (1972).

(38) H. B. Chin and R. Bau, *J. Am. Chem. Soc.*, **95**, 2508 (1973).

(39) L. J. Todd, J. P. Hickey, J. R. Wilkinson, J. C. Huffman, and K. Folting, *J. Organomet. Chem.*, **112**, 167 (1976).

(40) L. J. Todd and J. R. Wilkinson, *J. Organomet. Chem.*, **80**, C31 (1974).

Bis(dimethylamido)tris(*N,N*-dimethylcarbamato)tantalum(V). Structure and Dynamical Solution Behavior of a Compound Containing Seven-Coordinate Tantalum

MALCOLM H. CHISHOLM,* F. ALBERT COTTON,* and MICHAEL W. EXTINE

Bis(dimethylamido)tris(*N,N*-dimethylcarbamato)tantalum(V), Ta(NMe₂)₂(O₂CNMe₂)₃, crystallizes in the monoclinic system with $a = 15.488$ (3) Å, $b = 8.214$ (1) Å, $c = 17.808$ (3) Å, $\beta = 115.25$ (1)°, $V = 2049$ (1) Å³, $Z = 4$, and space group $P2_1/c$. The structure was solved and refined to $R_1 = 0.070$ and $R_2 = 0.088$ using 2247 reflections having $I > 3\sigma(I)$. Tantalum is seven-coordinate and the central TaN_2O_5 moiety corresponds closely to a pentagonal bipyramid. Two bidentate O_2CNMe_2 ligands occupy four of the sites of the pentagonal plane while the fifth is occupied by a dimethylamido ligand. The other dimethylamido ligand and a monodentate O_2CNMe_2 ligand occupy the axial positions. The short Ta–N bond distances (1.96 (1) and 1.97 (1) Å), the planar Ta–NC₂ units, and the 90° dihedral angle between the two Ta–NC₂ planes are indicative of N-to-Ta π bonding, which, together with the formation of the seven σ bonds, allow tantalum to achieve an 18-valence shell electronic configuration. The compound shows an interesting dynamical solution behavior. Above 0 °C intramolecular site exchange is rapid on the NMR time scale (¹H and ¹³C) and leads to the appearance of one type of NMe₂ ligand and one type of O₂CNMe₂ ligand. At low temperature (<–60 °C) there are two types of NMe₂ groups and two types of O₂CNMe₂ ligands. If certain assumptions are made, the latter observation may be reconciled with the adoption in solution of a structure akin to that found in the crystal.

Introduction

Previous work has shown[1-4] that early transition metal dimethylamides react with carbon dioxide to give *N,N*-dimethylcarbamato compounds according to eq 1, where M =

$$M(NMe_2)_n + nCO_2 \rightarrow M(O_2CNMe_2)_n \tag{1}$$

Ti or Zn for $n = 4$ and M = Nb or Ta for $n = 5$. In some cases it was possible to detect and even isolate intermediates $M(NMe_2)_{n-m}(O_2CNMe_2)_m$ in these reactions. In a study of the reactions between $M(NMe_2)_5$ (M = Nb and Ta) and CO_2 we found that no single $M(NMe_2)_{5-n}(O_2CNMe_2)_n$ compound was favored exclusively by kinetic and thermodynamic factors.[4] For M = Ta the compound Ta(NMe₂)₂(O₂CNMe₂)₃ was the only mixed dimethylamido(carbamato)tantalum compound which could be isolated in a pure state.[4] We report here the crystal and molecular structure of Ta(NMe₂)₂(O₂CNMe₂)₃ together with the results of a variable-temperature NMR study (¹H and ¹³C).

*To whom correspondence should be addressed: M.H.C., Princeton University; F.A.C., Texas A&M University.

Results and Discussion

Solid-State Structure of Ta(NMe₂)₂(O₂CNMe₂)₃. The compound is composed of discrete molecules of Ta-(NMe₂)₂(O₂CNMe₂)₃ in the solid state. A perspective drawing showing the coordination geometry of the tantalum atom and the atom labeling scheme is shown in Figure 1. The final atomic coordinates and thermal parameters are given in Table I. Pertinent bond distances and angles are given in Table II. Table III lists a number of least-squares planes calculated for this molecule.

Ta(NMe₂)₂(O₂CNMe₂)₃ contains seven-coordinate tantalum. Two of the carbamato ligands are bidentate and one is monodentate. The TaO₅N₂ moiety can be described as a distorted pentagonal bipyramid, with O(5) and N(5) occupying the axial coordination sites. The tantalum and remaining five atoms are approximately planar (see Table III). All three *N,N*-dimethylcarbamato ligands are planar; note that the tantalum atom lies in the planes defined by the bidentate carbamato ligands. The two TaNC₂ moieties are also planar.

Bonding Considerations. Among the higher coordination numbers, seven-coordinate species represent a commonly found