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Registry No. $(C_4H_4)Fe(dppe)(CO)$, 72318-19-5.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes and of fractional coordinates and isotropic thermal parameters (28 pages). Ordering information is given on any current masthead page.

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Structural Characterization of the (Methylcyclopentadienyl)- and Cyclopentadienylnickel Carbonyl Dimers, $[Ni(\eta^5\text{-}C_5H_4R)(\mu\text{-}CO)]_2$ (R = CH_3, H): Stereochemical Analysis of Planar and Nonplanar $Ni_2(CO)_2$ Cores Containing Metal–Metal Single Bonds

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X-ray diffraction studies of $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$ and $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ show, in accordance with their different solid-state infrared spectra, that the methyl-substituted cyclopentadienylnickel dimer crystallizes with a planar $Ni_2(CO)_2$ framework, in contrast to the unsubstituted dimer which crystallizes with *two* independent molecules A and B containing differently bent $Ni_2(CO)_2$ cores. The crystallographically imposed C_{2h}-$2/m$ site symmetry on the $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$ molecule requires that each of the two centrosymmetrically related methylcyclopentadienyl rings is bisected by the mirror plane coincident with the planar $Ni_2(CO)_2$ core. This unsymmetrical ring orientation produces nonequivalent Ni–CO bond lengths of 1.840 (3) and 1.889 (3) Å (mean 1.864 Å). Molecules A and B of $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ each conform within experimental error to C_{2v}-$2mm$ symmetry; the symmetrically disposed C_5H_5 rings, which are tilted such as to be almost perpendicular to their bonding planar NiC_2 fragments of the bent $Ni_2(CO)_2$ core, give rise to equivalent Ni–CO distances of range 1.853 (5)–1.874 (5) Å (mean 1.863 Å). An examination reveals that a bending deformation of the $Ni_2(CO)_2$ core from a planar one in the methylcyclopentadienyl carbonyl molecule to the differently bent ones in the cyclopentadienyl carbonyl molecules A and B (which possess torsional angles of 146.0 and 139.2°, respectively, for the CNi_2–Ni_2C' fragment) generates essentially no change in the Ni–C bond lengths and only a small alteration in the Ni–Ni distance (from 2.390 (1) to 2.363 (1) and 2.351 (1) Å for molecules A and B, respectively). Hence, an angular deformation of the $Ni_2(CO)_2$ core in molecules A and B may be simply considered as a bending vibrational mode of the two bridging carbonyl ligands about the Ni–Ni axis. The two independent molecules of crystalline $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ are then regarded as individual frames in a motion picture of a dynamic butterfly-like inversion, which is presumed from energetic considerations to occur in solution. In order to lead to an equivalent C_{2v} molecular configuration, an inversion of the nonplanar $Ni_2(CO)_2$ core must be accompanied by a concomitant rotation (together with a slight tilting) of each cyclopentadienyl ring by 36° about its Ni–Cp(centroid) axis. In this case, the intermediate structure corresponds to that of crystalline $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$ with a planar $Ni_2(CO)_2$ core and perpendicular rings which have been rotated by 18°. The solid-state existence of this intermediate configuration thereby provides direct evidence that such a butterfly interconversion is structurally allowed with bridge retention. Both $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$ and $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ were characterized by solution and solid-state infrared, by ^1H and $^{13}C\{^1H\}$ NMR, and by mass spectral measurements under matching conditions. $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$: mol wt = 331.68, monoclinic, $C2/m$, a = 8.009 (2) Å, b = 8.794 (3) Å, c = 9.971 (3) Å, β = 113.87 (1)°, V = 642.2 (7) Å^3, ρ_o = 1.71 g/cm^3 (flotation), ρ_c = 1.715 g/cm^3 for Z = 2. For 1612 independent diffractometry-collected reflections with $I > 2\sigma(I)$, $R_1(F)$ = 5.0% and $R_2(F)$ = 5.7%. $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$: mol wt = 303.63, triclinic, $P\bar{1}$, a = 10.990 (2) Å, b = 13.704 (2) Å, c = 7.860 (2) Å, α = 99.12 (1)°, β = 101.54 (2)°, γ = 75.94 (1)°, V = 1117.4 (4) Å^3, ρ_o = 1.77 g/cm^3 (flotation), ρ_c = 1.805 g/cm^3 for Z = 4. For 3879 independent diffractometry-collected reflections with $I > 2\sigma(I)$, $R_1(F)$ = 4.5% and $R_2(F)$ = 5.2%.

Introduction

In the course of research dealing with a resolution of crystallographic twinning and/or crystal disorder problems in triangular organometallic compounds of cobalt and nickel,[1] the (methylcyclopentadienyl)nickel carbonyl dimer,[2] $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$, was isolated. Our stereochemical interest in this methyl-substituted cyclopentadienyl derivative was aroused by its unexpectedly exhibiting a markedly different color and transparency in the crystalline state from that of the classical parent dimer, $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$.

This latter compound was first prepared in 1958 by Fischer and Palm[3] who from magnetic susceptibility measurements established its diamagnetic character and from its infrared spectrum proposed a carbonyl-bridged structure with a Ni–Ni bond. They also reported[3] from dielectric constant measurements[4] in benzene solution at 25 °C a permanent dipole moment of $\mu = 0 \pm 0.38$ D. The first suggestion of a bent geometry similar to that of the electronically equivalent $Co_2(CO)_8$ was made by Tilney-Bassett and Mills[5] on the basis of the compound exhibiting two carbonyl stretching frequencies in the bridging carbonyl region. Unpublished infrared investigations by Miller and Fritz and independently by Palm (both quoted by Miller[6]) showed the compound to possess two carbonyl stretching bands both in the solid state and in solution but only one band in the vapor at 100 °C. It is noteworthy that Miller[6] in 1962 mentioned that the proposed bent structure for $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ was difficult to reconcile with the compound's zero dipole moment, and consequently he suggested the possibility that the "free" molecule indeed has a center of symmetry but is slightly distorted in solution thereby allowing the second carbonyl frequency to become

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active. He also presumed that the splitting of one of these bands in the crystalline state was due to the presence of two different molecular sites in the crystal. In 1971 McArdle and Manning[7] carried out a detailed infrared analysis including simple force-constant calculations, from which they concluded the presence in solution of only one species containing a puckered $Ni_2(CO)_2$ core with an estimated dihedral angle of ca. 140° between the two Ni–C(carbonyl)–Ni planes fused along the Ni–Ni bond. This geometry was proposed to be analogous to that found by Nice and Mills in the crystalline state from an unpublished X-ray diffraction measurement quoted by Mills and Shaw[8] in 1968 (along with a reported Ni–Ni distance and mean Ni–C(ring) distances) in their X-ray determination of the structurally related (diphenylacetylene)bis(cyclopentadienylnickel) compound.

Measurements of the temperature-dependent proton and carbon-13 NMR spectra of $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ carried out by Gansow, Burke, and Vernon[9] in 1976 showed no evidence of a structural rearrangement in solution over a temperature range between −160 and 100 °C.

In 1968 Brunner[10] reported the preparation and spectral characterization of the corresponding cyclopentadienylcobalt nitrosyl dimer. The diamagnetism of this black compound was established from a ^1H NMR spectrum. From its solution and KBr-pellet IR spectra, which each showed two distinct nitrosyl bands, and from its high dipole moment of 1.64 ± 0.15 D in benzene solution, Brunner[10] proposed that the isoelectronic $[Co(\eta^5\text{-}C_5H_5)(\mu\text{-}NO)]_2$ molecule is structurally analogous to the $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ molecule in containing a bent geometry. However, a recent X-ray diffraction determination of a monoclinic crystalline phase of this cobalt dimer by Bernal et al.[11] in 1977 revealed a centrosymmetric planar rather than a bent $Co_2(NO)_2$ core, which is not consistent with Brunner's KBr-pellet nitrosyl spectrum of $[Co(\eta^5\text{-}C_5H_5)(\mu\text{-}NO)]_2$. Although no explanation and no solid-state IR data were given by Bernal et al.[11] to account for this apparent anomaly, it certainly is conceivable (vide infra) that $[Co(\eta^5\text{-}C_5H_5)(\mu\text{-}NO)]_2$ can crystallize in another solid-state phase with a bent $Co_2(NO)_2$ core. A theoretical analysis involving calculations of Walsh-type diagrams was recently presented by Pinhas and Hoffmann[12] to account for the presence or absence of the ring-puckering deformation in $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$, $[Co(\eta^5\text{-}C_5H_5)(\mu\text{-}NO)]_2$, and related dimers.

This paper reports the single-crystal X-ray diffraction study of $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$ together with that of $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ which was subsequently carried out in order to obtain a detailed comparison of their contrasting solid-state structures. These results together with experimentally matched measurements of their solid-state and solution IR spectra, their ^1H and $^{13}C\{^1H\}$ NMR spectra, and their mass spectra have provided a reconciliation of the previously reported physical measurements of the $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ compound in the vapor, solution, and crystalline states.

Experimental Section

Preparation and Properties. A sample of $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ was synthesized by the method of King;[13a] a sample of $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$ was prepared analogously. The starting nickelocenes required for the above procedures were also produced by the synthetic route of King[13b] with methylcyclopentadiene dimer (Aldrich Chemical Co., 95%) and dicyclopentadiene (Aldrich Chemical Co., 95%), each cracked to monomer immediately before use through a 15-cm Vigreux column. The resulting dimeric carbonyl compounds were purified by several in vacuo sublimations at ca. 90 °C. Whereas microscopic examination showed that the cyclopentadienylnickel carbonyl dimer consists of dark red, often opaque, crystals which appear dark green by reflected light, the methyl-substituted analogue forms clear, bright orange crystals.

Single-Crystal X-ray Data Collection. Relatively large single crystals of both compounds were grown by slow sublimation in vacuo at ca. 70 °C in a 30 cm (length) × 22 mm (diameter) straight glass tube, which was surrounded by a copper tube in order to obtain a relatively uniform, extended temperature gradient.

(a) $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$. A large irregular prism of approximate dimensions 0.54 mm × 0.60 mm × 0.42 mm was chosen, fixed to a glass fiber with water-soluble glue, and mounted on a goniometer. The X-ray measurements were performed on a NOVA automated Syntex $P\bar{1}$ diffractometer with Mo $K\bar{\alpha}$ radiation ($\lambda(\alpha_1) = 0.709\,26$ Å, $\lambda(\alpha_2) = 0.713\,54$ Å).[14] After optical alignment of the crystal, fifteen independent reflections chosen from a Polaroid rotation photograph were computer centered. The angular coordinates thus obtained were autoindexed (from which a monoclinic cell was found and confirmed by axial photographs) and least squares refined to determine an approximate orientation matrix from which angle settings for all reflections could be generated. ω scans of a few reflections showed well-defined peaks with peak widths at half-height measured to be ca. 0.2°. At this point a short data set in the range $25° \leq 2\theta \leq 30°$ was obtained, and fifteen independent medium-intensity reflections, scattered evenly among the eight octants (of $C_{2h}\text{-}2/m$ Laue symmetry), were recentered to obtain a precise orientation matrix and accurate cell parameters together with their associated standard errors. The θ–2θ step scan technique was used to measure intensities with a variable scan speed in 2θ of 4.00–24.00°/min from 1.00° below $K\alpha_1$ to 1.00° above $K\alpha_2$ and with (stationary-crystal)–(stationary-counter) background counting at both extremes of the scan for one-third of the total scan time. The actual scan speed for each reflection was computer determined from an initial 3-s scan over the central one-third of the peak. The intensities of three standard reflections, measured after every 47 data, showed no evidence of significant crystal decay during the entire data collection. Data, sampled once in the reciprocal lattice octants hkl and $\bar{h}kl$ for $3.00° \leq 2\theta \leq 90.00°$, were reduced to $|F_{obsd}|$ and $\sigma(F_{obsd})$.[15] Lorentz–polarization corrections included the polarization effect arising from the monochromator crystal being presumed to be half-mosaic and half-ideal.[16]

Observed systematic absences for $\{hkl\}$ data of $h + k = 2n + 1$ indicated a C-centered lattice compatible with three probable monoclinic space groups:[17] $C2$ (C_2^3, No. 5), Cm (C_s^3, No. 8), and $C2/m$ (C_{2h}^3, No. 12); the centric space group, $C2/m$, was used and subsequently confirmed by the successful solution and refinement of the crystal structure. An absorption correction[18] was made, based on a calculated linear absorption coefficient (μ) of 29.37 cm^{-1} for Mo $K\bar{\alpha}$ radiation ($\lambda = 0.7107$ Å)[19] and estimated absorption coefficients which ranged between 0.211 and 0.370. A sorting and merging[20] of the data gave 1612 independent reflections with $I > 2\sigma(I)$.

(b) $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$. A seven-sided, cylindrical-shaped prism with an approximate width of 0.26 mm and height of 0.74 mm was selected for X-ray examination. The procedures for crystal alignment and data collection were the same as described for the methyl-substituted analogue with a few exceptions. The selection of a triclinic cell led to the sampling of data in the hkl, $\bar{h}kl$, $h\bar{k}l$, and $\bar{h}\bar{k}l$ octants

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Table I. Atomic Parameters for $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$[a]

A. Positional Parameters

atom	*x*	*y*	*z*
Ni	0.14186 (5)	0	0.10533 (4)
O	0.1742 (4)	0	−0.1694 (3)
C	0.0920 (4)	0	−0.0967 (3)
C(1)	0.2794 (4)	0	0.3376 (4)
C(2)	0.3333 (4)	0.1311 (4)	0.2810 (3)
C(3)	0.4117 (3)	0.0808 (4)	0.1852 (3)
C(11)	0.1964 (7)	0	0.4475 (4)
H(2)	0.317 (5)	0.238 (5)	0.295 (4)
H(3)	0.460 (5)	0.149 (4)	0.136 (4)
H(11)	0.276 (10)	0	0.523 (8)
H(12)	0.101 (7)	0.089 (7)	0.430 (6)

B. Anisotropic Thermal Parameters $(\times 10^4)$[b]

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	83 (1)	83 (1)	70 (1)	0	21 (1)	0
O	145 (5)	250 (7)	108 (3)	0	70 (3)	0
C	109 (4)	129 (5)	77 (3)	0	34 (3)	0
C(1)	112 (5)	156 (6)	78 (3)	0	19 (3)	0
C(2)	139 (4)	127 (4)	102 (3)	−32 (3)	19 (2)	−23 (3)
C(3)	106 (3)	180 (5)	115 (3)	−36 (3)	35 (3)	1 (3)
C(11)	178 (8)	294 (12)	67 (3)	0	29 (4)	0

C. Isotropic Temperature Factors (Å^2)

H(2)	4.2 (8)	H(11)	5.8 (15)
H(3)	3.5 (7)	H(12)	7.4 (12)

[a] The standard deviation of the last significant figure is given in parentheses after the number. [b] The anisotropic thermal parameters are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Table II. Interatomic Distances and Bond Angles for $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$[a-d]

A. Intramolecular Distances (Å)

Ni–Ni^1	2.3902 (8)	Ni–C	1.889 (3)
Ni–C(1)	2.124 (3)	Ni–C^1	1.840 (3)
Ni–C(2)	2.139 (2)	Ni–Cp	1.745
Ni–C(3)	2.101 (2)	C(1)–C(2)	1.425 (4)
C–O	1.160 (4)	C(2)–C(3)	1.410 (4)
C(1)–C(11)	1.495 (6)	C(3)–C(3)^2	1.421 (8)
C(11)–H(11)	0.77 (7)	C(2)–H(2)	0.97 (4)
C(11)–H(12)	1.06 (6)	C(3)–H(3)	0.95 (4)
O···H(12)^1	2.76	C···C^1	2.863
		C···C(1)^1	2.973

B. Intermolecular Distances (Å)

O···H(2)^3	2.63	H(2)···H(3)^7	2.82
O···H(2)^4	2.63	H(12)···H(12)^8	2.52
H(2)···H(12)^5	2.61	H(12)···H(12)^9	2.97
H(2)···H(12)^6	2.97		

C. Bond Angles (Deg)

Cp–Ni–C	128.3	Ni^1–Ni–C	49.2 (1)
Cp–Ni–C^1	131.4	Ni–Ni^1–C	51.0 (1)
C–Ni–C^1	100.3 (1)	Ni–C–Ni^1	79.7 (1)
Ni–C–O	137.6 (3)	C(2)^2–C(1)–C(2)	108.1 (3)
Ni^1–C–O	142.7 (3)	C(1)–C(2)–C(3)	107.6 (3)
C(2)–C(1)–C(11)	125.9 (2)	C(2)–C(3)–C(3)^2	108.3 (2)
C(1)–C(2)–H(2)	131 (2)	C(2)–C(3)–H(3)	122 (2)
C(3)–C(2)–H(2)	122 (2)	C(3)^2–C(3)–H(3)	129 (2)
C(1)–C(11)–H(11)	106 (5)	H(11)–C(11)–H(12)	115 (4)
C(1)–C(11)–H(12)	113 (3)	H(12)–C(11)–H(12)^2	95 (6)

[a] The standard deviation of the last significant figure is given in parentheses after the number. [b] Relevant distances are given out to a maximum of 3.0 Å. [c] The numerical superscripts refer to the symmetry-related positions: (1) $-x, -y, -z$; (2) $x, -y, z$; (3) $^1/_2 - x, {}^1/_2 - y, -z$; (4) $^1/_2 - x, -{}^1/_2 + y, -z$; (5) $^1/_2 + x, {}^1/_2 - y, z$; (6) $^1/_2 - x, {}^1/_2 - y, 1 - z$; (7) $-{}^1/_2 + x, {}^1/_2 - y, z$; (8) $-x, y, 1 - z$; (9) $-x, -y, 1 - z$. [d] Cp refers to the centroid of the [C(1), C(2), C(3), C(3)^2, C(2)^2] ring.

for $3° \leq 2\theta \leq 60°$. Of the two possible triclinic space groups (viz., $P1$ (C_1^1, No. 1) and $P\bar{1}$ (C_i^1, No. 2)), the centric one, $P\bar{1}$, was used and subsequently substantiated by the successful solution and refinement of the crystal structure. An absorption correction, based upon estimated absorption coefficients of range 0.420–0.502 resulting from a linear absorption coefficient (μ) of 33.67 cm^{-1} for Mo K$\bar{\alpha}$ radiation, was applied to the corrected intensities. A sorting and merging of the data yielded 3879 independent reflections with $I > 2\sigma(I)$.

Unit Cell Data. (a) $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$. The measured lattice constants and estimated standard deviations for the monoclinic cell at ca. 22 °C are as follows: $a = 8.009$ (2) Å, $b = 8.794$ (3) Å, $c = 9.971$ (3) Å, $\beta = 113.87$ (1)°. The unit cell volume is 642.2 (7) Å^3. The observed density of 1.71 g/cm^3, measured by the flotation method in aqueous zinc bromide, is in agreement with a calculated density of 1.715 g/cm^3 for $Z = 2$ and a fw = 331.68. The total number of electrons in the unit cell, $F(000)$, is 340. The structural determination necessitated the location of one-fourth of one independent dimer consisting of 1 nickel, 1 oxygen, 3 carbon, and 1 hydrogen atoms, each occupying the fourfold set of special equivalent positions of (0, 0, 0; $^1/_2$, $^1/_2$, 0) ± (x, 0, z), and of 2 carbon and 3 hydrogen atoms, each occupying the eightfold set of general equivalent positions of (0, 0, 0; $^1/_2$, $^1/_2$, 0) ± (x, y, z; x, $-y$, z).

(b) $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$. The lattice constants and estimated standard deviations obtained at ca. 22 °C for the triclinic cell are $a = 10.990$ (2) Å, $b = 13.704$ (2) Å, $c = 7.860$ (2) Å, $\alpha = 99.12$ (1)°, $\beta = 101.54$ (2)°, and $\gamma = 75.94$ (1)°. The unit cell volume is 1117.4 (4) Å^3. The observed density of 1.77 g/cm^3, measured in aqueous zinc bromide, is in accord with a calculated density of 1.805 g/cm^3 for $Z = 4$ and a fw = 303.63. The total number of electrons in the unit cell, $F(000)$, is 616. The structural analysis required the location of two independent dimers comprised of 4 nickel, 4 oxygen, 24 carbon, and 20 hydrogen atoms, each occupying the twofold set of general equivalent positions: ±(x, y, z).

Structural Determination and Refinement. For both compounds, the atomic scattering factor tables for the nonhydrogen atoms were generated from the nine-parameter equation and parameters for neutral atoms given by Cromer and Mann,[21] while those for the hydrogen atoms are from Stewart, Davidson, and Simpson.[22] Anomalous dispersion corrections were made for Ni ($\Delta f' = 0.285$, $\Delta f'' = 1.113$), O ($\Delta f' = 0.008$, $\Delta f'' = 0.006$), and C ($\Delta f' = 0.002$, $\Delta f'' = 0.002$).[23]

(a) $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$. The structure was solved via the Patterson method followed by Fourier and difference Fourier syntheses[24] which established coordinates for all nonhydrogen atoms. Least-squares refinement[25,26] reduced the $R_1(F)$ value below 10%. At this point the hydrogen atoms were inserted at idealized positions,[27] and least-squares refinement with varying positional and anisotropic thermal parameters for the nonhydrogen atoms and with varying positional and varying isotropic temperature parameters for the hydrogen atoms was then continued. The last, full-matrix least-squares cycle converged to $R_1(F) = 5.0\%$ and $R_2(F) = 5.7\%$ with no parameter shift-to-error ratio being greater than 0.01.[25]

The standard deviation in an observation of unit weight ("goodness-of-fit"), defined by $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, was 1.26, the number of reflections (m) was 1612, and the number of parameters varied in the refinement (n) was 64, from which $m/n = 25.2$. A final difference Fourier map showed the largest peak to be ca. 0.36 e/Å^3, thereby indicating no significant residual density.

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(24) Calabrese, J. C. "MAP, A FORTRAN Fourier Summation and Molecular Assemblage Program"; University of Wisconsin—Madison: Madison, Wis., 1972.

(25) The unweighted and weighted discrepancy factors used are $R_1(F) = [\sum||F_o| - |F_c||/\sum|F_o|] \times 100$ and $R_2(F) = [\sum w_i||F_o| - |F_c||^2/\sum w_i|F_o|^2]^{1/2} \times 100$. All least-squares refinements were based on the minimization of $\sum w_i||F_o| - |F_c||^2$ with individual weights of $w_i = 1/\sigma^2(F_o)$ assigned on the basis of the esd's of the observed structure factors.

(26) Busing, W. R.; Martin, K. O.; Levy, H. A. "OR FLS, A FORTRAN Crystallographic Least Squares Program", Report ORNL-TM-305; Oak Ridge National Laboratory: Oak Ridge, Tenn., 1962.

(27) Calabrese, J. C. "MIRAGE", Ph.D. Thesis, University of Wisconsin—Madison, 1971; Appendix III.

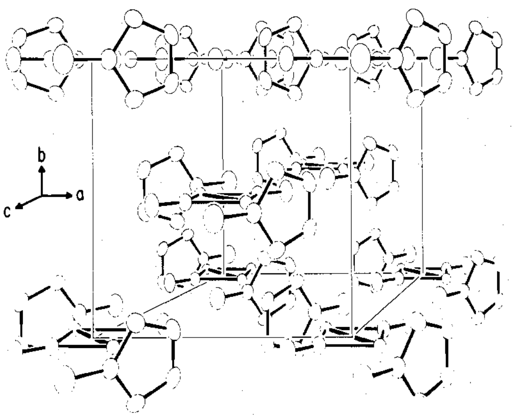

Figure 1. View of the monoclinic unit cell of $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$ showing the arrangement under C_{2h}-$2/m$ symmetry of two molecules, each of which is located at the centrosymmetric intersection of a crystallographic mirror plane and twofold axis in the *b* direction.

Final positional and thermal parameters are given in Table I. Interatomic distances and bond angles with estimated standard deviations[28] are listed in Table II. Selected least-squares planes and interplanar angles were calculated.[29] Observed and calculated structure factor amplitudes are given as supplementary material.

(b) $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$. The heavy-atom method, analytically applied[30] to a computed three-dimensional Patterson synthesis, initially gave several possible solutions containing three heavy atoms. The correct solution was ultimately established from Fourier and difference Fourier syntheses, coupled with least-squares refinement.[31] Idealized hydrogen positions were inserted into the structure,[27] and refinement was continued with varying positional and anisotropic thermal parameters for the nonhydrogen atoms and varying positional and fixed isotropic temperature parameters for the hydrogen atoms. The last, full-matrix least-squares cycle[26] led to $R_1(F) = 4.51\%$ and $R_2(F) = 5.23\%$ with no parameter shift-to-error ratio being greater than 0.19 (i.e., this particular value corresponds to a positional coordinate of the hydrogen atom H(11); all other shift/error values were less than 0.10).[25]

The "goodness-of-fit" value was 1.17; the ratio of the number of reflections (*m*) of 3879 to the number of varied parameters (*n*) of 349 was $m/n = 11.1$. A final difference Fourier map, which showed the largest residual peak to be ca. 0.41 e/Å^3, indicated no anomalous features.

Final positional and thermal parameters are given in Table III. Interatomic distances and bond angles[28] are listed in Table IV. Selected least-squares planes and interplanar angles[29] are found in Table V. Observed and calculated structure factor amplitudes appear as supplementary material. All molecular figures were computer generated and computer drawn.[32]

Results and Discussion

Structural Features of $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$. (a) General Description of the Crystal and Molecular Structure. Crystalline (methylcyclopentadienyl)nickel carbonyl dimer is comprised of discrete molecules with no abnormally short intermolecular contacts. A unit-cell drawing showing the molecular orientations under monoclinic $C2/m$ symmetry is presented in Figure 1. Figure 2 shows that the solid-state configuration of the dimeric molecule of crystallographic C_{2h}-$2/m$ site symmetry consists of a planar central $Ni_2(CO)_2$ core containing two bridging carbonyls with each nickel coordinated in a η^5 manner to a methylcyclopentadienyl ring.

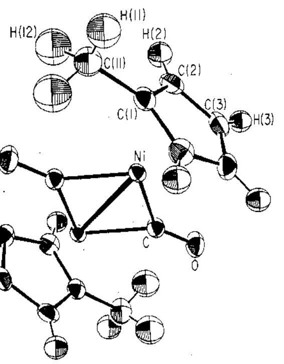

Figure 2. Molecular configuration of $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$, shown with 30% probability thermal ellipsoids. This centrosymmetric dimer possesses crystallographic C_{2h}-$2/m$ site symmetry with the mirror plane, which contains the $Ni_2(CO)_2$ core, bisecting each methylcyclopentadienyl ring. This unsymmetrical ring orientation, which results in the methyl-attached C(1) ring atom being trans to a carbonyl ligand, is assumed to account for the observed asymmetric coordination of the indepenent carbonyl ligand with the two nickel atoms.

(b) The $Ni_2(CO)_2$ Core. The entire $Ni_2(CO)_2$ fragment is constrained to exact planarity by its lying on a crystallographic mirror plane. Its Ni–Ni distance of 2.390 (1) Å is in accord with an electron-pair Ni–Ni bond. An asymmetry in the coordination of the independent bridging carbonyl is evidenced by the two independent Ni–CO bond lengths of 1.840 (3) and 1.889 (3) Å. This bonding difference of 0.05 Å may be readily ascribed to the resulting effect of the particular perpendicular orientation of the methylcyclopentadienyl ligand relative to the $Ni_2(CO)_2$ core (vide infra). The independent C–O distance of 1.160 (4) Å is normal for a doubly bridging carbonyl ligand.

(c) The Localized Methylcyclopentadienyl–$Ni(CO)_2$ Interaction and Resulting Bonding Implications. Each of the two centrosymmetrically related methylcyclopentadienyl rings is bisected by the mirror plane (coincident with the planar $Ni_2(CO)_2$ core) which passes through one ring atom C(1), its attached methyl carbon atom C(11), and one methyl hydrogen atom H(11). This ring disposition results in the methyl-attached C(1) atom being trans to one carbonyl ligand, while the midpoint of the C(3)–C(3′) bond (where the prime indicates the mirror-related atom) is trans to the other carbonyl ligand. Of the three independent Ni–C(ring) distances, the fact that the two identical Ni–C(2) and Ni–C(2′) distances of 2.139 (2) Å are significantly longer than the two identical Ni–C(3) and Ni–C(3′) distances of 2.101 (2) Å is in accord with the methylcyclopentadienyl ring being slightly skewed away from the C(1)-attached methyl substituent on account of steric effects with the carbonyl ligands. However, the fact that the Ni–C(1) distance of 2.124 (3) Å is actually less rather than significantly greater than the Ni–C(2) distances points to the ring C(1) atom being bent toward the nickel atom, and this is confirmed by its perpendicular displacement of 0.04 Å toward the nickel from the exact plane defined by the other four ring atoms (viz., C(2), C(3), C(3′), and C(2′)).[33] This ring bending may be attributed to the stronger than expected interaction of C(1) with the nickel atom resulting at least in part from the relative electron-releasing ability of the methyl substituent. In contrast to the predicted difference from steric considerations, the longer Ni–CO distance is trans rather than

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[28] Busing, W. R.; Martin, K. O.; Levy, H. A. "OR FFE, A FORTRAN Crystallographic Function and Error Program", Report ORNL-TM-306; Oak Ridge National Laboratory: Oak Ridge, Tenn., 1964.

[29] "PLANES", a revised version of "PLANE 1" written by: Smith, D. L. Ph.D. Thesis, University of Wisconsin—Madison, 1962; Appendix IV.

[30] Calabrese, J. C. "PHASE", Ph.D. Thesis, University of Wisconsin—Madison, 1971; Appendix II.

[31] Calabrese, J. C. "A Crystallographic Variable Matrix Least-Squares Refinement Program"; University of Wisconsin—Madison: Madison, Wis., 1972.

[32] Johnson, C. K. "OR TEP-II, A FORTRAN Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations", Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, Tenn., 1976.

[33] Inclusion of all five carbon ring atoms in a least-squares plane calculation[29] reveals perpendicular displacements of +0.016 Å for C(1), −0.013 Å for C(2) and C(2′), and +0.005 Å for C(3) and C(3′) from the mean plane.

Table III. Atomic Parameters for $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$[a, b]

A. Positional Parameters

atom	x	y	z	atom	x	y	z
Ni(1)	0.10163 (5)	0.15320 (4)	0.40903 (8)	C(35)	0.4290 (6)	−0.2472 (5)	−0.3029 (9)
Ni(2)	0.22387 (5)	0.03019 (4)	0.22765 (8)	C(41)	0.6884 (7)	−0.6021 (6)	−0.0249 (13)
Ni(3)	0.60870 (5)	−0.34742 (4)	−0.27053 (8)	C(42)	0.7128 (12)	−0.5358 (7)	0.1236 (14)
Ni(4)	0.73144 (6)	−0.46707 (5)	−0.08514 (8)	C(43)	0.8457 (10)	−0.5282 (6)	0.1332 (11)
O(1)	0.1123 (5)	0.2168 (3)	0.0844 (6)	C(44)	0.8834 (7)	−0.5842 (5)	−0.0087 (12)
O(2)	0.3150 (4)	0.0243 (4)	0.5937 (5)	C(45)	0.7904 (9)	−0.6269 (5)	−0.1011 (10)
O(3)	0.8278 (4)	−0.4731 (4)	−0.3993 (6)	H(11)	−0.159 (6)	0.126 (5)	0.390 (8)
O(4)	0.6359 (5)	−0.2725 (4)	0.0920 (6)	H(12)	−0.131 (6)	0.264 (5)	0.270 (9)
C(1)	0.1347 (5)	0.1622 (4)	0.1901 (6)	H(13)	0.043 (6)	0.361 (5)	0.489 (8)
C(2)	0.2479 (5)	0.0549 (4)	0.4694 (7)	H(14)	0.118 (6)	0.259 (5)	0.724 (9)
C(3)	0.7585 (5)	−0.4439 (4)	−0.3003 (7)	H(15)	0.016 (7)	0.115 (5)	0.656 (9)
C(4)	0.6521 (5)	−0.3321 (4)	−0.0284 (7)	H(21)	0.139 (6)	−0.148 (5)	0.069 (8)
C(11)	−0.0881 (6)	0.1720 (5)	0.4697 (10)	H(22)	0.336 (6)	−0.167 (5)	0.278 (8)
C(12)	−0.0794 (6)	0.2532 (5)	0.3962 (9)	H(23)	0.454 (6)	−0.057 (5)	0.207 (9)
C(13)	0.0122 (8)	0.2981 (5)	0.4991 (13)	H(24)	0.365 (6)	0.021 (5)	−0.035 (8)
C(14)	0.0675 (7)	0.2449 (9)	0.6379 (10)	H(25)	0.153 (6)	−0.028 (5)	−0.118 (9)
C(15)	0.0039 (9)	0.1631 (7)	0.6164 (11)	H(31)	0.355 (6)	−0.373 (5)	−0.419 (8)
C(21)	0.1977 (6)	−0.1126 (4)	0.0784 (8)	H(32)	0.518 (6)	−0.399 (5)	−0.607 (8)
C(22)	0.3102 (6)	−0.1261 (4)	0.1961 (9)	H(33)	0.631 (6)	−0.247 (5)	−0.551 (8)
C(23)	0.3872 (6)	−0.0679 (6)	0.1542 (11)	H(34)	0.546 (6)	−0.136 (5)	−0.279 (8)
C(24)	0.3197 (8)	−0.0171 (5)	0.0158 (10)	H(35)	0.382 (6)	−0.226 (5)	−0.232 (9)
C(25)	0.2010 (7)	−0.0438 (5)	−0.0292 (8)	H(41)	0.610 (6)	−0.626 (5)	−0.082 (8)
C(31)	0.4150 (5)	−0.3338 (5)	−0.4149 (9)	H(42)	0.683 (7)	−0.511 (5)	0.184 (9)
C(32)	0.5014 (6)	−0.3496 (5)	−0.5251 (8)	H(43)	0.904 (6)	−0.494 (5)	0.201 (9)
C(33)	0.5660 (6)	−0.2684 (6)	−0.4884 (10)	H(44)	0.978 (6)	−0.585 (5)	−0.018 (8)
C(34)	0.5206 (7)	−0.2057 (5)	−0.3505 (11)	H(45)	0.794 (6)	−0.662 (5)	−0.209 (9)

B. Anisotropic Thermal Parameters ($\times 10^4$)[c]

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni(1)	65 (1)	41 (1)	117 (1)	−3 (1)	22 (1)	4 (1)	C(15)	182 (11)	101 (7)	219 (16)	54 (7)	129 (11)	72 (8)
Ni(2)	60 (1)	38 (1)	119 (1)	−3 (1)	19 (1)	4 (1)	C(21)	103 (6)	50 (4)	215 (13)	−11 (4)	19 (7)	−15 (5)
Ni(3)	60 (1)	37 (1)	131 (1)	−2 (1)	5 (1)	16 (1)	C(22)	125 (7)	42 (3)	222 (14)	21 (4)	12 (8)	15 (5)
Ni(4)	67 (1)	42 (1)	136 (1)	−2 (1)	8 (1)	24 (1)	C(23)	77 (6)	82 (5)	321 (20)	−4 (5)	53 (9)	−60 (8)
O(1)	193 (6)	67 (3)	196 (9)	29 (3)	82 (6)	58 (4)	C(24)	170 (10)	67 (4)	242 (16)	−24 (5)	137 (11)	−15 (7)
O(2)	154 (6)	124 (4)	143 (8)	48 (4)	−21 (5)	34 (5)	C(25)	161 (9)	63 (4)	120 (11)	17 (5)	14 (7)	−3 (5)
O(3)	132 (5)	95 (4)	243 (10)	36 (3)	96 (6)	59 (5)	C(31)	69 (5)	72 (4)	243 (14)	−18 (4)	−28 (7)	36 (6)
O(4)	210 (7)	78 (3)	161 (9)	26 (4)	8 (6)	−28 (4)	C(32)	116 (7)	75 (5)	140 (11)	22 (5)	−11 (7)	6 (5)
C(1)	91 (5)	50 (3)	117 (9)	3 (3)	31 (5)	8 (4)	C(33)	91 (6)	108 (6)	247 (16)	1 (5)	8 (8)	104 (8)
C(2)	94 (5)	55 (3)	128 (10)	6 (3)	21 (6)	13 (4)	C(34)	114 (7)	42 (3)	345 (19)	−12 (4)	−58 (9)	52 (7)
C(3)	85 (5)	50 (3)	164 (11)	3 (3)	35 (6)	30 (5)	C(35)	85 (6)	74 (5)	217 (14)	30 (4)	20 (7)	14 (6)
C(4)	104 (6)	56 (4)	150 (11)	1 (4)	11 (6)	12 (5)	C(41)	111 (7)	89 (6)	377 (22)	−31 (5)	−3 (11)	112 (10)
C(11)	89 (6)	85 (5)	274 (16)	−8 (4)	86 (8)	0 (7)	C(42)	317 (19)	94 (7)	319 (24)	88 (9)	229 (18)	120 (11)
C(12)	107 (7)	82 (5)	218 (14)	20 (5)	70 (8)	18 (7)	C(43)	232 (13)	65 (5)	237 (18)	−40 (7)	−112 (13)	64 (8)
C(13)	153 (9)	43 (4)	388 (23)	−11 (5)	135 (13)	−38 (7)	C(44)	104 (7)	57 (4)	378 (22)	3 (4)	−1 (10)	82 (8)
C(14)	97 (7)	170 (10)	182 (15)	−13 (7)	23 (8)	−98 (11)	C(45)	214 (12)	42 (4)	256 (17)	−15 (5)	51 (12)	33 (6)

[a] The standard deviation of the last significant figure is given in parentheses after the number. [b] The hydrogen atoms were refined with isotropic temperature factors fixed at 6.0 Å^2. [c] The anisotropic thermal parameters are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

cis to C(1). Hence, the bridging carbonyl asymmetry is presumed to be electronically induced due primarily to the trans influence of the methyl-linked C(1) atom.

The three independent C(ring)–C(ring) distances of range 1.410 (4) to 1.425 (4) Å are statistically equivalent and approach the expected value of ca. 1.43 Å cited by Churchill and Kalra[34] for librationally damped cyclopentadienyl ring C–C distances. The methyl substituent presumably locks the ring into one rotational orientation thereby damping out the normally large librational motion (and hence artificially shortened distances) observed in most unsubstituted cyclopentadienyl rings.

The methyl carbon atom, C(11), deviates out of the *mean* least-squares plane[29] of all five ring carbon atoms by 0.04 Å away from the nickel atom. This outward bending of the methyl substituent is not unexpected in comparison with *penta*methylcyclopentadienyl–metal systems which uniformly exhibit a bending of all five methyl carbons from the ring plane away from the metal (e.g., $Co[\eta^5\text{-}C_5(CH_3)_5](CO)_2$[35] shows perpendicular carbon displacements ranging from 0.04 to 0.13 Å).

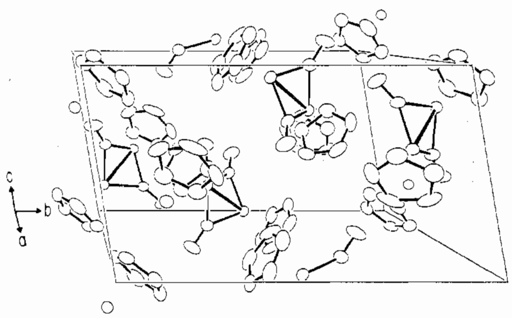

Figure 3. View of the triclinic unit cell of $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ showing the orientations of four dimers under $P\bar{1}$ symmetry. There are two crystallographically independent molecules A and B.

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(34) Churchill, M. R.; Kalra, K. L. *Inorg. Chem.* **1973**, *12*, 1650–6.

(35) Byers, L. R.; Dahl, L. F. *Inorg. Chem.*, in press.

Table IV. Interatomic Distances and Bond Angles for $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-CO})]_2$ $^{a-d}$

A. Distances, Å

dimer A		dimer B		dimer A		dimer B	
			Bonding Intramolecular Distances				
Ni(1)–Ni(2)	2.3627 (9)	Ni(3)–Ni(4)	2.3510 (9)	C(11)–C(12)	1.362 (9)	C(31)–C(32)	1.367 (9)
Ni(1)–C(1)	1.856 (5)	Ni(3)–C(3)	1.874 (5)	C(11)–C(15)	1.374 (11)	C(31)–C(35)	1.382 (9)
Ni(1)–C(2)	1.862 (5)	Ni(3)–C(4)	1.858 (6)	C(21)–C(22)	1.380 (9)	C(41)–C(42)	1.384 (14)
Ni(2)–C(1)	1.874 (5)	Ni(4)–C(3)	1.862 (5)	C(21)–C(25)	1.373 (9)	C(41)–C(45)	1.322 (10)
Ni(2)–C(2)	1.853 (5)	Ni(4)–C(4)	1.868 (6)		1.372 (av)		1.364 (av)
	1.861 (av)		1.865 (av)	C(12)–C(13)	1.365 (10)	C(32)–C(33)	1.422 (10)
C(1)–O(1)	1.156 (6)	C(3)–O(3)	1.156 (6)	C(15)–C(14)	1.430 (13)	C(35)–C(34)	1.404 (10)
C(2)–O(2)	1.169 (6)	C(4)–O(4)	1.160 (6)	C(22)–C(23)	1.408 (11)	C(42)–C(43)	1.475 (15)
	1.162 (av)		1.158 (av)	C(25)–C(24)	1.403 (10)	C(45)–C(44)	1.331 (10)
Ni(1)–C(11)	2.177 (6)	Ni(3)–C(31)	2.182 (5)		1.401 (av)		1.408 (av)
Ni(2)–C(21)	2.167 (6)	Ni(4)–C(41)	2.160 (7)	C(13)–C(14)	1.365 (12)	C(33)–C(34)	1.369 (10)
	2.172 (av)		2.171 (av)	C(23)–C(24)	1.373 (11)	C(43)–C(44)	1.328 (11)
Ni(1)–C(12)	2.118 (6)	Ni(3)–C(32)	2.109 (6)		1.369 (av)		1.348 (av)
Ni(1)–C(15)	2.095 (6)	Ni(3)–C(35)	2.108 (5)	C(11)–H(11)	1.14 (6)	C(31)–H(31)	0.94 (6)
Ni(2)–C(22)	2.118 (5)	Ni(4)–C(42)	2.082 (7)	C(21)–H(21)	0.88 (6)	C(41)–H(41)	1.00 (6)
Ni(2)–C(25)	2.107 (6)	Ni(4)–C(45)	2.118 (6)		1.01 (av)		0.97 (av)
	2.109 (av)		2.104 (av)	C(12)–H(12)	1.05 (6)	C(32)–H(32)	0.87 (6)
Ni(1)–C(13)	2.072 (6)	Ni(3)–C(33)	2.084 (6)	C(15)–H(15)	0.74 (7)	C(35)–H(35)	0.81 (7)
Ni(1)–C(14)	2.069 (6)	Ni(3)–C(34)	2.082 (6)	C(22)–H(22)	0.87 (6)	C(42)–H(42)	0.64 (7)
Ni(2)–C(23)	2.088 (6)	Ni(4)–C(43)	2.075 (6)	C(25)–H(25)	0.81 (6)	C(45)–H(45)	0.91 (7)
Ni(2)–C(24)	2.081 (6)	Ni(4)–C(44)	2.080 (6)		0.87 (av)		0.81 (av)
	2.077 (av)		2.080 (av)	C(13)–H(13)	1.02 (6)	C(33)–H(33)	1.06 (6)
Ni(1)–Cp(1)	1.750	Ni(3)–Cp(3)	1.752	C(14)–H(14)	0.81 (7)	C(34)–H(34)	1.09 (6)
Ni(2)–Cp(2)	1.752	Ni(4)–Cp(4)	1.752	C(23)–H(23)	0.80 (6)	C(43)–H(43)	0.92 (6)
	1.751 (av)		1.752 (av)	C(24)–H(24)	0.98 (6)	C(44)–H(44)	1.06 (6)
					0.90 (av)		1.03 (av)
			Nonbonding Intermolecular Distances^{e}				
O(1)···H(14)^{1}	2.99	O(3)···H(13)^{5}	2.58	H(11)···H(25)^{6}	2.35	H(22)···H(41)^{8}	2.99
O(1)···H(44)^{2}	2.91	O(4)···H(14)^{3}	2.84	H(11)···H(35)^{6}	2.67	H(22)···H(45)^{8}	2.96
O(2)···H(23)^{3}	2.80	O(4)···H(33)^{4}	2.78	H(12)···H(21)^{6}	2.88	H(23)···H(24)^{5}	2.79
O(2)···H(24)^{4}	2.86	C(33)···H(22)^{1}	2.99	H(12)···H(31)^{6}	2.92	H(23)···H(34)^{5}	2.62
C(25)···H(11)^{6}	2.87			H(12)···H(35)^{6}	2.88	H(24)···H(24)^{5}	2.84
				H(13)···H(43)^{3}	2.85	H(24)···H(34)^{5}	2.84
				H(15)···H(21)^{7}	2.93	H(31)···H(42)^{8}	2.77
				H(15)···H(25)^{4}	2.81	H(32)···H(41)^{9}	2.59
				H(21)···H(45)^{8}	2.86	H(32)···H(42)^{1}	2.72

B. Bond Angles, Deg

dimer A		dimer B		dimer A		dimer B	
Cp(1)–Ni(1)–Ni(2)	165.9	Cp(3)–Ni(3)–Ni(4)	163.5	C(15)–C(11)–C(12)	107.2 (7)	C(35)–C(31)–C(32)	107.1 (6)
Cp(2)–Ni(2)–Ni(1)	166.6	Cp(4)–Ni(4)–Ni(3)	162.0	C(25)–C(21)–C(22)	108.2 (6)	C(45)–C(41)–C(42)	107.9 (8)
	166.2 (av)		162.8 (av)		107.7 (av)		107.5 (av)
Cp(1)–Ni(1)–C(1)	130.5	Cp(3)–Ni(3)–C(3)	133.1	C(11)–C(12)–C(13)	109.3 (7)	C(31)–C(32)–C(33)	109.0 (6)
Cp(1)–Ni(1)–C(2)	133.5	Cp(3)–Ni(3)–C(4)	132.8	C(11)–C(15)–C(14)	108.5 (7)	C(31)–C(35)–C(34)	109.2 (6)
Cp(2)–Ni(2)–C(1)	131.5	Cp(4)–Ni(4)–C(3)	130.4	C(21)–C(22)–C(23)	107.8 (7)	C(41)–C(42)–C(43)	105.0 (6)
Cp(2)–Ni(2)–C(2)	132.8	Cp(4)–Ni(4)–C(4)	135.7	C(21)–C(25)–C(24)	108.5 (6)	C(41)–C(45)–C(44)	111.3 (8)
	132.1 (av)		133.0 (av)		108.5 (av)		108.6 (av)
C(1)–Ni(1)–C(2)	95.4 (4)	C(3)–Ni(3)–C(4)	93.4 (4)	C(12)–C(13)–C(14)	109.7 (7)	C(32)–C(33)–C(34)	107.1 (6)
C(1)–Ni(2)–C(2)	95.1 (4)	C(3)–Ni(4)–C(4)	93.4 (4)	C(15)–C(14)–C(13)	105.2 (6)	C(35)–C(34)–C(33)	107.6 (6)
	95.2 (av)		93.4 (av)	C(22)–C(23)–C(24)	107.9 (6)	C(42)–C(43)–C(44)	105.6 (7)
Ni(1)–C(1)–Ni(2)	78.6 (2)	Ni(3)–C(3)–Ni(4)	78.0 (2)	C(25)–C(24)–C(23)	107.6 (6)	C(45)–C(44)–C(43)	110.1 (8)
Ni(1)–C(2)–Ni(2)	79.0 (2)	Ni(3)–C(4)–Ni(4)	78.2 (2)		107.6 (av)		107.6 (av)
	78.8 (av)		78.1 (av)				
Ni(1)–C(1)–O(1)	141.9 (4)	Ni(3)–C(3)–O(3)	140.7 (4)				
Ni(2)–C(1)–O(1)	139.5 (4)	Ni(4)–C(3)–O(3)	141.3 (4)				
Ni(1)–C(2)–O(2)	139.9 (4)	Ni(3)–C(4)–O(4)	140.9 (5)				
Ni(2)–C(2)–O(2)	141.0 (4)	Ni(4)–C(4)–O(4)	140.8 (5)				
	140.6 (av)		140.9 (av)				

[a] The standard deviation of the last significant figure is given in parentheses after the number. [b] Values are averaged according to pseudo C_{2v}-2*mm* symmetry. [c] Cp(*n*) refers to the centroid of the *n*th cyclopentadienyl ring. [d] Relevant distances are given out to a maximum of 3.0 Å. [e] The numerical superscripts refer to the symmetry-related positions: (1) $x, y, -1 + z$; (2) $-1 + x, 1 + y, z$; (3) $1 - x, -y, 1 - z$; (4) $x, y, 1 + z$; (5) $1 - x, -y, -z$; (6) $-x, -y, -z$; (7) $-x, -y, 1 - z$; (8) $1 - x, -1 - y, -z$; (9) $1 - x, -1 - y, -1 - z$.

Structural Features of $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-CO})]_2$. (a) General Description of the Crystal and Molecular Structure. The solid-state structure of the cyclopentadienylnickel carbonyl dimer consists of dimeric molecules separated from each other by normal intermolecular distances. The unit cell (Figure 3) of $P\bar{1}$ symmetry contains *two totally independent molecules*

Table V. Mean Planes and Interplanar Angles for $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$[a,b]

A. Planes and Perpendicular Distances (A) of Selected Atoms from These Planes

1. Plane through Ni(1), Ni(2), C(1), O(1)

$$-0.8524X - 0.3013Y - 0.4273Z + 2.6838 = 0$$

Ni(1)	0.002	C(1)	−0.007
Ni(2)	0.001	O(1)	0.004

2. Plane through Ni(1), Ni(2), C(2), O(2)

$$0.7629X + 0.6463Y - 0.0187Z - 1.7797 = 0$$

Ni(1)	−0.002	C(2)	0.011
Ni(2)	−0.002	O(2)	−0.006

3. Plane through Ni(3), Ni(4), C(3), O(3)

$$-0.6426X - 0.6119Y - 0.4611Z + 0.1876 = 0$$

Ni(3)	0.001	C(3)	−0.005
Ni(4)	0.001	O(3)	0.003

4. Plane through Ni(3), Ni(4), C(4), O(4)

$$0.9511X + 0.3013Y - 0.0674Z - 4.4835 = 0$$

Ni(3)	−0.002	C(4)	0.010
Ni(4)	−0.002	O(4)	−0.006

5. Plane through C(11), C(12), C(13), C(14), C(15)

$$0.6674X - 0.5169Y - 0.5361Z + 3.6348 = 0$$

Ni(1)	1.748	Cp(1)	0.000
C(11)	−0.016	H(11)	0.05
C(12)	0.014	H(12)	0.18
C(15)	0.012	H(15)	0.13
C(13)	−0.006	H(13)	−0.03
C(14)	−0.004	H(14)	−0.10

6. Plane through C(21), C(22), C(23), C(24), C(25)

$$0.3426X - 0.6921Y - 0.6353Z - 1.2629 = 0$$

Ni(2)	−1.753	Cp(2)	0.000
C(21)	0.017	H(21)	0.13
C(22)	−0.014	H(22)	0.02
C(25)	−0.013	H(25)	0.10
C(23)	0.006	H(23)	−0.08
C(24)	0.004	H(24)	0.11

7. Plane through C(31), C(32), C(33), C(34), C(35)

$$-0.4717X + 0.6075Y - 0.6391Z + 2.4018 = 0$$

Ni(3)	−1.751	Cp(3)	0.000
C(31)	0.019	H(31)	0.09
C(32)	−0.016	H(32)	−0.04
C(35)	−0.014	H(35)	0.04
C(33)	0.007	H(33)	0.10
C(34)	0.005	H(34)	−0.01

8. Plane through C(41), C(42), C(43), C(44), C(45)

$$-0.0484X + 0.8513Y - 0.5224Z + 6.9675 = 0$$

Ni(4)	1.753	Cp(4)	0.000
C(41)	−0.017	H(41)	0.03
C(42)	0.017	H(42)	0.03
C(45)	0.009	H(45)	0.12
C(43)	−0.013	H(43)	0.03
C(44)	0.004	H(44)	−0.01

9. Plane through Ni(1), C(1), C(2)

$$-0.6204X - 0.6744Y - 0.4003Z + 2.9951 = 0$$

O(1)	−0.294	O(2)	−0.304

10. Plane through Ni(2), C(1), C(2)

$$-0.9659X - 0.2591Y - 0.0017Z + 2.1826 = 0$$

O(1)	−0.311	O(2)	−0.292

11. Plane through Ni(3), C(3), C(4)

$$0.6711X + 0.7397Y - 0.0492Z - 0.8512 = 0$$

O(3)	0.364	O(4)	0.349

12. Plane through Ni(4), C(3), C(4)

$$-0.8891X - 0.1524Y - 0.4316Z + 4.6619 = 0$$

O(3)	−0.356	O(4)	−0.352

13. Plane through Ni(1), Ni(2), C(1)

$$-0.8519X - 0.2973Y - 0.4312Z + 2.6871 = 0$$

O(1)	0.017

14. Plane through Ni(1), Ni(2), C(2)

$$0.7591X + 0.6504Y - 0.0263Z - 1.7566 = 0$$

O(2)	−0.028

15. Plane through Ni(3), Ni(4), C(3)

$$-0.6399X - 0.6129Y - 0.4636Z + 0.1609 = 0$$

O(3)	0.012

16. Plane through Ni(3), Ni(4), C(4)

$$0.9522X + 0.2962Y - 0.0742Z - 4.5240 = 0$$

O(4)	−0.026

B. Dihedral Angles (Deg) between Normals to Planes

planes	angle	planes	angle	planes	angle	planes	angle
1–2	33.2	13–14	34.0	7–11	80.5	8–12	82.0
3–4	40.1	15–16	40.8	9–10	39.2	11–12	46.5
5–9	81.4	6–10	81.3	5–6	158.0	7–8	150.9

[a] The equations of the planes are given in an angstrom orthogonal coordinate system (X, Y, Z), which is related to the triclinic crystallographic fractional coordinates (x, y, z) by the transformations $X = ax + (b \cos\gamma)y + (c \cos\beta)z$, $Y = (b \sin\gamma)y + (c\tau/\sin\gamma)z$, and $Z = (c\Delta/\sin\gamma)z$ (where $\tau = (\cos\alpha - \cos\beta\cos\gamma)$ and $\Delta = (1 + 2\cos\alpha\cos\beta\cos\gamma - \cos^2\alpha - \cos^2\beta - \cos^2\gamma)^{1/2}$). Unit weights were used in the calculations of the planes. [b] Cp(n) refers to the centroid of the nth cyclopentadienyl ring.

(A and B) whose detailed geometries are depicted in Figure 4. Even though the site symmetry of each molecule is strictly C_1-1, they both experimentally conform with C_{2v}-2*mm* geometry; hence, the molecular parameters of each molecule A and B have been averaged under C_{2v} symmetry in Table IV.

In accordance with the solid-state infrared characterization (Figure 5) of $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$,[6,7] the two independent molecular configurations possess bent $Ni_2(CO)_2$ cores analogous to the bent $Co_2(CO)_2$ cores of the two independent molecules in the solid-state structure of the electronically equivalent dicobalt octacarbonyl.[36] The cyclopentadienyl ligands are η^5 coordinated to their respective nickel atoms and tilt somewhat in a direction opposite to the bending of the doubly bridging carbonyls such that each cyclopentadienyl ring is almost perpendicular to the bonding planar NiC_2 fragment. The localized environment about each nickel atom in the dimer thereby corresponds approximately to that about the cobalt atom in the structurally related $Co[\eta^5\text{-}C_5(CH_3)_5](CO)_2$ monomer (vide infra).

(b) The Bent $Ni_2(CO)_2$ Core and Its Stereochemical Relationship with the Planar $Ni_2(CO)_2$ Core of $[Ni_2(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$ and the Bent $Ni_2(CNCH_3)_2$ Core of $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CNCH_3)]_2$. The two crystallographically independent molecules A and B of $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ have single-bond Ni–Ni distances of 2.363 (1) and 2.351 (1) Å in agreement with the reported Mills–Shaw value[8] of 2.36 Å. In contrast to the distinct symmetry found in the bridging car-

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(36) Sumner, G. G.; Klug, H. P.; Alexander, L. E. *Acta Crystallogr.* **1964**, *17*, 732–42.

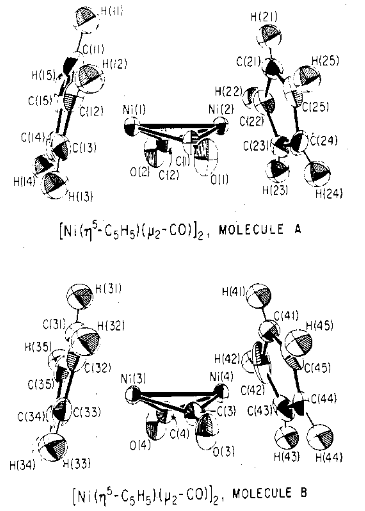

Figure 4. Molecular configurations of the two independent dimeric units of $[Ni(\eta^5-C_5H_5)(\mu-CO)]_2$, shown with 30% probability thermal ellipsoids. Each molecule conforms within experimental error to C_{2v}-$2mm$ symmetry with one mirror plane passing through the two nickel atoms and bisecting the bent $Ni_2(CO)_2$ core and each of the two mirror-related cyclopentadienyl rings.

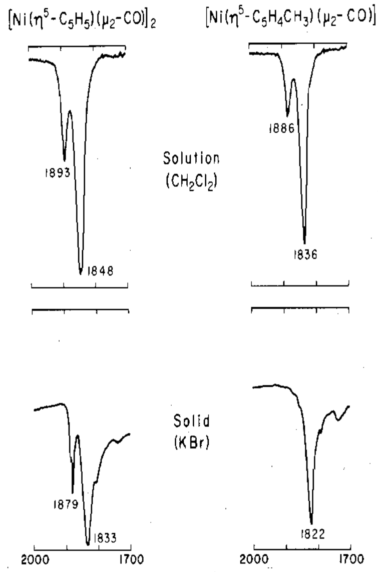

Figure 5. Infrared spectra in the 1700–2000-cm^{-1} region for $[Ni(\eta^5-C_5H_5)(\mu-CO)]_2$ and $[Ni(\eta^5-C_5H_4CH_3)(\mu-CO)]_2$ both in solution (CH_2Cl_2) and in the solid state (KBr). The observance in the solid-state spectra of only one bridging carbonyl frequency for the methylcyclopentadienyl carbonyl dimer vs. two bridging carbonyl frequencies for the unsubstituted cyclopentadienyl carbonyl dimer is in complete harmony with their different geometries in the crystal state. Their similar solution spectra with two bridging carbonyl frequencies of similar intensity ratio point to both compounds possessing analogously bent $Ni_2(CO)_2$ cores in solution.

bonyls in the methyl-substituted cyclopentadienyl analogue, each of the bridging carbonyl ligands in molecules A and B is symmetrically coordinated within experimental error to the nickel atoms. The Ni–CO bond lengths range from 1.853 (5) to 1.874 (5) Å; the mean of 1.863 Å is within 2σ of all individual values. These equivalent Ni–CO linkages in the bent $Ni_2(CO)_2$ cores may be ascribed to the essentially symmetrical orientations of the unsubstituted cyclopentadienyl ligands. The C–O distances range from 1.156 (6) to 1.169 (6) Å with the average value of 1.160 Å being the same as that found in the methyl-substituted analogue.

Of prime interest is a comparison given in Table VI of the mean molecular parameters of the bent $Ni_2(CO)_2$ cores in molecules A and B not only with each other and with the planar $Ni_2(CO)_2$ core in the $[Ni(\eta^5-C_5H_4CH_3)(\mu-CO)]_2$ molecule but also with the bent $Ni_2(CNCH_3)_2$ core of the structurally analogous and electronically equivalent $[Ni(\eta^5-C_5H_5)(\mu-CNCH_3)]_2$ molecule which was structurally characterized by Adams, Cotton, and Rusholme.[37] An examination of Table VI reveals that a bending deformation of the $Ni_2(CX)_2$ core (X = O, NCH_3) from a planar one in the methylcyclopentadienyl carbonyl dimer to nonplanar ones in the unsubstituted cyclopentadienyl carbonyl and cyclopentadienyl methyl isocyanide dimers produces essentially no change in the Ni–C bond lengths and only a small but unidirectional alteration in the Ni–Ni bond lengths and Ni–C–Ni bond angles. Hence, this angular deformation of the $Ni_2(CX)_2$ core may be simply regarded as a bending or flapping vibrational mode of the bridging ligands about the Ni–Ni axis. Table VI also points to a concomitant motion of the cyclopentadienyl rings in the opposite direction to that of the bridging ligands in order to maintain a nearly perpendicular orientation between each NiC_2 fragment and its nickel-coordinated cyclopentadienyl ligand. This geometrical constraint is evidenced by each cyclopentadienyl ring, which is perpendicular to the planar $Ni_2(CO)_2$ core in the methylcyclopentadienyl carbonyl dimer, being analogously oriented with its locally planar NiC_2 center (corresponding to virtually identical torsional angles of range 97.0–99.5°) in the three differently bent $Ni_2(CX)_2$ cores for molecules A and B of the unsubstituted cyclopentadienyl carbonyl dimer and for the cyclopentadienyl methyl isocyanide dimer.

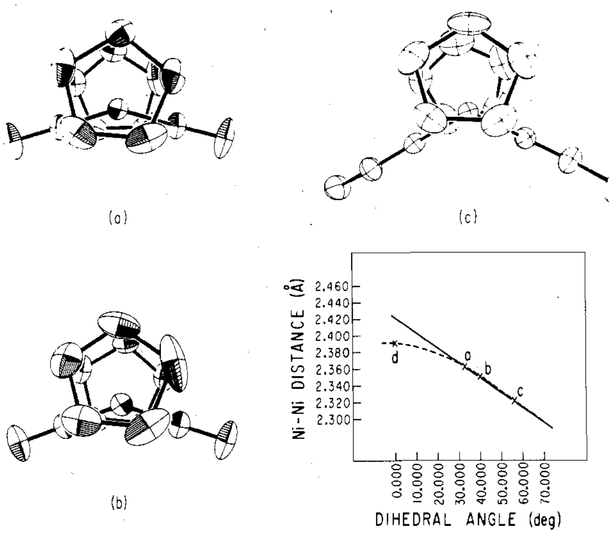

Figure 6. Comparison of the Ni–Ni distance vs. the dihedral angle of the two Ni–C(bridging)–Ni planes in (a) dimer A of $[Ni(\eta^5-C_5H_5)(\mu-CO)]_2$, (b) dimer B of $[Ni(\eta^5-C_5H_5)(\mu-CO)]_2$, (c) $[Ni(\eta^5-C_5H_5)(\mu-CNCH_3)]_2$, and (d) $[Ni(\eta^5-C_5H_4CH_3)(\mu-CO)]_2$ (planar, end-on view not illustrated). Note that Table VI lists the interplanar torsional angles (which are the supplements of the above dihedral angles) for the CNi_2–Ni_2C' fragments.

The geometrical consequences (described above) in a bending deformation of the bridging ligands about the Ni–Ni axis appear to require bonding overlap alterations which show up in a correlation of the Ni–Ni bond distance with the torsional angle of the CNi_2–Ni_2C' fragment (Table VI). On the basis of the assumption that the perturbation of the $Ni_2(CX)_2$ core either by methyl substitution for a cyclopentadienyl hydrogen substituent or by methyl isocyanide substitution for carbonyl ligands is negligible, Figure 6 has been constructed to show the small but definite change in the Ni–Ni distance

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[37] Adams, R. D.; Cotton, F. A.; Rusholme, G. A. *J. Coord. Chem.* **1971**, *1*, 275–83.

Table VI. Comparison of Mean Geometrical Parameters for $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$, Molecules A and B of $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$, and $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CNCH_3)]_2$[a]

	$[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu_2\text{-}CO)]_2$	$[Ni(\eta^5\text{-}C_5H_5)(\mu_2\text{-}CO)]_2$ A	$[Ni(\eta^5\text{-}C_5H_5)(\mu_2\text{-}CO)]_2$ B	$[Ni(\eta^5\text{-}C_5H_5)(\mu_2\text{-}CNCH_3)]_2$
Crystallographic Site Symmetry	C_{2h}-2/m	C_1-1		C_1-1
Virtual Symmetry	C_{2h}-2/m	C_{2v}-2mm		C_2-2
Ni_2C_2 Core	C_{2h}(planar)	C_{2v}(bent)		C_2(bent)
A. Distances (Å)				
Ni-Ni	2.390(1)	2.363(1)	2.351(1)	2.322(1)
Ni-CX (X = O; NCH_3)	1.864[c]	1.861(5)[b]	1.865(5)[b]	1.881[d]
Ni-Cp[e]	1.745	1.751	1.752	1.770
B. Bond Angles (deg)				
Ni-C-Ni'	79.7(1)	78.8(2)[b]	78.1(2)[b]	76.2(2)[b]
C-Ni-C'	100.3(1)	95.2(4)[b]	93.4(4)[b]	87.8(2)[b]
C. Torsional Angles (deg)[f]				
NiC_2-C_2Ni' fragment	180.0	140.8	133.5	117.9
CNi_2-Ni_2C' fragment	180.0	146.0	139.2	123.6
Two C_5(ring)-NiC_2 fragments	90.0;90.0	98.6;98.7	99.5;98.0	98.9;97.0
C_5(ring)-C_5(ring)'	0.0	22.0	29.1	46.3

[a] Ref. 37.

[b] Each esd given in parentheses after the mean of equivalent observations represents the estimated standard deviation of an individual observation rather than that of the mean.

[c] The average of two non-equivalent distances, 1.840(3) and 1.889(3) Å, of the one independent, asymmetrically coordinated bridging carbonyl.

[d] The average of two non-equivalent means, 1.864(4) and 1.899(4) Å. The smaller value is the average of the two equivalent $Ni\text{-}CNCH_3$ bond lengths anti to the methyl substituents, while the larger value is the average of the two equivalent $Ni\text{-}CNCH_3$ bond lengths syn to the methyl substituents.

[e] Cp denotes the centroid of the cyclopentadienyl ring.

[f] Torsional angle denotes the angle between the two planes P and Q defined by the P-Q fragment. The corresponding dihedral angle, defined in Table V (and Figure 6) as the angle between the normals of the two planes, is the supplement of the torsional angle.

as the core bends. The shape of the curve drawn through the four examples is meant only to relate the observed variation of distance with angular change and not to be a specific functional form. The line drawn through points *a*, *b*, and *c* has a correlation coefficient of 0.998, thereby indicating a linear correlation of the points of greater than 95% probability. The actual curve suggests that the extrapolation of the linear increase in the Ni–Ni bond distance is hampered by a more important energetic requirement to maintain the bridging ligands at a relatively fixed Ni–Ni distance. That is, the analogous, short metal–metal distances in this series of dimers are presumed from recently available structural data of related dimers[38] to be primarily governed by the particular electronic and steric constraints of the bridging carbonyl ligands due to the direct metal–metal interactions being much weaker.

(c) The Localized Cyclopentadienyl–$Ni(CO)_2$ Interaction and Resulting Bonding Implications. Figure 4 shows that each cyclopentadienyl ligand *n* (where *n* = 1–4) in molecules A and B of the $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ dimer is symmetrically oriented relative to the nonplanar $Ni_2(CO)_2$ core such that the pseudo mirror plane bisecting the entire molecule passes through the nickel atoms, one ring carbon atom C(*n*1), and its attached hydrogen atom H(*n*1). Of the other four carbon atoms in each ring, C(*n*2) and C(*n*5) are mirror related and likewise C(*n*3) and C(*n*4). The resulting nickel coordination of each local $(\eta^5\text{-}C_5H_5)NiC_2$ moiety, in which the NiC_2 fragment is nearly perpendicular (i.e., within 8–10° in each case) to the cyclopentadienyl ring, is not only analogous to that found[37] in the $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CNCH_3)]_2$ dimer but also approximates the cobalt coordination determined[35] in $[Co(\eta^5\text{-}C_5(CH_3)_5](CO)_2$. The fact that a relatively precise X-ray diffraction study[35] of this latter cobalt monomer, in which the cyclopentadienyl ring has been effectively anchored from librational motion in the solid state by the five methyl substituents, provided definite bond-length evidence for a statistically significant and theoretically meaningful distortion of the cyclopentadienyl ring makes it worthwhile to perform a similar comparative analysis.

An examination of a resulting numerical comparison, which is summarized in Table VII, reveals the following structural features.

(1) The tilt by ca. 8–10° of each cyclopentadienyl ring from perpendicularity with its local NiC_2 center in the $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ and $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CNCH_3)]_2$ dimers gives rise to a uniform variation in the Ni–C(ring) distances with the equivalent Ni–C(*n*3) and Ni–C(*n*4) distances being ca. 0.10 Å shorter than the unique Ni–C(*n*1) bond length. In

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(38) Cf.: Ginsburg, R. E.; Cirjak, L. M.; Dahl, L. F. *J. Chem. Soc., Chem. Commun.* **1979**, 468–70 and references cited therein.

Table VII. Comparison of Mean Geometrical Parameters for the Structurally Similar $(\eta^5\text{-}C_5H_5)NiC_2$ Centers in Molecules A and B of $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ and in $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CNCH_3)]_2$[a] with Those for $Co[\eta^5\text{-}C_5(CH_3)_5](CO)_2$[b]

	$[Ni(\eta^5\text{-}C_5H_5)(\mu_2\text{-}CO)]_2$				$[Ni(\eta^5\text{-}C_5H_5)(\mu_2\text{-}CNCH_3)]_2$		$Co[\eta^5\text{-}C_5(CH_3)_5](CO)_2$
	A		B				
A. Metal-C(Ring) Distances (Å)	$(n = 1,2)^c$		$(n = 3,4)^c$		$(n = 1,2)^{c,d}$		$(n = 1)^c$
M-C(n1)[e]	[2][f] 2.172		[2] 2.171		[2] 2.190		[1] 2.102
M-C(n2) -C(n5)[e]	[4] 2.109		[4] 2.104		[4] 2.136		[2] 2.067
M-C(n3) -C(n4)[e]	[4] 2.077		[4] 2.080		[4] 2.098		[2] 2.103
B. C(Ring)-C(Ring) Distances (Å)							
C(n1)-C(n2) C(n1)-C(n5)	[4] 1.372		[4] 1.364		[4] 1.383		[2] 1.410
C(n2)-C(n3) C(n4)-C(n5)	[4] 1.401		[4] 1.408		[4] 1.412		[2] 1.446
C(n3)-C(n4)	[2] 1.369		[2] 1.348		[2] 1.396		[1] 1.392
C. Atomic Displacements[g] From Mean Pentacarbon(Ring) Plane (Å)	n = 1	n = 2	n = 3	n = 4	n = 1	n = 2	n = 1
C(n1)	-0.016	-0.017	-0.019	-0.017	-0.018	-0.010	-0.021
C(n2) C(n5)	+0.014 +0.012	+0.014 +0.013	+0.016 +0.014	+0.017 +0.009	+0.016 +0.012	+0.012 +0.004	+0.016 +0.017
C(n3) C(n4)	-0.006 -0.004	-0.006 -0.004	-0.007 -0.005	+0.013 -0.004	-0.009 -0.002	-0.009 +0.004	-0.006 -0.007
Metal	+1.743	+1.753	+1.751	+1.753	+1.766	+1.768	+1.703

[a] Ref. 37. [b] Ref. 35. [c] n denotes the number of the cyclopentadienyl ring for a given molecule.

[d] For this comparison, the atoms of $[Ni(\eta^5\text{-}C_5H_5)(\mu_2\text{-}CNCH_3)]_2$ have been relabeled in accordance with the same atomic designation used here for the other molecules. The new atomic labeling relative to the original one[37] is as follows: C_{14}, C_{15}, C_{11}, C_{12}, C_{13} are replaced by C(11), C(12), C(13), C(14), C(15), respectively, while C_{25}, C_{21}, C_{22}, C_{23}, C_{24} are replaced by C(21), C(22), C(23), C(24), C(25), respectively.

[e] It is presumed that C(n2) and C(n5) are symmetry equivalent, and likewise C(n3) and C(n4), by a virtual mirror plane which bisects each NiC_2 center (or the $Co(CO)_2$ fragment) and passes through C(n1).

[f] Brackets [ ] enclose the number of equivalent distances having the values listed in the right columns.

[g] The signs of the perpendicular displacements of the individual C(ring) atoms from their mean pentacarbon plane are designated for each ring on the common basis that the coordinated metal atom is located in a positive direction from a given ring.

contrast, for $Co[\eta^5\text{-}C_5(CH_3)_5](CO)_2$ in which the cyclopentadienyl ring is perpendicular to the planar $Co(CO)_2$ fragment, these same three Ni–C(ring) distances possess identical values.

(2) The two chemically equivalent cyclopentadienyl rings in each of the three independent nickel molecules presented in Table VII display similar C(ring)–C(ring) bond-length patterns with the equivalent C(*n*2)–C(*n*3) and C(*n*4)–C(*n*5) bonds being invariably longer by 0.02–0.05 Å than the unique C(*n*3)–C(*n*4) bond and the equivalent C(*n*1)–C(*n*2) and C(*n*1)–C(*n*5) bonds. It is noteworthy that the considerably smaller values for the C(ring)–C(ring) bonds in molecules A and B of $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ and in $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CNCH_3)]_2$ compared to those for the corresponding bonds in (pentamethylcyclopentadienyl)cobalt dicarbonyl are a consequence[34] of the much greater librational motion (as evidenced from the sizes, shapes, and orientations of the atomic thermal ellipsoids) of the unsubstituted cyclopentadienyl rings. Nevertheless, the stereochemical feature of prime interest is that this particular C(ring)–C(ring) distortion in each of the three nickel molecules is completely consistent within the limits of experimental error with that determined[35] for $Co[\eta^5\text{-}C_5(CH_3)_5](CO)_2$, in which the two equivalent, adjacent C(11)–C(12) and C(11)–C(15) bonds of 1.410 Å (average) are separated from the C(13)–C(14) bond of 1.392 Å by two equivalent, long C(12)–C(13) and C(14)–C(15) bonds of 1.446 Å (average). This small but pronounced deformation of the pentamethylcyclopentadienyl ring in $Co[\eta^5\text{-}C_5(CH_3)_5](CO)_2$ from a regular pentagonal geometry toward an "allyl–ene" geometry may be readily ascribed to a resulting localization of π-electron density in the ring by its noncylindrical bonding interaction with the planar $Co(CO)_2$ center. Although this static distortion pattern is not unlike the distortions previously indicated and interpreted from X-ray diffraction studies[39] of metal complexes containing unsubstituted cyclopentadienyl rings in other asymmetric metal environments, the structural investigation of $Co[\eta^5\text{-}C_5(CH_3)_5](CO)_2$ furnished the first experimentally convincing evidence for a clear-cut ring distortion by a planar ML_2 fragment.[40]

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(39) (a) Dahl, L. F.; Wei, C. H. *Inorg. Chem.* **1963**, *2*, 713–21. (b) Gerloch, M.; Mason, R. *J. Chem. Soc.* **1965**, 296–304. (c) Bennett, M. J.; Churchill, M. R.; Gerloch, M.; Mason, R. *Nature* (*London*) **1964**, *201*, 1318–20. (d) Churchill, M. R. *Inorg. Chem.* **1965**, *4*, 1734–9. (e) Coleman, J. M.; Dahl, L. F. *J. Am. Chem. Soc.* **1967**, *89*, 542–52. (f) Smith, A. E. *Inorg. Chem.* **1972**, *11*, 165–70.

(40) Bis[cyclopentadienyl(π-allyl)nickel], containing two centrosymmetrically related *nonplanar* $Ni(\eta^3\text{-allyl})$ fragments each coordinated to an unsubstituted cyclopentadienyl ring, is the only other statistically significant example (to our knowledge) which was shown from an X-ray crystallographic determination[39f] to possess a similar cyclopentadienyl ring deformation in the solid state.

(3) The observed perpendicular displacements of the C(ring) atoms from their mean plane are small (i.e., less than 0.02 Å) in each of the six cyclopentadienyl rings in the three nickel molecules. Yet, they reinforce one another in indicating a slight ring puckering, as evidenced by the extensive mirror-plane correlation of comparable C(ring) deviations toward and away from the nickel atom (see Table VII). Furthermore, an analogous ring puckering is observed in the pentamethylcyclopentadienyl ligand of (pentamethylcyclopentadienyl)cobalt dicarbonyl. Here, the equivalent C(12) and C(15) atoms deviate from the mean plane by 0.016 and 0.017 Å, respectively, toward the cobalt, while the equivalent C(13) and C(14) atoms deviate by 0.006 and 0.007 Å, respectively, and C(11) by 0.021 Å away from the cobalt. The directional shifts of these perpendicular displacements are also indicated by the equivalent Co–C(12) and Co–C(15) bonds of 2.067 Å (average) being shorter than the Co–C(11) bond of 2.102 Å and the equivalent Co–C(13) and Co–C(14) bonds of 2.103 Å (average). Hence, it is evident that the electronically induced distortion of a cyclopentadienyl ring due to its interaction with a planar Co(CO)$_2$ or NiC$_2$ fragment also includes a slight ring puckering.

Infrared, Proton and Proton-Decoupled Carbon-13 Nuclear Magnetic Resonance, and Mass Spectral Characterization. As indicated in the introduction, an extensive amount of physical characterization has already been done on $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$. Although the results of the spectral analyses reported here reproduce those previously obtained for $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$, it is still worthwhile to assess the influence of the methyl ring substituent upon the system by a comparison of the two compounds under matched experimental conditions.

The solution IR spectra, for both compounds in CH_2Cl_2 (Figure 5) and also in a variety of other solvents, clearly display the two bridging carbonyl bands in the 1800–1900 cm^{-1} region characteristic of the entire family of alkyl-substituted $[Ni(\eta^5\text{-}C_5H_4R)(\mu\text{-}CO)]_2$ compounds.[2] The higher carbonyl frequency can be assigned to a symmetric stretching mode and the lower carbonyl frequency to the corresponding asymmetric stretching mode. Of particular note is that the appearance of the symmetric C-O stretching mode in the methylcyclopentadienyl compound requires a breakdown in the C_{2h}-$2/m$ symmetry shown by the molecule in the crystal lattice in that this *centric* point group strictly forbids any IR activity of the symmetric modes. This observation, along with other evidence to be discussed more fully later, suggests that these molecules are fluxional in solution. The solid-state IR carbonyl bands (Figure 5) are not only completely consistent with the known crystalline geometries but also substantiate the assignment of the higher frequency to the *symmetric* C–O stretching mode. The effect of a methyl substitution for one cyclopentadienyl hydrogen atom in the dimer is to lower the comparable carbonyl frequencies by approximately 10 cm^{-1}, which implies from simple electronic considerations that the relative electron-releasing ability of the ring substituent energetically produces a greater back-bonding from the nickel d orbitals into the antibonding π^* carbonyl orbitals. Such behavior is not unexpected in having been observed previously, for example, with a 45 cm^{-1} decrease in the ν(N–O) frequency of $Ni(\eta^5\text{-}C_5H_4R)NO$ when R = CH_3 is substituted in place of a H atom.[41] The relative intensities of the two carbonyl frequencies of $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ show very little solvent dependence in solvents encompassing a wide range of dipole moments. On the basis of the intensity ratio of these two carbonyl bands, McArdle and Manning[7] have calculated via the method of Beck, Melnikoff, and Stahl[42] that the OC···CO angle for $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ in solution is ca. 140°. The appropriate torsional angle[43] (i.e., supplement of the corresponding dihedral angle in Table V) between the two mean $Ni_2(CO)$ planes is 146.8° for molecule A and 139.9° for molecule B in crystalline $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$; this excellent agreement indicates a similar degree of bending of the $Ni_2(CO)_2$ core in the solid and solution phases. An intensity-ratio comparison of the corresponding two solution IR carbonyl bands of $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$ points to its $Ni_2(CO)_2$ core being bent in solution by an analogous angle of ca. 140°.

The 100-MHz ^{1}H NMR spectrum of $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ in $CDCl_3$, with internal Me_4Si as reference, shows a sharp singlet at δ 5.41 for the cyclopentadienyl protons. A corresponding spectrum of $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$ exhibits a sharp singlet assigned to the methyl protons at δ 1.89 (relative intensity 3) and a broad peak at δ 5.24 (relative intensity 4) which can be assigned as the unresolved AA′BB′ pattern expected for a monosubstituted cyclopentadienyl ring. A 270-MHz ^{1}H NMR measurement[44] of the same sample of $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$ shows the methyl singlet at δ 1.895 (1) and an apparent doublet for the AA′BB′ pattern at δ 5.225 (1) and 5.278 (1). The upfield shift of the remaining cyclopentadienyl ring protons upon methyl substitution implies an overall increase in their diamagnetic shielding.

The 15-MHz $^{13}C\{^1H\}$ NMR spectrum of $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ in acetone-d_6, with internal Me_4Si as reference and with ca. 0.1 M Cr(acac)$_3$ as a paramagnetic relaxation reagent[45] (for observing CO carbon absorptions) shows resonances for the cyclopentadienyl carbons at δ 94.5 (1) and for the carbonyl carbons at δ 226.9 (1). The methyl analogue, run under the same conditions, exhibits the following resonances: methyl carbon, δ 12.1 (1); ring carbons, δ 93.5 (1) [relative intensity 2], 95.1 (1) [relative intensity 2], 107.9 (1) [relative intensity 1]; carbonyl carbons, δ 230.7 (1). An assignment of the δ 107.9 resonance to the methyl-attached ring carbon (i.e., C(1)) is based upon the relative intensities. Only the decoupled spectrum was taken, but by analogy with a study on 1,1′-dimethylferrocene[46] it seems likely that the δ 95.1 and 93.5 resonances correspond to the mirror-related pairs of C(2) and C(3), respectively.

A previous carbon-13 temperature study on the unsubstituted dimer by Gansow, Burke, and Vernon[9] revealed no unusual character in the single observed carbonyl resonance from −160 to +100 °C, thereby indicating no apparent environmental changes over this temperature range. As found by other authors[47] for several different types of organometallic systems, the expected increase in occupation of the antibonding π^* carbonyl orbitals (as previously evidenced by the decreased ν(C–O) of $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$ vs. $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$) shows up as an apparent deshielding of the carbonyl carbon atom, *counter* to diamagnetic shielding predictions. This apparent anomaly has been attributed to a paramagnetic term resulting from "a decrease in the magnitude of the separation between the ground state and the lowest lying electronic excited states with increasing transition metal → carbonyl π back-donation."[47b]

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(41) Bailey, R. T. *Spectrochim. Acta, Part A* **1969**, *25a*, 1127–33.

(42) Beck, W.; Melnikoff, A.; Stahl, R. *Chem. Ber.* **1966**, *99*, 3721–7.

(43) The torsional angles between the two mean $Ni_2(CO)$ planes provides a reasonably precise estimate of the OC···CO angle in that least-squares calculations (Table V) showed that all atoms for each of the four Ni(CO)Ni′ fragments in molecules A and B are coplanar within 0.011 Å.

(44) Courteously run by Dr. David F. Hillenbrand (University of Wisconsin—Madison) using a Bruker WH-270 Fourier transform nuclear magnetic resonance spectrometer.

(45) Cf.: Gansow, O. A.; Burke, A. R.; La Mar, G. N. *J. Chem. Soc., Chem. Commun.* **1972**, 456–7.

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Table VIII. Mass Spectral Data

ion	m/e	intensity[a]
A. $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$		
$(C_5H_5)_2Ni_2(CO)_2^+$	302	4.9
$(C_5H_5)_2Ni_2(CO)^+$	274	2.3
$(C_5H_5)_2Ni_2^+$	246	32.1
$(C_5H_5)_2Ni^+$	188	100.0
$(C_5H_5)Ni^+$	123	70.2
Ni^+	58	22.1
B. $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$		
$(C_5H_4CH_3)_2Ni_2(CO)_2^+$	330	8.4
$(C_5H_4CH_3)_2Ni_2(CO)^+$	302	2.5
$(C_5H_4CH_2)_2Ni_2^+$	272	80.2
$(C_5H_5CH_3)Ni(CO)_2^+$	194	13.6
$(C_5H_4CH_2)Ni^+$	136	100.0
Ni^+	58	46.5

[a] Peak heights given relative to base peak as 100.0.

The mass spectra,[48] examined with each sample introduced into a 70-eV ion source by a direct inlet system at 130 °C, show interestingly different fragmentation sequences. The major peaks for nickel-containing ions are given in Table VIII. The use of a mass spectral program[49] (written to generate theoretical isotopic abundance envelopes for any ion) greatly facilitated the identification of the ion peaks by comparison with the considerably different isotopic envelope patterns calculated for mononickel and dinickel ions (since carbon, hydrogen, and oxygen all have major isotopes whose abundances are greater than 99%). In agreement with previous mass spectral measurements[50] of $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$, Table VIII shows the existence of its parent ion which undergoes successive loss of CO followed by splitting to the nickelocenium ion (base peak) and ultimately to species involving loss of the rings. On the other hand, the mass spectral data reveal that $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$ possesses a more diversified fragmentation pattern. Loss of the first CO from the observed parent ion occurs, but loss of the second CO is apparently accompanied by simultaneous loss of two hydrogens (proposed as one from each methyl group) to change the methylcyclopentadienyl rings into fulvene rings. This fulvene structure also appears after the fission of the Ni–Ni bond to yield mononuclear entities. The loss of hydrogen atoms in the two preceding ions is partially accounted for by the appearance of the *cyclopentadiene* species, $[Ni(C_5H_5CH_3)(CO)_2]^+$, which is formally analogous to $[Ni(CO)_4]^+$.

A Case for Fluxional Behavior Involving a Butterfly-Like Interconversion in the $[Ni(\eta^5\text{-}C_5H_4R)(\mu\text{-}CO)]_2$ Dimers (R = H, CH_3). The crystallographic data previously discussed show that a bending deformation of the $Ni_2(CO)_2$ core about the Ni–Ni axis from a planar one in the methylcyclopentadienyl carbonyl molecule to the differently bent ones in the cyclopentadienyl carbonyl molecules A and B (which possess torsional angles of 146.0 and 139.2°, respectively, for the CNi_2–Ni_2C' fragment) produces only a small change in either the Ni–Ni or Ni–CO distances. Therefore, the two independent dimers observed in crystalline $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ may be considered as merely *individual frames in a motion picture of a dynamic butterfly-like inversion which occurs in solution.* The middle frame is represented by crystalline $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$ with its planar $Ni_2(CO)_2$ core. In order to lead to an equivalent C_{2v} molecular configuration, an inversion of the nonplanar $Ni_2(CO)_2$ core must be accompanied by a concomitant rotation (together with a slight tilting) of each cyclopentadienyl ring by 36° about its Ni–Cp(centroid) axis. In this case, the intermediate structure corresponds to that of crystalline $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$ with a planar $Ni_2(CO)_2$ and perpendicular rings which have been rotated by 18°. The important aspect is that the solid-state existence of such an intermediate configuration demonstrates directly that such a butterfly interconversion is structurally allowed with bridge retention. This proposal of fluxional behavior in solution is realistic because the bending deformation required for facile interconversion in this case must be very small (i.e., at most only a few kilocalories per mole).

Further support that an intramolecular interconversion of $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ in solution would occur via a butterfly motion through a planar bridged intermediate rather than via a bridge-opening mechanism involving a nonbridged intermediate is based upon the sole existence (to our knowledge) of all related dimers in a bridged form which may be either planar or nonplanar. An analysis of the shapes and orientations of the carbonyl oxygen thermal ellipsoids in $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$ shows no unusual distribution of their electron density normal to the $Ni_2(CO)_2$ plane. Indeed, the planar core is definitely indicated as the favored configuration in the gaseous state in that the vapor phase IR spectrum of the unsubstituted $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$ dimer at 100 °C is reported[6] to show only the asymmetric carbonyl band. If so, its observed bent conformation in solution is then presumed to be a consequence of solvent–solute interactions. The fact that the relative intensities of the two carbonyl bands are essentially invariant to a change of solvent encompassing a large variation in dipole moment supports the assertion of a small energy difference between the planar and the bent geometries.

The isoelectronic $[Co(\eta^5\text{-}C_5H_5)(\mu\text{-}NO)]_2$ dimer, which displays the two infrared-active nitrosyl modes in solution[10] indicative of a bent configuration, was found by an X-ray diffraction study[11] to have a planar $Co_2(NO)_2$ core in the solid state. Curiously, a KBr-pellet IR spectrum[10] of this compound exhibited both nitrosyl bands, indicating the possibility of a second crystalline form containing a bent $Co_2(NO)_2$ core. It appears then that this ambivalent behavior of a planar core vs. bent core is fairly general for dimers with metal–metal bond orders equal to one, in sharp contrast to analogous metal–metal multiple-bonded dimers, whose out-of-plane $d\pi$–$d\pi$ dimetal-bonding interaction[13,38,51] favors a planar core. Structurally characterized examples of the latter dimers include $[Fe(\eta^5\text{-}C_5H_5)(\mu\text{-}NO)]_2$[52] (with an Fe–Fe bond order of 2) and the $[Co(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2^-$ monoanion (with a Co–Co bond order of 1.5) as the bis(triphenylphosphin)iminium salt[51] and as the tetraphenylarsonium salt;[53] these two dimers are expectedly planar in the crystalline state, and their infrared solution spectra exhibit only the asymmetric bridging ligand stretching mode in harmony with the maintenance of a planar centrosymmetric core in solution.

Fluxional Behavior in Structurally Analogous Dimeric Systems and the Interrelated Adams–Cotton Pseudorotation Mechanism Proposed for $[Co(CO)_3(\mu\text{-}Ge(CH_3)_2)]_2$. The above postulated mechanism for a rapid intramolecular rearrangement of the $[Ni(\eta^5\text{-}C_5H_4R)(\mu\text{-}CO)]_2$ dimers (R = H, CH_3)

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(48) Courteously run by Mr. Kerry L. Spear (University of Wisconsin—Madison).

(49) Byers, L. R. "MSEG, A FORTRAN Mass Spectral Envelope Generator", Ph.D. Thesis, University of Wisconsin—Madison, 1978; Appendix I.

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(51) Schore, N. E.; Ilenda, C. S.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 1781–7. Ilenda, C. S.; Schore, N. E.; Bergman, R. G. *Ibid.* **1976**, *98*, 255–6. Schore, N. E.; Ilenda, C. S.; Bergman, R. G. *Ibid.* **1976**, *98*, 256–8.

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(53) Ginsburg, R. E. Ph.D. Thesis, University of Wisconsin—Madison, 1978. Ginsburg, R. E.; Dahl, L. F., unpublished research.

in solution bears a close resemblance to the pseudorotation mechanism proposed on the basis of a temperature-dependent ^{1}H NMR study by Adams and Cotton[54] for the axial–equatorial methyl group exchange in $[Co(CO)_3(\mu\text{-}Ge(CH_3)_2)]_2$, which (with its bent Co_2Ge_2 core and an electron-pair metal–metal bond) may be regarded as a structural analogue of molecules A and B. They suggested that the methyl site-exchange process may occur via an inversion of the bent Co_2Ge_2 core accompanied by some rearrangement of the $Co(CO)_3$ groups (tantamount to a rotation about the local approximate threefold axis) such that the transition state or intermediate consists of a trigonal-bipyramidal ligand configuration about each cobalt atom. The possibility of a bridge-opening mechanism involving an intermediate or transition state in which the dimethylgermanium ligands went to terminal-type bonding positions was also suggested.[54,55] An extensive investigation was subsequently reported by Cotton, Cullen, and their coworkers[56] on the fluxional behavior of the metal–metal-bonded $[M(CO)_3(\mu\text{-}X)]_2$ dimers (with X = PMe_2, $AsMe_2$, AsMePh, SMe, and SEt for M = Fe and X = $GeMe_2$ and $SnMe_2$ for M = Co). They concluded from their ^{13}C and ^{1}H measurements that no information can be obtained concerning the process by which carbonyl ligands undergo site exchange during the occurrence of the R group site exchange on account of independent carbonyl scrambling being too rapid at temperatures required for R group exchange. They also concluded that axial–equatorial R group exchange occurs simultaneously in both ligand-bridged groups but that the mechanism for this process (which may involve either bridge retention or bridge opening) remains debatable.[57]

In order to find any evidence of a dynamic rearrangement in the $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CNR)]_2$ dimers, Adams and Cotton[58] examined the ^{1}H NMR spectra of the methyl isocyanide and isopropyl isocyanide compounds. Although the spectrum of the $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CNCH_3)]_2$ dimer did not undergo any change on cooling to −107 °C, the room-temperature spectrum of the $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CNCH(CH_3)_2)]_2$ dimer exhibited a doublet which, upon cooling, collapsed and appeared as a broad singlet at −107 °C. Adams and Cotton[58] suggested several possible mechanisms for methyl site exchange including: (1) opening and reclosing of bridges; (2) simple inversion at the nitrogen atoms with bridge retention; (3) a butterfly inversion of the $Co_2(CNR)_2$ core of the type postulated[54] to occur in $[Co(CO)_3(\mu\text{-}Ge(CH_3)_2)]_2$.

Other Stereochemical Implications Based upon the Structures of the $[Ni(\eta^5\text{-}C_5H_4R)(\mu\text{-}CO)]_2$ Dimers (R = H, CH_3). The structural results presented here provide a clarification concerning possible structures previously proposed by others.[7,59] First, Jolly and Wilke[59] stated that two "structures are possible differing in the cis or trans arrangement of the π-cyclopentadienyl groups" in $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$. It is now evident that the near perpendicularity of the cyclopentadienyl ligands to their coordinated NiC_2 moieties does not allow for the formation of a trans configuration. Second, McArdle and Manning[7] concluded from an infrared spectral analysis that $(\eta^5\text{-}C_5H_5)Fe(CO)(\mu\text{-}CO)_2Ni(\eta^5\text{-}C_5H_5)$ should have a virtually planar $Fe(CO)_2Ni$ core. The determined configuration for the $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$ dimer provides definite support that the cyclopentadienyl ring bonded to the nickel atom should also be perpendicularly disposed to a planar $Fe(CO)_2Ni$ core rather than oriented either on the opposite side (trans isomer) or on the same side (cis isomer) as the iron-coordinated cyclopentadienyl ring.

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Registry No. $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$, 12170-92-2; $[Ni(\eta^5\text{-}C_5H_4CH_3)(\mu\text{-}CO)]_2$, 32028-28-7.

Supplementary Material Available: A listing of the observed and calculated structure factor amplitudes (30 pages). Ordering information is given on any current masthead page.

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(57) On the basis of the Adams–Cotton mechanism[54] for the axial–equatorial methyl group exchange in $[Co(CO)_3(\mu\text{-}Ge(CH_3)_2)]_2$, the corresponding intermediate (or transition state) for methyl group site exchange in the structurally analogous Fe–Fe-bonded neutral $[Fe(CO)_3(\mu\text{-}P(CH_3)_2)]_2$ dimer (containing a bent Fe_2P_2 core) would possess an idealized C_{2h} geometry with a planar Fe_2P_2 core and trigonal-bipyramidal iron atoms. Its near conformity to the C_{2h}-distorted geometry recently determined in the solid state for the planar Fe–Fe-nonbonded $[Fe(CO)_3(\mu\text{-}P(C_6H_5)_2)]_2^{2-}$ dianion from an X-ray diffraction study (Ginsburg, R. E.; Rothrock, R. K.; Finke, R. G.; Collman, J. P.; Dahl, L. F. *J. Am. Chem. Soc.* **1979**, *101*, 6550–62) provides support for the Adams–Cotton mechanism with non bridge opening.

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