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Synthesis and Stereochemical Analysis of the Triangular Cobalt–Dinickel Clusters $(\eta^5\text{-}C_5H_{5-n}Me_n)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ (Where $n = 0, 1, 5$): Direct Evidence for the Antibonding Trimetal Character of the Unpaired Electron in the Fischer–Palm $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ and Resulting Geometrical Effects upon Formal Oxidation by Replacement of a Nickel with a Cobalt Atom

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Abstract: The preparation of three members ($n = 0, 1, 5$) of this mixed-metal $(\eta^5\text{-}C_5H_{5-n}Me_n)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ series in nearly quantitative yields from the analogous reactions of equimolar quantities of $Ni_2(\eta^5\text{-}C_5H_5)_2(\mu_2\text{-}CO)_2$ and $Co(\eta^5\text{-}C_5H_{5-n}Me_n)(CO)_2$ in refluxing hexane and their characterization by X-ray diffraction and other physical techniques were performed in order to provide a convincing operational test in experimentally discriminating between the Longuet–Higgins–Stone bonding trimetal HOMO model vs. the Strouse–Dahl antibonding trimetal HOMO model proposed for the unpaired electron in the classical Fischer–Palm $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ cluster. In light of the Strouse–Dahl model being based upon a direct metal–metal bond length comparison (and subsequent dilute single-crystal ESR analysis) of the isostructural $Co_3(CO)_9(\mu_3\text{-}S)$-$FeCo_2(CO)_9(\mu_3\text{-}S)$ pair in which the unpaired electron in the paramagnetic C_{3v}—$3m$ tricobalt molecule was formally removed by substitution of an iron atom in place of a cobalt atom, a similar experimental strategy was utilized in formally oxidizing the $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ molecule (which defied our attempts of direct oxidation to the monocation) by replacement of one nickel atom with a cobalt atom. A resulting geometrical comparison revealed a metal–metal bond length of 2.358 (2) Å for $CoNi_2(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ (whose expected diamagnetic character was ascertained from a magnetic susceptibility measurement at room temperature) vs. that of 2.389 (2) Å for the isostructural $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$, whose architecture, initially determined by Hoch and Mills from film data, was refined from diffractometry data in order to provide more precise molecular parameters. Although this significant decrease of 0.031 Å in the metal–metal distance is consistent with the unpaired electron in the trinickel molecule populating a HOMO with highly antibonding trinickel character, the presence of a crystallographically imposed threefold disorder in the $CoNi_2$ molecule gives rise to an averaged structure of C_{3h}—$3/m$ site symmetry, and thus it was not possible to deduce the actual configuration of the $CoNi_2(CO)_2$ framework. An attempt to overcome this crystal disorder was made by the subsequent synthesis of $(\eta^5\text{-}C_5H_4Me)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$, but unfortunately an X-ray diffraction examination of several crystals showed that the cobalt-attached C_5H_4Me ring was not sufficiently different from the other two C_5H_5 rings to prevent analogous crystal disordering of each molecule. An ultimate solution to this problem involved the preparation of the (pentamethylcyclopentadienyl)cobalt–dinickel analogue, $(\eta^5\text{-}C_5Me_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ *which was found by* crystallographic study to be ordered and which thereby furnished a detailed description of its molecular configuration. The $CoNi_2(CO)_2$ core was determined to conform within experimental error to C_{2v}—$2mm$ symmetry with a considerably shorter Ni–Ni bond length of 2.326 (2) Å relative to two equivalent Co–Ni bond lengths of 2.371 Å (average) together with two markedly shorter Co–CO distances of 1.86 Å (average) relative to four equivalent Ni–CO distaces of 2.01 Å (average); these distinct variations may be rationalized from electronic considerations. The fact that the mean length of 2.356 Å for the three metal–metal bonds is virtually identical with that of 2.358 (2) Å previously found for the three metal–metal bonds in the averaged structure of $CoNi_2(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ provides additional bond length support for the Strouse–Dahl model (which places the unpaired electron in a HOMO of a_2 representation) applied to $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$. A comparative analysis of the $(\eta^5\text{-}C_5H_{5-n}Me_n)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ series ($n = 0, 1, 5$) by infrared, by ^1H and $^{13}C\{^1H\}$ NMR, and by cyclic voltammetric measurements allowed a direct assessment of the degree of perturbation of various physical properties of these three cobalt–dinickel clusters due to the more electron-releasing methyl substituent on the unsubstituted and monomethyl- and pentamethyl-substituted cyclopentadienyl ring coordinated to the cobalt atom.

Introduction

In 1958 Fischer and Palm[1] reported the synthesis and characterization by infrared spectral and magnetic measurements of a new type of molecular trimetal cluster of formula $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$. Its proposed D_{3h} geometry containing two triply bridging carbonyl ligands capping an equilaterial triangle of nickel atoms was substantiated from an X-ray diffraction analysis by Hock and Mills[2] in 1961. An ESR examination of this paramagnetic complex containing one unpaired electron was reported in 1962 by Longuet-Higgins and Stone,[3] who suggested from a qualitative bonding model that the measured $g_\perp$ and $g_\parallel$ values were consistent with the unpaired electron residing primarily in a *bonding out-of-plane* nondegenerate trimetal orbital of d_π character. However, a dilute single-crystal ESR investigation by Strouse and Dahl[4,5] of the related paramagnetic $Co_3(CO)_9(\mu_3\text{-}S)$ molecule doped into the diamagnetic $FeCo_2(CO)_9(\mu_3\text{-}S)$ host material unambiguously showed from an analysis of the hyperfine structure that the unpaired electron was in a predominantly *antibonding in-plane* nondegenerate trimetal orbital of a_2 representation under C_{3v} symmetry. Their definitive results substantiated the previous conclusions[6] based on X-ray diffraction de-

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terminations[6,7] of $Co_3(CO)_9(\mu_3\text{-}S)$[8] and $FeCo_2(CO)_9(\mu_3\text{-}S)$[9] that the unpaired electron in $Co_3(CO)_9(\mu_3\text{-}S)$ has an appreciable conjugative destabilization effect (or antibonding character) in considerably lengthening by 0.083 Å the average metal–metal distance in the tricobalt molecule relative to that in the corresponding crystal-disordered iron–dicobalt molecule. Hence, Strouse and Dahl[4] proposed an alternative qualitative MO model for the Fischer–Palm $Ni^3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ molecule and asserted that it likewise contains its unpaired electron in an *antibonding in-plane* nondegenerate trimetal orbital of the same type d-orbital character as the one containing the unpaired electron in $Co_3(CO)_9(\mu_3\text{-}S)$.[10,11] Our efforts to ascertain experimentally the antibonding trimetal nature of the HOMO in $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ through an attempted removal of the unpaired electron by its oxidation to the monocation were unsuccessful.

An operational test of the alternative bonding hypothesis was devised by Uchtman and Dahl[12] by the synthesis and X-ray structural determination of $(\eta^5\text{-}C_5H_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$, in which the electron has been formally removed by the replacement of one nickel with a cobalt atom. A comparison of its geometry with that of $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$, whose structure was simultaneously redetermined[12] in order to obtain more precise molecular parameters, gave clear-cut bond length evidence on the basis of the significant decrease in the *mean* metal–metal distance that the unpaired electron in the trinickel molecule was indeed in an antibonding metal cluster orbital. However, a crystallographically imposed threefold disorder of the $CoNi_2$ molecules resulted in its actual configuration being averaged to D_{3h} symmetry, and thus it was not possible to assess the detailed geometrical effect upon the $CoNi_2(CO)_2$ core due to the mixed-metal atoms.

Our subsequent work led to the synthesis and structural analyses of other $M_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}X)(\mu_3\text{-}Y)$ systems together with the development of a metal cluster model[5,13] for predicting geometries and distances in these M_3 clusters containing different numbers of *antibonding* electrons. These include $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}O)$[14] and $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}S)$[15] which possess no antibonding metal cluster electrons, the $[Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}S)_2]^+$ monocation[15] with one antibonding electron, $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}S)_2$[15] with two antibonding electrons, and $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}S)_2$[16] with five antibonding electrons. Consistently, however, the structural analyses in each of the latter neutral compounds were again greatly complicated by crystallographic twinning and crystal order–disorder problems arising from these triangular metal frameworks crystallizing into hexagonal lattices with crystallographically imposed equilateral symmetry.

One original objective of the work reported here was to prepare and structurally characterize analogous mono-substituted cyclopentadienyl trimetal clusters.[17] It was hoped that the C_5H_4R ligands with suitable bulky R substituents would prevent twinning problems from arising, and furthermore it was deemed desirable to vary the relative electron-donating (or withdrawing) ability of the R groups in order to change the redox characteristics sufficiently that different charged species could be stabilized for structural elucidation. In this regard, initial work involved the preparation of $Co(\eta^5\text{-}C_5H_4R)(CO)_2$ complexes [R = Me, $SiMe_3$, CH_2Ph, CPh_3, COMe, and C(O)Ph] by the reaction of sodium cyclopentadienide with RCl to give C_5H_5R in situ followed by its reaction with $Co_2(CO)_8$. Each of these monomeric liquid $Co(\eta_5\text{-}C_5H_4R)(CO)_2$ complexes was in turn reacted with propylene sulfide in the hope of producing both $Co_3(\eta^5\text{-}C_5H_4R)_3(\mu_3\text{-}S)(\mu_3\text{-}CO)$ and $Co_3(\eta^5\text{-}C_5H_4R)_3(\mu_3\text{-}S)_2$. Definite evidence for these triangular cobalt species was provided by ^1H NMR and/or IR analyses. Unfortunately, despite extensive efforts to purify the products by column chromatography, noncrystalline oils invariably were obtained except for one crystalline product, $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}S)(\mu_3\text{-}CO)$, which was found from preliminary X-ray examination to also be twinned.[17]

Our research then shifted to an attempt to prepare an ordered solid-state analogue of the crystal-disordered $(\eta^5\text{-}C_5H_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ by an attachment of a C_5H_4R ligand only to the cobalt atom. The cobalt-labeled molecule $(\eta^5\text{-}C_5H_4Me)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ was synthesized, but X-ray diffraction examination of several crystals revealed them to be disordered. At approximately this time, Threlkel and Bercaw[18] developed a more convenient preparative route to the ligand precursor pentamethylcyclopentadiene. Therefore, $(\eta^5\text{-}C_5Me_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ was prepared and a relatively precise X-ray structural determination showed the desired attainment of a crystal-ordered $CoNi_2(CO)_2$ core geometry.

Herein are reported the results of our preparation and characterization of three electronically equivalent members of a cobalt–dinickel cluster series, $(\eta^5\text{-}C_5H_{5-n}Me_n)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ (where n = 0, 1, 5). A comparative analysis of these mixed-metal clusters by infrared, proton and carbon-13 magnetic resonance, and cyclic voltammetric studies has furnished a self-consistent set of trends which distinctly reflect the influence of methyl substitution on the cobalt-coordinated cyclopentadienyl ring. Also presented are the details of our X-ray diffraction studies of the crystal-ordered $(\eta^5\text{-}C_5Me_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ and crystal-disordered $(\eta^5\text{-}C_5H_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ molecules and of the $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ molecule (whose overall geometry was initially ascertained by Hoch and Mills[2]). Of prime importance is that a comparative analysis of these *three* molecules has fulfilled our expectations in providing experimentally convincing evidence that the HOMO containing the unpaired electron in the Fischer–Palm trinickel molecule indeed has large *antibonding* rather than *bonding* trimetal orbital character.

It is especially noteworthy that from symmetry-based arguments supported by extended Hückel calculations for $M_3(CO)_9$(ligand) and $M_3(\eta^5\text{-}C_5H_5)_3$(ligand) complexes (where M = Fe), Schilling and Hoffman[19] recently performed a systematic examination of the frontier orbitals for $Co_3(CO)_9(\mu_3\text{-}S)$ and $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ as well as for a large number of other triangular M_3L_9(ligand) complexes; they likewise concluded that the unpaired electron in the above two paramagnetic molecules is in the antibonding trimetal a_2 orbital.

Experimental Section

Preparation and Properties. All reactions, column-chromatographic separations, and crystallizations were performed under a nitrogen atmosphere via standard Schlenk techniques. Reagent grade solvents were dried by standard procedures before use.

(a) $(\eta^5\text{-}C_5H_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$. Initial attempts to prepare the desired complex by UV irradiation of a benzene solution of $Co_2(CO)_8$ and $Ni(C_5H_5)_2$ were unsuccessful; only mixtures of $Co(C_5H_5)(CO)_2$ and unreacted $Ni(C_5H_5)_2$ were formed. A sodium amalgam reduction of $Ni_2(C_5H_5)_2(CO)_2$ and $Co(C_5H_5)_2$ in methanol was also attempted, but no isolable products could be obtained. The reaction of $Co(C_5H_5)(CO)_2$ and $Ni_2(C_5H_5)_2(CO)_2$ in refluxing hexane yielded the desired cobalt–dinickel complex.

In a typical reaction, 1.8 g (10 mmol) of cyclopentadienylcobalt dicarbonyl and 3.0 g (10 mmol) of cyclopentadienylnickel carbonyl di-

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mer[1,20] were refluxed in 100 mL of hexane for a period of 7 days. A small portion of the reaction solution periodically was removed for an infrared analysis (Infracord spectrometer). When the bands at 1880 and 1840 cm^{-1} due to $Ni_2(C_5H_5)_2(CO)_2$ had disappeared, filtration of the reaction solution gave a brownish green solution and a black residue. The black residue was washed with 100 mL of hexane and dried under vacuum. The brownish green solution was evaporated to complete dryness in water-aspirator vacuum, and the resulting residue sublimed in high vacuum at 75 °C to give large crystals identified as mixtures of $Ni(C_5H_5)_2$ and $Co(C_5H_5)_2$ (50% yield) from their single-crystal X-ray diffraction patterns. Anal. Calcd for $(C_5H_5)_2(Ni,Co)$: C, 63.5; H, 5.3. Found: C, 63.0; H, 5.2.

The black hydrocarbon-insoluble residue was recrystallized from a 1:1 chloroform–octane solution to give dark green needle crystals of $(C_5H_5)CoNi_2(C_5H_5)_2(CO)_2$ (10% yield; dec ~180 °C). Anal. (by Alfred Bernhardt, Max Planck Institut, Mülheim (Ruhr), West Germany) Calcd for $CoNi_2C_{17}H_{15}O_2$: C, 47.3; H, 3.48; O, 7.42. Found: C, 47.6; H, 3.57; O, 7.29. An attempt to analyze the metal content by atomic absorption spectrometry indicated that significant amounts of both Co and Ni were present; the reproducibility of the measurements was poor (e.g., 29.9% Ni, 29.0% Co; 16% Ni, 23% Co), and hence an exact metal content could not be determined. Convincing evidence for the compound possessing the desired cobalt–dinickel stoichiometry (instead of a nonstoichiometric mixture) was furnished from magnetic susceptibility measurements[21] via the Faraday method which conclusively showed the compound to be diamagnetic ($\chi_g = 0.78 \times 10^{-6}$ cgs units, 25 °C). Its infrared spectrum (Beckman IR-8 spectrometer) in $CHCl_3$ solution exhibited only one carbonyl stretching frequency at 1723 cm^{-1} compared to a frequency of 1729 cm^{-1} observed in an infrared spectrum of $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ run under identical conditions and superimposed on the spectrum of $(C_5H_5)CoNi_2(C_5H_5)_2(CO)_2$.

(b) $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$. This compound was synthesized via the originally described procedure.[1]

(c) $(\eta^5\text{-}C_5H_4Me)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$. This compound was prepared in an analogous fashion to that of $(C_5H_5)CoNi_2(C_5H_5)_2$ by the reaction of equimolar quantities of $Co(C_5H_4Me)(CO)_2$ and $Ni_2(C_5H_5)_2(CO)_2$. Details of the preparation of $Co(C_5H_4Me)(CO)_2$ closely followed those previously described[22] for $Co(C_5Me_5)(CO)_2$; methylcyclopentadienyl dimer (Aldrich Chemical Co., 95%) was thermally cracked to monomer immediately before use through a 15-cm Vigreux column.

(d) $(\eta^5\text{-}C_5Me_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$. Details of the synthesis of this compound are analogous to those utilized to obtain $(C_5H_5)CoNi_2(C_5H_5)_2(CO)_2$ and $(C_5H_4Me)CoNi_2(C_5H_5)_2(CO)_2$. A mass spectrum (AEI MS902C high-resolution mass spectrometer) confirmed the molecular formulation with the appearance of a molecular ion envelope at *m/e* values of 496, 497, 498, 499, 500, 501, and 502 with relative intensities of 100.00 (100.00), 22.17 (25.10), 78.91 (80.62), 20.78 (23.40), 27.91 (29.29), 5.74 (8.26), and 5.43 (8.90), respectively, where the theoretically calculated[23] relative intensities are given in parentheses.

(e) General Comments on the Isolation and Properties of $(\eta^5\text{-}C_5H_{5-n}Me_n)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ (Where $n = 0, 1, 5$). Presumably the slow reaction rate associated with the rather low boiling hexane solvent is important to eliminate or minimize the trimerization of the nickel dimer to the paramagnetic Fischer–Palm compound, $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$. The observation that essentially none of this trinickel species was obtained suggests that the probable mechanism for the reaction proceeds *via* the thermal (or photolytic) decarbonylation of the cobalt monomer to $Co(C_5H_{5-n}Me_n)CO$ followed by attack of this entity upon the nickel dimer with concomitant loss of a second carbonyl. Solutions were transferred to an alumina (5 wt % H_2O added) column packed by the use of hexane and eluted with hexane in order to remove small amounts of the starting materials. Further elution with an 80% hexane/20% benzene mixture (v/v) gave the desired products as dark greenish brown bands. All three compounds can be formed in nearly quantitative yield. They each display an intense yellow brown coloration in solution in solvents such as benzene, dichloromethane, and chloroform but are insoluble in hexane or in water. From qualitative observations such as those derived from the column chromatography (e.g., $(C_5H_5)CoNi_2(C_5H_5)_2(CO)_2$ is efficiently removed from the column only with 100% benzene) as well as from relative intensities of saturated solutions in the nuclear magnetic resonance studies, it was found that the solubility in this series markedly increases with increasing methyl substitution on the cobalt–cyclopentadienyl ring.

Spectral values reported in the Discussion were obtained, unless otherwise indicated, with the following instruments: infrared (Beckman IR 4240 spectrophotometer); proton nuclear magnetic resonance (JEOL JMN-MH-100 nuclear magnetic resonance spectrometer); and proton-decoupled carbon-13 nuclear magnetic resonance (JEOL JNM-FX60 Fourier transform nuclear magnetic resonance spectrometer). Cyclic voltammetric values were recorded with an electrochemical system consisting of a Model 173 Potentiostat/Galvanostat, a Model 175 Universal Programmer, and a Model 179 Digital Coulometer, all manufactured by Princeton Applied Research, with a Tektronix R5103N storage oscilloscope and a Houston Instrument OMNIGRAPHIC 2000 (x-y) recorder.

X-ray Diffraction Analyses and Structural Refinements. (a) $(\eta^5\text{-}C_5H_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ and $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$. Single crystals of the cobalt–dinickel compound suitable for X-ray diffraction measurements were obtained by slow evaporation of a chloroform–octane solution, while suitable crystals of $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ were obtained directly from the reaction mixture. Needle-shaped crystals of dimensions 0.10 × 0.25 × 0.10 mm for the $CoNi_2$ compound and 0.25 × 0.20 × 0.20 mm for the Ni_3 compound were each mounted with epoxy cement on a thin glass fiber, such that the needle axis (in both cases the unique *c* axis) was the axis of rotation. Preliminary oscillation and Weissenberg X-ray photographs of both crystals possessed hexagonal C_{6h}—$6/m$ Laue symmetry, and their similar lattice constants substantiated our expectations that both crystal structures are isomorphous. In turn, each of the two crystals was then optically aligned on a General Electric Datex-controlled diffractometer with an E&A full circle. For each compound 36 reflections were carefully centered and the angle settings used to obtain lattice constants and angle settings for all reflection data. Details of the data collection for each crystal by the θ–2θ scan mode with Zr-filtered Mo Kα radiation and their subsequent data reduction to give structure factor amplitudes and their standard deviations paralleled those previously described for $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}O)$,[14] with the following exceptions. Intensity data (hkl, $\bar{h}\bar{k}l$) corresponding to three equivalent forms of hexagonal (C_{6h}) data were collected to a maximum 2θ value of 40°. A total of 762 observed and 79 unobserved (i.e., $I < 2\sigma(I)$) reflections were obtained for the $CoNi_2$ cluster, while 740 observed and 104 unobserved reflections were obtained for the Ni_3 cluster. The differences in intensities for equivalent reflections were found almost without exception to be less than 5%, and therefore all equivalent reflections were averaged to give a total of 253 independent observed intensity maxima for the $CoNi_2$ cluster and 248 for the Ni_3 cluster.

For $(\eta^5\text{-}C_5H_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$, the determined hexagonal lattice constants at 23 °C are $a = b = 9.158$ (3) Å, $c = 10.739$ (4) Å, and $V = 780.1$ Å^3. The experimental density (measured by the flotation method) of 1.82 g/cm^3 is identical with the calculated density of 1.82 g/cm^3 for $Z = 2$ and a fw = 427.7. The total number of electrons in the unit cell, $F(000)$, is 216.

For $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ the hexagonal lattice constants are as follows (with the previously determined values of Hock and Mills[2] given in brackets): $a = b = 9.246$ (3) Å [9.26 (5) Å], $c = 10.698$ (4) Å [10.70 (6) Å], $V = 792.0$ Å^3 [794 Å^3]. The observed density (flotation method) of 1.81 g/cm^3 [1.81 g/cm^3] is in agreement with a calculated density of 1.80 g/cm^3 [1.79 g/cm^3] for $Z = 2$ and a fw = 427.4. $F(000) = 217$.

Observed systematic absences for both hexagonal data sets of $\{00l\}$ with l odd indicated the probable space group to be either $P6_3$ (C_6^6, No. 173)[24a] or $P6_3/m$ (C_{6h}^2, No. 176);[24b] our choice of the latter centrosymmetric group (which is the same one selected by Hoch and Mills[2]) was verified by the successful refinements of both structures. For each compound the six metal atoms were found to occupy the special sixfold set of positions, $\pm(x, y, {}^1/_4; -y, x - y, {}^1/_4; y - x, - x, {}^1/_4)$, while the four carbon and four oxygen atoms of the carbonyl groups occupy the special fourfold sets of positions, $\pm({}^1/_3, {}^2/_3, z; {}^2/_3, {}^1/_3, {}^1/_2 + z)$. The cyclopentadienyl groups were found to be disordered such that of the 60 half-carbon atoms, 24 occupy the special sixfold sets of positions $\pm(x, y, {}^1/_4; -y, x - y, {}^1/_4; y - x, - x, {}^1/_4)$, while the other 36 occupy the general twelvefold sets of positions $\pm(x, y, z; -y, x - y, z; y - x, -x, z; x, y, {}^1/_2 - z; -y, x - y, {}^1/_2 - z; y - x, -x, {}^1/_2 - z)$. Thus, the solution of the structure required the location of one metal atom, one carbonyl group, and one disordered cyclopentadienyl group.

The published parameters of Hock and Mills[2] for $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ were used as a starting point for the solution of each structure. Both complexes were treated in an identical fashion. The positional parameters of the cyclopentadienyl carbon atoms were used to define a rigid body which in effect consisted of two regularly shaped coplanar C_5H_5 rings (each of D_{5h} symmetry) which are related to each other by a center of symmetry located at the common centroid of each ring; the

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(21) We are indebted to Dr. M. Camp of the University of Wisconsin—Madison for making this measurement.

(22) Byers, L. R.; Dahl, L. F. *Inorg. Chem.* **1980**, *19*, 277–284.

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

(24) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1952; Vol. I: (a) p 280; (b) p 283; (c) p 93; (d) p 79.

Table I. Positional and Thermal Parameters for the Crystal-Disordered $(\eta^5\text{-}C_5H_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$[a]

	x	y	z	B, Å^2
M	0.5098 (1)	0.3153 (1)	1/4	*b*
C(carbonyl)	2/3	1/3	0.3778 (13)	3.5 (3)
O(carbonyl)	2/3	1/3	0.4879 (9)	4.4 (2)
C(1)[c]	0.2499	0.1407	1/4	6.7 (7)
C(2)[c]	0.2910	0.2441	0.3559	5.8 (4)
C(3)[c]	0.3574	0.4114	0.3155	4.0 (3)
C(4)[c]	0.3687	0.4399	1/4	3.6 (5)
C(5)[c]	0.2613	0.1692	0.3155	1.8 (2)
C(6)[c]	0.3277	0.3365	0.3559	2.7 (3)
H(1)[c]	0.1958	0.0042	1/4	*d*
H(2)[c]	0.2744	0.2023	0.4524	*d*
H(3)[c]	0.4012	0.5218	0.3751	*d*
H(4)[c]	0.4229	0.5764	1/4	*d*
H(5)[c]	0.2175	0.0588	0.3751	*d*
H(6)[c]	0.3443	0.3783	0.4524	*d*

[a] Estimated standard deviations are given in parentheses in this and the following tables. [b] Anisotropic thermal parameters 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 for the disordered metal atom (i.e., one-third-weighted Co and two-thirds-weighted Ni). The resulting thermal coefficients (×10^4) are as follows: β_{11}, 78 (3); β_{22}, 90 (3); β_{33}, 82 (2); β_{12}, 43 (2); $\beta_{13} = \beta_{23} = 0$. [c] Atoms of twofold disordered cyclopentadienyl ring. The rigid-group atomic positions are defined relative to an orthonormal coordinate system x', y', z' as follows: The origin of the coordinate system lies on the centroid of the ring, $+x'$ passes through one atom of the ring, and all atoms lie in the $x'y'$ plane. The rigid-group angles ϕ, θ, ρ (given below) define the position (other than translation to the crystallogrphic origin) of the rigid-group coordinate system with respect to the crystallographic axis system. The hydrogen atoms of the cyclopentadienyl ring lie along vectors extended from the ring centroid through the carbon atoms such that the ring conforms to D_{5h} symmetry with C–C = 1.405 Å and C–H = 1.08 Å. The rigid-group angles (degrees) are as follows: ϕ, 96.7 (3); θ, 90.0; ρ, 0.0. [d] All hydrogen atoms are arbitrarily assigned fixed isotropic temperature factors of 8.0 Å^2.

Table II. Positional and Thermal Parameters for $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$

	x	y	z	B, Å^2
Ni	0.5091 (1)	0.3148 (1)	1/4	*a*
C(carbonyl)	2/3	1/3	0.3764 (12)	3.2 (2)
O(carbonyl)	2/3	1/3	0.4871 (9)	4.7 (2)
C(1)[b]	0.2487	0.1412	1/4	7.1 (6)
C(2)[b]	0.2895	0.2437	0.3563	6.9 (4)
C(3)[b]	0.3555	0.4094	0.3157	4.5 (3)
C(4)[b]	0.3667	0.4377	1/4	3.3 (4)
C(5)[b]	0.2599	0.1695	0.3157	1.9 (2)
C(6)[b]	0.3259	0.3352	0.3563	3.1 (3)
H(1)[b]	0.1948	0.0060	1/4	*c*
H(2)[b]	0.2729	0.2023	0.4532	*c*
H(3)[b]	0.3990	0.5188	0.3756	*c*
H(4)[b]	0.4206	0.5729	1/4	*c*
H(5)[b]	0.2163	0.0601	0.3756	*c*
H(6)[b]	0.3424	0.3767	0.4532	*c*

[a] Anisotropic thermal parameters of the form given in Table I were used for the independent nickel atom. The resulting thermal coefficients (×10^4) are as follows: β_{11}, 81 (3); β_{22}, 95 (3); β_{33}, 83 (2), β_{12}, 47 (2); $\beta_{13} = \beta_{23} = 0$. [b] Atoms of twofold disordered cyclopentadienyl ring. See footnote c of Table I. The rigid-group angles (degrees) are as follows: ϕ, 96.7 (3); θ, 90.0°, ρ, 0.0°. [c] All hydrogen atoms were arbitrarily assigned fixed isotropic temperature factors of 8.0 Å^2.

Table III. Intramolecular Distances and Bond Angles for the Crystal-Disordered $(\eta^5\text{-}C_5H_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ and Crystal-Ordered $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ Which Are Isomorphous Compounds

	$CoNi_2$-$(\eta^5\text{-}C_5H_5)_3$-$(\mu_3\text{-}CO)_2$	$Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$	
		a	b
	A. Distances (Å)		
M–M[c]	2.358 (2)	2.389 (2)	[2.39 (1)]
M–CO	1.933 (10)	1.932 (9)	[1.93 (1)]
C–O	1.183 (13)	1.183 (13)	[1.19 (2)]
M–C(ring)	2.105 (av)	2.125 (av)	[2.12]
M–Cp(centroid)	1.733	1.757	
OC···CO	2.745 (27)	2.706 (26)	
M···O	2.895 (9)	2.887 (9)	
	B. Bond Angles (deg)		
M–M–M	60.0	60.0	
M–C–O	135.2 (3)	134.4 (3)	[134]
M–C(O)–M	75.1 (4)	76.4 (4)	[77]
OC–M–CO	90.5 (6)	88.9 (5)	

[a] Values are from the redetermined least-squares refinement based upon diffractometry data. [b] Values are from the original Hock–Mills structural analysis[2] based upon three-dimensional Weissenberg film data. [c] M denotes either the crystal-disordered metal atom (i.e., one-third-weighted Co and two-thirds-weighted Ni) in the $CoNi_2$ molecule or the nickel atom in the Ni_3 molecule. The crystallographically imposed site symmetry for each of these molecules is C_{3h}–$3/m$.

rings were so oriented that one carbon atom of each ring lay on the horizontal crystallographic mirror plane of the unit cell. (See Table I for a description of the rigid-body system.)[25c] Hydrogen atoms were included in the rigid-body least-squares refinement, but during the refinement their isotropic thermal parameters were not varied. Anisotropic thermal parameters were assigned to the metal atoms and isotropic ones to all other atoms. Four cycles of full-matrix rigid-body isotropic-anisotropic least-squares refinement,[25d] of which the last cycle in each case exhibited no positional parameter shifts greater than 0.2σ, resulted in $R_1(F)$ = 4.6% and $R_2(F)$ = 5.5%[26] for the $CoNi_2$ cluster and $R_1(F)$ = 4.1% and $R_2(F)$ = 4.8%[26] for the Ni_3 cluster. Final difference Fourier maps revealed in both cases no peaks greater than 0.75 e/Å^3, thereby justifying the disordered rigid-body treatment of the cyclopentadienyl groups.

Atomic parameters from the output of the last cycle are given in Table I for $(\eta^5\text{-}C_5H_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ and in Table II for $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$. Interatomic distances and bond angles along with their estimated standard deviations, which were calculated from the full inverse matrix,[25e] are presented in Table III for both compounds. Observed and calculated structure factor amplitudes are given as supplementary material.

(b) $(\eta^5\text{-}C_5Me_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$. Single crystals were grown by slow sublimation in vacuo at ca. 130 °C in a 30 cm (long) × 22 mm (diameter) straight-tube, glass apparatus surrounded by a 15 cm (long) × 30 mm (diameter) piece of copper tubing, used to create a more uniform and extended temperature gradient. A hexagonal-shaped prismatic crystal of approximate dimensions 0.52 mm (side-to-side) × 0.12 mm (top to bottom) was utilized for the X-ray diffraction measurements with Mo Kα radiation on a Syntex P1 diffractometer. Details of the crystal alignment, data collection, and data treatment are analogous to those reported[22] for $Co(\eta^5\text{-}C_5Me_5)(CO)_2$. Intensities were sampled once for two monoclinic reciprocal lattice octants hkl and $hk\bar{l}$ for 3.0° ≤ 2θ ≤ 70.0°. Two standard reflections showed evidence during the data collection of a slight linear crystal decay, for which a correction was made. Since estimated absorption coefficients (based upon a calculated linear absorption coefficient[27] of 25.9 cm^{-1} for Mo Kα radiation) varied

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(25) (a) Blount, J. F. "DEAR, A FORTRAN Absorption-Correction Program", 1965, based on the method given by Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1957**, *10*, 180–182. (b) Broach, R. W. "QUICKSAM, A FORTRAN Program for Sorting and Merging Structure Factor Data", Ph.D. Thesis, University of Wisconsin—Madison, 1977, Appendix II. (c) Watkins, S. F. Ph.D. Thesis, University of Wisconsin—Madison, 1967, Appendix. (d) "ORFLSR, A Local Rigid-Body Least-Squares Program" adapted from the Busing–Martin–Levy ORFLS, Report ORNL-TM-305; Oak Ridge National Laboratory: Oak Ridge, TN, 1962. (e) Busing, W. R.; Martin, K. O.; Levy, H. A. "ORFFE, A FORTRAN Crystallographic Function and Error Program", Report ORNL-TM-306; Oak Ridge National Laboratory: Oak Ridge, TN, 1964. (f) "PLANES", a revised version of "PLANE 1" written by: Smith, D. L. Ph.D. Thesis, University of Wisconsin—Madison, 1962, Appendix IV. (g) Johnson, C. K. "ORTEP-II, A FORTRAN Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations", Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(26) 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 estimated standard deviations of the observed structure factors. The standard deviation in an observation of unit weight ("goodness-of-fit") is defined by $[\sum w_i(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

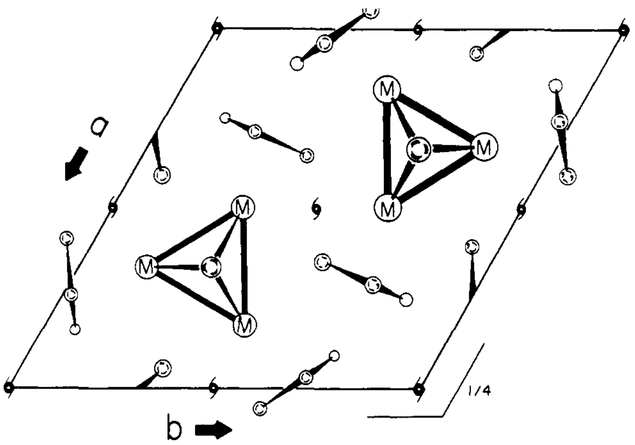

Figure 1. [001] projection of the hexagonal unit cell of the crystal-disordered $(\eta^5\text{-}C_5H_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ and crystal-ordered $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ which are isomorphous molecular compounds. The imposed crystallographic site symmetry of each molecule is C_{3h}—$3/m$. Hydrogen atoms have been omitted for clarity.

between 0.29 and 0.64, an analytical absorption correction[25a] was applied to the intensity data. A sorting and merging[25b] of the data gave 2584 independent reflections with $I > 2\sigma(I)$.

The measured lattice constants and estimated standard deviations for the monoclinic unit cell at ca. 22 °C are a = 9.227 (6) Å, b = 9.283 (6) Å, c = 12.556 (5) Å, and β = 103.63 (5)°. The unit-cell volume is 1045.2 (11) Å^3. The observed density of 1.58 g/cm^3, measured in aqueous zinc bromide, is in agreement with a calculated density of 1.58 g/cm^3 for Z = 2 and a fw = 497.8 g/mol. The total number of electrons in the unit cell, $F(000)$, is 512.

Observed systematic absences for $\{0k0\}$ data with $k = 2n + 1$ indicated two possible space groups: $P2_1/m$ (C_{2h}^2, No. 11)[24c] or $P2_1$ (C_2^2, No. 4);[24d] the noncentrosymmetric space group, $P2_1$, was subsequently confirmed by the successful solution and refinement of the structure. The crystal structure analysis required the location of one independent cluster molecule consisting of 2 nickel, 1 cobalt, 2 oxygen, 22 carbon, and 25 hydrogen atoms, each occupying the twofold set of general equivalent positions $(x, y, z; -x, {}^1/_2 + y, -z)$.

An analytical interpretation[28a] of a computed three-dimensional Patterson synthesis yielded under $P2_1$ symmetry a reasonable trimetal solution (i.e., a triangle with chemically consistent side lengths). Subsequent Fourier and difference Fourier syntheses, coupled with least-squares refinement,[25d] led to positions for all nonhydrogen atoms. At this point, idealized positions for the hydrogen atoms[28b] were inserted into the structure, and refinement was then continued. After the $R_1(F)$ value had decreased to 9.0%, the correct enantiomer was determined to have the inverted coordinates by a testing of the two possibilities with the anomalous dispersion corrections.[29,30] Refinement ultimately converged in the final, full-matrix least-squares cycle to $R_1(F)$ = 8.2% and $R_2(F)$ = 7.9%[26] with no parameter shift-to-error ratio (Δ/σ) being greater than 1.13; all Δ/σ values for nonhydrogen atoms were less than 0.47).

The "goodness-of-fit" value[26] was 1.60, the number of reflections (m) was 2584, and the number of varied parameters (n) was 318, which gave m/n = 8.1. A final difference Fourier map showed the largest positive residual peaks to be associated with the trimetal plane at 0.86 Å (1.66 e/Å^3) from Ni(1), and 0.85 Å (1.44 e/Å^3) from Ni (2), and 0.88 and 0.84 Å (1.17 and 1.10 e/Å^3, respectively) from the Co atom.

Final positional and thermal parameters are given in Table IV. Interatomic distances and bond angles with estimated standard deviations[25e] are reported in Table V. Selected least-squares planes and interplanar angles[25f] were calculated. Observed and calculated structure factor amplitudes are given as supplementary material. Most of the molecular figures were computer drawn.[25g]

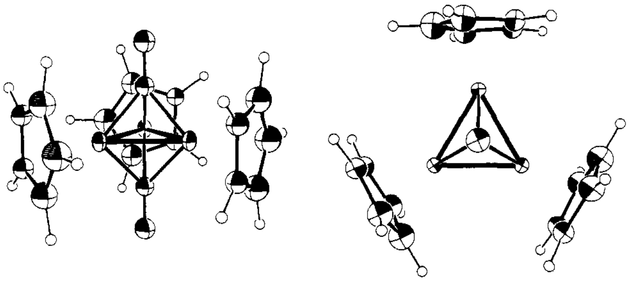

Figure 2. Two views of the solid-state configuration of the crystal-disordered, diamagnetic $(\eta^5\text{-}C_5H_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ molecule which is isomorphic with the crystal-ordered, paramagnetic Fischer–Palm $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ molecule. The crystallographically demanded site symmetry is C_{3h}—$3/m$, while the pseudosymmetry of the $M_3(CO)_2$ core is D_{3h}—$\bar{6}2m$.

Results and Discussion

Structural Features of $(\eta^5\text{-}C_5H_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ and $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$. The crystal structure of the crystal-disordered $CoNi_2$ molecule is virtually *identical* with that of the Fischer–Palm $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ molecule. Figure 1 shows a unit-cell projection down the c axis; the crystallographically demanded site symmetry of each of the two molecules, which are related to each other by an inversion center, is C_{3h}—$3/m$ (or S_3—$\bar{6}$). This symmetry necessitates that each cobalt–dinickel molecule be randomly distributed at a given crystal site over its three statistical orientations. In accordance with this C_{3h} description, the *averaged* structure (Figure 2) of $(\eta^5\text{-}C_5H_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ corresponds to the presumed crystal-ordered structure of $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ in possessing an equilateral metal triangle with each of the two mirror-related carbonyl ligands positioned on the principal threefold axis being symmetrically coordinated to the three metal atoms. The $CoNi_2(CO)_2$ core of the *averaged* structure approximates D_{3h}—$\bar{6}2m$ symmetry which with *no disorder* is reduced to either C_{2v}—$2mm$ or C_s—m, depending upon whether the two carbonyl ligands in a given molecule are actually symmetry related or not. A similar crystallographic threefold disordering in the solid-state structures of the triangular mixed-metal clusters, $FeCo_2(CO)_9(\mu_3\text{-}X)$ (where X = S[6], Se[5], Te[5]) has been assumed (i.e., the crystallographic site symmetry in each case is C_1—1) on the basis of the experimental conformity of all corresponding distances and bond angles to a C_{3v}—$3m$ geometry. As in the case of the cobalt–dinickel molecule, such a crystal disorder is undoubtedly an effect of the nearly identical covalent radii of the metal atoms involved.

With the exception of the metal–metal bond length change (vide infra), there is no significant difference between the corresponding molecular parameters (Table III) of $(\eta^5\text{-}C_5H_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ and $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$.

The M–CO and C–O bond lengths of 1.93 (1) and 1.18 (1) Å, respectively, in $(\eta^5\text{-}C_5H_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ are identical with those found in $Ni_3(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$. These values are in the expected range for a triply bridging carbonyl ligand.

Each of the three symmetry-equivalent C_5H_5 rings in the $CoNi_2$ molecule (and likewise in the Ni_3 molecule) is bisected by the crystallographically imposed mirror plane which passes through one carbon atom and relates the other two independent atoms to their corresponding mirror-image partners. However, each ring in the solid state possesses an orientational disorder imposed by a noncrystallographic twofold axis which is directed through the cyclopentadienyl-attached metal atom and the midpoint of the triangular side of the other two metal atoms. None of the M–C (ring) distances in either the $CoNi_2$ or Ni_3 molecule is significantly different from their mean values of 2.105 or 2.125 Å, respectively. The corresponding M–Cp(centroid) distance of 1.73 Å in the $CoNi_2$ molecule is also somewhat shorter than the Ni–Cp (centroid) distance of 1.76 Å in the Ni_3 molecule. Although the twofold crystal disorder of the half-weighted C_5H_5 rings prevents an unambiguous assessment of the nearest intermolecular distances, calculations based upon crystal-ordered cyclopentadienyl models indicate that in all cases the shortest H···H separations

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(27) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 61–62.

(28) (a) Calabrese, J. C. "PHASE", Ph.D. Thesis, University of Wisconsin—Madison, 1971, Appendix II. (b) Calabrese, J. C. "MIRAGE", Ph.D. Thesis, University of Wisconsin—Madison, 1971, Appendix III.

(29) Anomalous dispersion corrections (Mo Kα radiation) were applied to the scattering factors of Ni ($\Delta f'$ = 0.285, $\Delta f''$ = 1.113), Co ($\Delta f'$ = 0.299, $\Delta f''$ = 0.973), O ($\Delta f'$ = 0.008, $\Delta f''$ = 0.006), and C ($\Delta f'$ = 0.002, $\Delta f''$ = 0.002).[30]

(30) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 149.

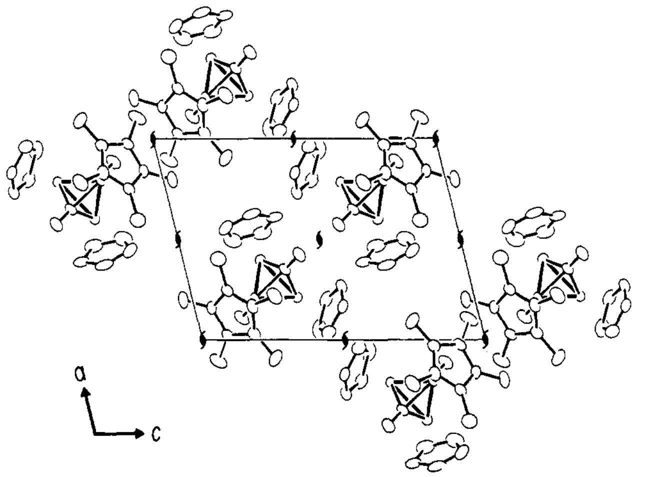

Figure 3. [010] projection of the unit cell of the crystal-ordered $(\eta^5\text{-}C_5Me_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ showing the arrangement of the two molecules per cell under monoclinic $P2_1$ symmetry. Hydrogen atoms have been omitted for clarity.

(2.4–2.5 Å) are close to the sum of van der Waals radii (2.4 Å).[31a] These H···H contacts undoubtedly have a large effect on the molecular packing, since all other nonbonding intermolecular distances in the molecular complexes are greater than normal van der Waals contacts.

The only prominent structural difference between the mean molecular parameters of $(\eta^5\text{-}C_5H_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ and $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ is that the metal–metal distance of 2.358 (2) Å in the $CoNi_2$ molecule is significantly shorter (by 15.5 times the individual estimated standard deviation of the M–M distance in either cluster) than that of 2.389 (2) Å in the Ni_3 molecule.[32] This 0.031-Å *decrease* in the mean metal–metal bond length formally corresponds to a loss of the unpaired electron from the paramagnetic Ni_3 molecule when one Ni atom is replaced by a Co atom to give the diamagnetic $CoNi_2$ molecule. This significant M–M bond length shortening (with no other influential molecular changes) upon formal oxidation of the Ni_3 molecule by metal substitution thereby provides direct experimental evidence that the unpaired electron in the Fischer–Palm $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ molecule must be accommodated in a MO which is strongly antibonding with respect to the trinickel AO's. The results of this operational test reinforce the theoretical models[4,19] which for the $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ molecule place the unpaired electron in the nondegenerate a_2 MO primarily composed of in-plane antibonding trinickel orbital character with no carbonyl orbital character allowed under threefold molecular symmetry.

Structural Features of $(\eta^5\text{-}C_5Me_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ and Resulting Bonding Implications. *triangulo*-(Pentamethylcyclopentadienyl)cobalt-bis(cyclopentadienylnickel) dicarbonyl exists as discrete molecules in the solid state with no unusual intermolecular contacts. A unit-cell projection parallel to the *b* axis (Figure 3) shows the orientations of the two molecules related by crystallographic $P2_1$ symmetry. The independent molecule (Figure 4) expectedly consists of a central isosceles $CoNi_2$ triangle with triply bridging carbonyl ligands above and below the trimetal plane and with the two nickel atoms η^5 coordinated to cyclopentadienyl rings and the cobalt atom η^5 coordinated to a pentamethylcyclopentadienyl ring. Although the molecule is not constrained by any crystallographic site symmetry, it does display an approximate C_{2v}—$2mm$ geometry within the central $CoNi_2(CO)_2$ core; hence, certain molecular parameters in Tables V and VI have been averaged accordingly.

The completely bonding metal triangle is defined by one Ni–Ni bond distance of 2.326 Å and two Co–Ni bond distances which average 2.371 Å. As shown in Figure 5, the bonding interaction of the two kinds of metal atoms with the carbonyl ligands is sufficiently different that a pronounced asymmetry between the Co–CO and Ni–CO bond lengths is seen. Both of the carbonyl carbon atoms are equally positioned closer to the cobalt atom to give a mean Co–CO bond length of 1.86 Å compared to a mean Ni–CO bond length of 2.01 Å. This considerable difference of 0.15 Å is deemed to be the result of a stronger $d_\pi(Co) \rightarrow \pi^*(CO)$ back-donation resulting from a closer matching of the higher cobalt d orbital energies with the π^* carbonyl orbital energies (i.e., the corresponding nickel d orbital energy levels are presumed to be stabilized below the cobalt ones by the extra proton in each nickel nucleus). The increased carbonyl interaction with the cobalt atom relative to that with each nickel atom also results in a tilting of each C–O bond from the normal of the trimetal plane toward the cobalt atom, as evidenced from the two noticeably larger Co–C–O bond angles of range 143 (1)–147 (1)° and mean 145° compared to the four Ni–C–O bond angles of range 129 (1) –132 (1)° and mean 130.5°. It is noteworthy that the crystallographic threefold disorder imposed on the corresponding unsubstituted cyclopentadienyl cobalt–dinickel molecule, $(\eta^5\text{-}C_5H_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$, completely masks these considerable bond length variations observed between the cobalt and nickel atoms in the $CoNi_2(CO)_2$ core of the (pentamethylcyclopentadienyl)cobalt–dinickel analog. At the same time, it is not difficult to reconcile from the structural differences why the unsubstituted cyclopentadienyl $CoNi_2$ molecule disorders in the solid state.

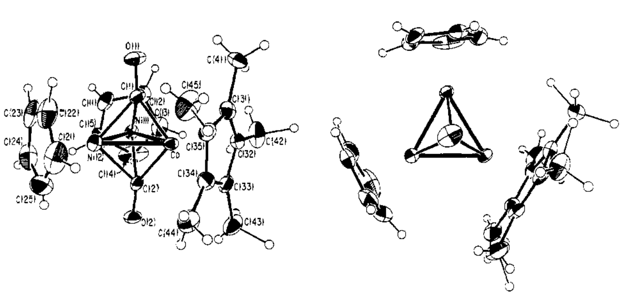

Figure 4. Two views of the configuration of the crystal-ordered $(\eta^5\text{-}C_5Me_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ molecule which is diamagnetic. The $CoNi_2(CO)_2$ core of this independent molecule of C_1 site symmetry conforms to an idealized C_{2v} geometry.

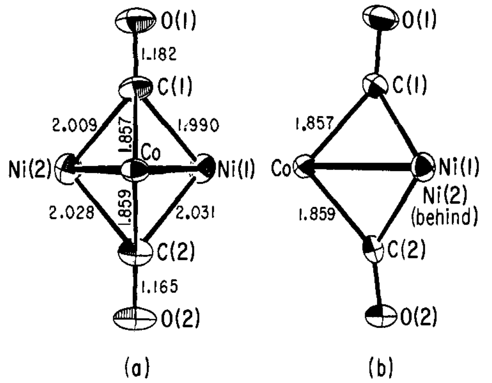

Figure 5. The $CoNi_2(CO)_2$ core in the $(\eta^5\text{-}C_5Me_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ molecule viewed: (a) along the bisector of the Ni(1)–Co–Ni(2) angle and (b) along the bond direction of the superimposed Ni(1) and Ni(2) atoms. The marked distortion of this core to C_{2v} symmetry is apparent from the mean of 1.86 Å for the two Co–CO bond lengths compared to the mean of 2.01 Å for the four Ni–CO bond lengths.

Even though the orientations of the two nickel-attached cyclopentadienyl rings also conform approximately to the pseudo C_{2v}—$2mm$ geometry of the $CoNi_2(CO)_2$ core, the errors associated with the ring carbon atoms are sufficiently large that the averages in Table V for these cyclopentadienyl rings are based on localized C_{5v} symmetry. The centroids of the two unsubstituted cyclopentadienyl rings from the nickel atoms lie within 0.01 Å of the 1.75-Å average, while the ten individual Ni–C(ring) distances range from 2.094 (15) to 2.132 (15) Å with a mean of 2.11 Å.

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(31) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960: (a) p 260; (b) p 256.

(32) The difference in the estimated single-bond covalent radii[31b] of cobalt (1.162 Å) and nickel (1.154 Å) is sufficiently small to be of little consequence.

Table IV. Atomic Parameters for $(\eta^5\text{-}C_5Me_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$[a]

A. Positional Parameters

atom	x	y	z	atom	x	y	z
Ni(1)	0.21299 (15)	0.3	0.37272 (10)	H(11)	0.327 (19)	0.226 (19)	0.586 (14)
Ni(2)	0.39680 (16)	0.28301 (22)	0.27445 (11)	H(12)	0.190 (16)	0.449 (22)	0.565 (12)
Co	0.20459 (16)	0.45599 (22)	0.22158 (11)	H(13)	−0.040 (19)	0.356 (18)	0.414 (13)
O(1)	0.4253 (11)	0.5365 (11)	0.4168 (7)	H(14)	0.043 (27)	0.151 (27)	0.404 (18)
O(2)	0.1125 (11)	0.1625 (9)	0.1587 (7)	H(15)	0.268 (17)	0.029 (17)	0.456 (12)
C(1)	0.3487 (12)	0.4590 (15)	0.3527 (8)	H(21)	0.531 (18)	0.328 (19)	0.117 (14)
C(2)	0.1752 (14)	0.2580 (12)	0.2097 (10)	H(22)	0.676 (18)	0.397 (17)	0.311 (14)
C(11)	0.2666 (18)	0.2352 (19)	0.5385 (11)	H(23)	0.636 (17)	0.216 (17)	0.451 (13)
C(12)	0.1681 (17)	0.3493 (17)	0.5266 (10)	H(24)	0.496 (16)	−0.012 (18)	0.353 (12)
C(13)	0.0395 (18)	0.3095 (23)	0.4541 (14)	H(25)	0.466 (22)	0.099 (21)	0.154 (16)
C(14)	0.0565 (36)	0.1651 (33)	0.4210 (19)	H(411)	0.311 (17)	0.793 (24)	0.333 (12)
C(15)	0.2030 (20)	0.1215 (16)	0.4739 (13)	H(412)	0.212 (18)	0.891 (18)	0.272 (13)
C(21)	0.5566 (22)	0.2687 (32)	0.1795 (17)	H(413)	0.107 (17)	0.761 (17)	0.344 (11)
C(22)	0.6252 (16)	0.3109 (25)	0.2823 (19)	H(421)	−0.055 (18)	0.649 (20)	0.318 (13)
C(23)	0.6110 (17)	0.2093 (23)	0.3611 (17)	H(422)	−0.149 (17)	0.746 (17)	0.209 (12)
C(24)	0.5317 (21)	0.0954 (19)	0.3036 (20)	H(423)	−0.124 (16)	0.495 (17)	0.283 (11)
C(25)	0.4978 (26)	0.1266 (35)	0.1939 (22)	H(431)	−0.154 (19)	0.419 (21)	0.091 (14)
C(31)	0.1681 (18)	0.6756 (13)	0.2062 (11)	H(432)	−0.168 (18)	0.497 (16)	−0.052 (13)
C(32)	0.0309 (14)	0.6072 (13)	0.1869 (10)	H(433)	−0.119 (20)	0.344 (18)	0.035 (15)
C(33)	0.0254 (14)	0.5147 (13)	0.0937 (10)	H(441)	0.148 (21)	0.371 (20)	−0.047 (14)
C(34)	0.1604 (15)	0.5247 (13)	0.0610 (9)	H(442)	0.159 (18)	0.476 (18)	−0.088 (14)
C(35)	0.2497 (14)	0.6274 (13)	0.1309 (9)	H(443)	0.282 (18)	0.497 (18)	−0.059 (14)
C(41)	0.2166 (21)	0.7900 (17)	0.2939 (12)	H(451)	0.398 (17)	0.711 (17)	0.022 (13)
C(42)	−0.0931 (22)	0.6284 (22)	0.2421 (15)	H(452)	0.414 (22)	0.736 (20)	0.101 (16)
C(43)	−0.1052 (21)	0.4219 (19)	0.0380 (17)	H(453)	0.475 (21)	0.662 (22)	0.166 (15)
C(44)	0.2006 (23)	0.4524 (24)	−0.0324 (11)				
C(45)	0.4051 (24)	0.6769 (24)	0.1257 (17)				

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

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni(1)	91 (2)	88 (2)	46 (1)	−3 (2)	15 (1)	15 (1)
Ni(2)	101 (2)	100 (2)	53 (1)	4 (2)	19 (1)	10 (1)
Co	101 (2)	69 (1)	34 (1)	−14 (2)	3 (1)	3 (1)
O(1)	169 (15)	146 (13)	61 (6)	−57 (13)	−10 (8)	−13 (8)
O(2)	164 (15)	94 (10)	75 (7)	−24 (10)	−24 (8)	−20 (7)
C(1)	104 (14)	89 (11)	51 (7)	−16 (14)	−11 (8)	7 (10)
C(2)	110 (17)	84 (14)	47 (7)	15 (11)	−13 (9)	12 (8)
C(11)	151 (22)	206 (25)	48 (8)	19 (20)	7 (11)	43 (12)
C(12)	158 (22)	160 (20)	53 (8)	4 (18)	43 (11)	19 (11)
C(13)	142 (21)	180 (26)	98 (13)	5 (23)	40 (13)	27 (17)
C(14)	293 (42)	290 (44)	93 (16)	−247 (36)	71 (23)	−1 (20)
C(15)	212 (28)	109 (17)	89 (12)	39 (20)	72 (16)	34 (13)
C(21)	185 (28)	326 (52)	101 (15)	67 (35)	82 (18)	62 (26)
C(22)	99 (19)	233 (32)	164 (21)	11 (24)	68 (16)	42 (25)
C(23)	88 (18)	250 (31)	123 (17)	56 (21)	40 (14)	53 (19)
C(24)	151 (26)	149 (24)	168 (23)	21 (21)	55 (20)	24 (20)
C(25)	184 (34)	322 (52)	148 (26)	40 (34)	11 (22)	−124 (31)
C(31)	178 (23)	70 (12)	56 (8)	3 (13)	15 (11)	23 (8)
C(32)	130 (18)	80 (13)	64 (8)	10 (13)	2 (10)	5 (9)
C(33)	106 (16)	99 (13)	59 (8)	6 (12)	−8 (9)	12 (9)
C(34)	144 (18)	99 (13)	43 (7)	8 (14)	21 (9)	8 (8)
C(35)	121 (17)	88 (13)	55 (8)	−18 (13)	1 (9)	26 (9)
C(41)	224 (27)	84 (14)	89 (11)	−9 (20)	−6 (14)	−23 (13)
C(42)	225 (31)	205 (27)	99 (13)	96 (26)	90 (18)	55 (17)
C(43)	169 (26)	137 (22)	114 (17)	−52 (20)	−41 (16)	30 (15)
C(44)	240 (32)	194 (23)	43 (8)	50 (29)	23 (13)	20 (15)
C(45)	184 (30)	198 (29)	108 (17)	−29 (25)	24 (17)	77 (18)

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

The centroid of the pentamethylcyclopentadienyl ring is 1.69 Å from the cobalt atom, while the five Co–C(ring) distances vary from 2.055 (11) to 2.098 (12) Å with a mean of 2.07 Å.

The ten C(ring)–C(ring) distances in the two cyclopentadienyl nickel rings range from 1.35 (3) to 1.45 (4) Å and average 1.39 Å. This large variation may readily be attributed to the relatively unhampered ring libration characteristic of most unsubstituted cyclopentadienyl rings at room temperature. The planarity of these rings is indicated by no carbon atoms in the two rings attached to Ni(1) and Ni(2) deviating by more than 0.011 and 0.010 Å, respectively, from the mean carbon planes.

The C(ring)–C(ring) distances in the relatively anchored pentamethylcyclopentadienyl ring attached to the cobalt atom vary from only 1.385 (19) to 1.420 (18) Å with a 1.41-Å average. The planarity of this ring is indicated by no ring carbon deviation being greater than 0.012 Å. All five methyl carbon atoms lie out of the mean ring plane to the side opposite the cobalt with a root-mean-square deviation of 0.052 Å. This kind of methyl deformation from the mean C(ring) plane is found almost without exception in other pentamethylcyclopentadienyl complexes.[22]

Table VI shows a comparison of mean geometrical parameters for this crystal-ordered pentamethylcyclopentadienyl $CoNi_2$ molecule and for the crystal-disordered cyclopentadienyl $CoNi_2$ and presumed crystal-ordered cyclopentadienyl Ni_3 molecule. An examination of these structural data reveals several important points. The close agreement of the corresponding mean distances

Table V. Interatomic Distances and Bond Angles for $(\eta^5\text{-}C_5Me_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$

A. Bonding Intramolecular Distances (Å)

Ni(1)–Ni(2)	2.3260 (23)	Ni(1)–C(1)	1.990 (12)
Ni(1)–Co	2.3740 (20)	Ni(2)–C(1)	2.009 (14)
Ni(2)–Co	2.3686 (24)	Ni(1)–C(2)	2.031 (12)
average	2.3713	Ni(2)–C(2)	2.028 (13)
C(1)–O(1)	1.182 (14)	average	2.014
C(2)–O(2)	1.165 (14)	Co–C(1)	1.857 (10)
average	1.173	Co–C(2)	1.859 (12)
Ni(1)–C(11)	2.110 (13)	average	1.858
Ni(1)–C(12)	2.118 (12)	Ni(1)–Cp(1)	1.742
Ni(1)–C(13)	2.094 (15)	Ni(2)–Cp(2)	1.752
Ni(1)–C(14)	2.105 (16)	average	1.747
Ni(1)–C(15)	2.103 (13)	Co–Cp(3)	1.690
average	2.106	Co–C(31)	2.068 (12)
Ni(2)–C(21)	2.107 (15)	Co–C(32)	2.098 (12)
Ni(2)–C(22)	2.103 (14)	Co–C(33)	2.087 (11)
Ni(2)–C(23)	2.132 (15)	Co–C(34)	2.062 (11)
Ni(2)–C(24)	2.122 (17)	Co–C(35)	2.055 (11)
Ni(2)–C(25)	2.108 (22)	average	2.074
average	2.114	C(31)–C(32)	1.385 (19)
C(11)–C(12)	1.381 (22)	C(32)–C(33)	1.443 (18)
C(12)–C(13)	1.365 (22)	C(33)–C(34)	1.404 (18)
C(13)–C(14)	1.423 (39)	C(34)–C(35)	1.420 (18)
C(14)–C(15)	1.417 (39)	C(35)–C(31)	1.413 (19)
C(15)–C(11)	1.375 (24)	average	1.413
average	1.392	C(31)–C(41)	1.520 (19)
C(21)–C(22)	1.354 (28)	C(32)–C(42)	1.484 (20)
C(22)–C(23)	1.396 (25)	C(33)–C(43)	1.512 (20)
C(23)–C(24)	1.388 (27)	C(34)–C(44)	1.473 (20)
C(24)–C(25)	1.370 (33)	C(35)–C(45)	1.522 (23)
C(25)–C(21)	1.453 (40)	average	1.502
average	1.392		

B. Bond Angles (Deg)

Ni(2)–Ni(1)–Co	60.5 (1)	Co–Ni(1)–C(1)	49.4 (3)
Ni(1)–Ni(2)–Co	60.7 (1)	Co–Ni(1)–C(2)	49.2 (3)
average	60.6	Co–Ni(2)–C(1)	49.4 (3)
Ni(1)–Co–Ni(2)	58.7 (1)	Co–Ni(2)–C(2)	49.3 (3)
Ni(1)–Co–C(1)	54.5 (4)	average	49.3
Ni(2)–Co–C(1)	55.2 (4)	Ni(2)–Ni(1)–C(1)	54.8 (4)
Ni(1)–Co–C(2)	55.8 (4)	Ni(2)–Ni(1)–C(2)	55.0 (4)
Ni(2)–Co–C(2)	55.8 (4)	Ni(1)–Ni(2)–C(1)	54.0 (3)
average	55.3	Ni(1)–Ni(2)–C(2)	55.1 (4)
C(1)–Ni(1)–C(2)	88.8 (5)	average	54.7
C(1)–Ni(2)–C(2)	88.3 (5)	Co–Ni(1)–Cp(1)	153.0
average	88.6	Co–Ni(2)–Cp(2)	152.3
C(1)–Co–C(2)	98.4 (6)	average	152.6
Ni(1)–C(1)–Ni(2)	71.1 (5)	Ni(2)–Ni(1)–Cp(1)	146.5
Ni(1)–C(2)–Ni(2)	69.9 (4)	Ni(1)–Ni(2)–Cp(2)	146.7
average	70.5	average	146.6
Ni(1)–C(1)–Co	76.1 (4)	Ni(1)–Co–Cp(3)	152.6
Ni(2)–C(1)–Co	75.5 (4)	Ni(2)–Co–Cp(3)	148.7
Ni(1)–C(2)–Co	75.1 (4)	average	150.6
Ni(2)–C(2)–Co	75.0 (4)	Ni(1)–C(1)–O(1)	131.2 (9)
average	75.4	Ni(2)–C(1)–O(1)	131.5 (10)
Co–C(1)–O(1)	143.2 (11)	Ni(1)–C(2)–O(2)	130.2 (10)
Co–C(2)–O(2)	147.2 (9)	Ni(2)–C(2)–O(2)	129.2 (10)
average	145.2	average	130.5
C(15)–C(11)–C(12)	110.2 (14)	C(25)–C(21)–C(22)	104.4 (20)
C(11)–C(12)–C(13)	108.2 (16)	C(21)–C(22)–C(23)	112.3 (22)
C(12)–C(13)–C(14)	108.1 (19)	C(22)–C(23)–C(24)	105.7 (18)
C(13)–C(14)–C(15)	106.9 (15)	C(23)–C(24)–C(25)	109.3 (20)
C(14)–C(15)–C(11)	106.6 (16)	C(24)–C(25)–C(21)	108.3 (18)
average	108.0	average	108.0
C(35)–C(31)–C(32)	110.3 (12)	C(35)–C(31)–C(41)	126.5 (14)
C(31)–C(32)–C(33)	105.7 (12)	C(32)–C(31)–C(41)	123.2 (14)
C(32)–C(33)–C(34)	109.5 (11)	C(31)–C(32)–C(42)	129.1 (14)
C(33)–C(34)–C(35)	106.8 (10)	C(33)–C(32)–C(42)	125.0 (14)
C(34)–C(35)–C(31)	107.7 (11)	C(32)–C(33)–C(43)	125.9 (15)
average	108.0	C(34)–C(33)–C(43)	124.6 (14)
		C(33)–C(34)–C(44)	127.6 (14)
		C(35)–C(34)–C(44)	125.4 (14)
		C(34)–C(35)–C(45)	126.2 (14)
		C(31)–C(35)–C(45)	126.1 (14)
		average	126.0

[a] Values involving the central $CoNi_2(CO)_2$ core are averaged according to pseudo $C_{2v}-2mm$ symmetry; values involving the cyclopentadienyl rings are averaged according to local pseudo $C_{5v}-5m$ symmetry. [b] Cp(n) refers to the centroid of the nth cyclopentadienyl ring.

Table VI. Comparison of Mean Geometrical Distances for $M_3(\eta^5\text{-}C_5R_5)_3(\mu_3\text{-}CO)_2$-Type Molecules

	$(\eta^5\text{-}C_{5\text{-}n}Me_n)CoNi_2\text{-}(\eta^5\text{-}C_5H_5)(\mu_3\text{-}CO)_2$		$Ni_3\text{-}(\eta^5\text{-}C_5H_5)_3\text{-}(\mu_3\text{-}CO)_2$	
	$n = 5^a$	$n = 0^a$	a	b
crystallographic site symmetry	C_1-1	$C_{3h}-3/m$ (disordered)	$C_{3h}-3/m$	
virtual symmetry of $M_3(CO)_2$ core	$C_{2v}-2mm$	$D_{3h}-\bar{6}2m$ (disordered)	$D_{3h}-\bar{6}2m$	
Co–Ni	[2][c] 2.371			
Ni–Ni	[1] 2.326			
M–M	[3] 2.356	2.358	2.389	2.39
M–CO	[6] 1.962	1.933	1.932	1.93
C–O	[2] 1.173	1.183	1.183	1.19
M–C(ring)	[15] 2.098	2.105	2.125	2.12
M–Cp(centroid)	[3] 1.728	1.733	1.757	

[a] This work based upon diffractometry data. [b] The original Hock–Mills structure[2] based upon film data. [c] Brackets enclose the number of equivalent distances having the values listed in the right columns.

between the pentamethylcyclopentadienyl $CoNi_2$ molecule and the cyclopentadienyl $CoNi_2$ molecule indicates an apparently insignificant geometrical perturbation of the molecular framework when the five hydrogen atoms of the C_5H_5 ring coordinated to the cobalt atom are replaced with methyl substituents. The fact that the crystallographic C_{3h}—$3/m$ site symmetry imposed on the crystal-disordered $(\eta^5\text{-}C_5H_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ molecule can effectively conceal the observed average molecule variations in the $Co_2Ni(CO)_2$ core of 0.045 Å between the one Ni–Ni and two Co–Ni distances and of 0.15 Å between the two Co–CO and four Ni–CO distances is not surprising. Fortunately, this structural comparison also points to the validity of the mean geometrical parameters in a crystal-disordered structure. The virtually identical value of 2.356 Å for the mean length of the three metal–metal bonds in the crystal-ordered pentamethylcyclopentadienyl $CoNi_2$ molecule with that of 2.358 (2) Å for the three metal–metal bonds in the cyclopentadienyl $CoNi_2$ analogue furnishes further experimental evidence in support of our rational explanation that the significantly longer length of 2.389 (2) Å for the three nickel–nickel bonds in the corresponding Fischer–Palm $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ molecule must be primarily due to its unpaired electron occupying a MO with highly antibonding trimetal orbital character.

Comparative Analysis of the Spectral and Electrochemical Data for the $(\eta^5\text{-}C_5H_{5-n}Me_n)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ Series (n = 0, 1, 5). (a) General Remarks. This series of three $CoNi_2$ compounds derived from the unsubstituted and monomethyl- and pentamethyl-substituted cyclopentadienyl ring on the cobalt atom allows the use of various physicochemical methods to determine the degree of this perturbation. In general, it is expected that the substitution of methyl substituents in place of hydrogen ones would make the C_5R_5 ring more electron releasing to the coordinated metal atom and thereby through greater net electron transfer to other parts of the molecule would affect its physical characteristics. The following results substantiate and quantify this presumed trend.

(b) Infrared Data. The prominent absorptions in both the solution (CH_2Cl_2) and solid-state (KBr) IR spectra are due to the triply bridging carbonyls. The occurrence in each case of only one rather broad band allows its assignment as the asymmetric stretching mode for the two approximately linear carbonyls. The solid-state ν_{CO} frequency of 1737 cm^{-1} for the cobalt-attached unsubstituted cyclopentadienyl ring ($n = 0$) is virtually identical with that of 1736 cm^{-1} for the cobalt-attached methylcyclopentadienyl ring ($n = 1$), whereas the corresponding frequency of 1720 cm^{-1} for the cobalt-attached pentamethylcyclopentadienyl ring ($n = 5$) is distinctly lower. These values presumably reflect an indistinguishable difference in the net charge transfer to the C–O bonds from the $(\eta^5\text{-}C_5H_4Me)CoNi_2(\eta^5\text{-}C_5H_5)_2$ fragment vs. the $(\eta^5\text{-}C_5H_5)CoNi_2(\eta^5\text{-}C_5H_5)_2$ fragment in contrast to a small detectable difference in the corresponding net charge transfer to the C–O bonds from the $(\eta^5\text{-}C_5Me_5)CoNi_2(\eta^5\text{-}C_5H_5)_2$ fragment vs. the $(\eta^5\text{-}C_5H_5)CoNi_2(\eta^5\text{-}C_2H_5)_2$ one.

However, the cobalt-dinickel compounds can readily be differentiated from one another by their solid-state (KBr) infrared spectra in the 1500–1200-cm^{-1} region, in which characteristic patterns due to increasing methyl substitution on the predominantly C–C cyclopentadienyl ring stretching frequencies arise which are similar to those observed in the 2000–1750-cm^{-1} region for substituted benzenes.[33] An absorption band at 1261 cm^{-1} is found for only the cobalt-attached methylcyclopentadienyl $CoNi_2$ molecule, while an absorption band at ca. 1380 cm^{-1} is observed for both the methylcyclopentadienyl $CoNi_2$ ($n = 1$) and pentamethylcyclopentadienyl $CoNi_2$ ($n = 5$) molecules. For the latter molecule, the intensity of the 1380-cm^{-1} band is unusually strong compared to the intensities of all the other bands in this region. These bands at 1261 and 1380 cm^{-1} are both absent for the unsubstituted cyclopentadienyl $CoNi_2$ molecule ($n = 0$).

(c) Proton and Proton-Decoupled Carbon-13 NMR Data. Proton NMR spectra indicate an apparent increase in the diamagnetic shielding of the protons throughout the molecule upon methyl substitution. The resonances (Varian A-60-A spectrometer) for the $n = 0$ compound in $CHCl_3$ solution vs. *external* Me_4Si fall at δ 5.23 for the ten equivalent nickel cyclopentadienyl ring protons and at δ 5.00 for the five equivalent cobalt cyclopentadienyl ring protons. Upon methyl substitution, the unsubstituted nickel cyclopentadienyl protons shield increasingly to give δ 5.22 for the $n = 1$ molecule and δ 5.07 for the $n = 5$ molecule. The AA′BB′ pattern expected for the methylcyclopentadienyl molecule ($n = 1$) is observed as a "doublet" at δ 4.86 and 4.81 with the methyl proton resonance at δ 1.88. For the pentamethylcyclopentadienyl molecule ($n = 5$) proton resonance occurs at δ 1.67. The values cited for the two methyl-substituted cyclopentadienyl molecules ($n = 1$ and 5) are for $CDCl_3$ solutions vs. internal Me_4Si.

Proton-decoupled carbon-13 resonances were obtained for the series with the use of 0.1 M $Cr(acac)_3$ as a paramagnetic relaxation reagent[34] in $CDCl_3$ solution vs. internal Me_4Si (except for the $n = 5$ molecule for which acetone-d_6 was used as solvent). The nickel cyclopentadienyl carbon atoms resonate at δ 94.6 for $n = 0$, at δ 93.2 for $n = 1$, and at δ 93.1 for $n = 5$. The cobalt ring carbons resonate at δ 87.8 for $n = 0$, at δ 101.8, 86.9, and 85.9 for $n = 1$, and at δ 96.6 for $n = 5$. The methyl carbon peaks occur at δ 13.1 for $n = 1$ and at 9.8 for $n = 5$.

The foregoing ^1H and $^{13}C\text{-}\{^1H\}$ NMR results closely parallel the trends noted by Materikova et al.[35] for the *sym*-polymethylferrocenes. Based upon their findings and the observed relative intensities, we can assign the three ring carbon resonances for the cobalt-attached methylcyclopentadienyl molecule ($n = 1$) to the C(1), C(2,5), and C(3,4) carbon atoms, respectively. Failure to observe the triply bridging carbonyl carbon resonance, even though the relaxation reagent was present and the observation window in the Fourier transform data collection extended beyond δ 310, is attributed to a broadening of the peak by scalar relaxation of the second kind[36] due to the quadrupole moment of the ^{59}Co nucleus ($I = {}^7/_2$).

(d) Electrochemical Data. The cyclic voltammetric results in this series are quite striking. Each of the three cobalt–dinickel molecules (denoted by $[CoNi_2]$) exhibited a reversible one-electron $[CoNi_2]^0/[CoNi_2]^-$ couple, thereby indicating the existence of its monoanion,[37] of which the one with $n = 0$ is isoelectronic with the paramagnetic Fischer–Palm $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ molecule. Each voltammogram was recorded in 1,2-dimethoxyethane at a stationary platinum-bead working electrode with a PAR Electrochemical System. Tetrabutylammonium perchlorate (0.1 M) was utilized as the supporting electrolyte, while the sample concentrations were ca. 1.0 mM. Solutions of each molecular compound were prepared under nitrogen; the electrochemical cell was also purged with nitrogen before and after each run. The $E_{1/2}$ values, which are uncorrected for junction potentials (although iR compensation for internal resistant potential drop was employed), are −1.525 V for $n = 0$, −1.558 V for $n = 1$, and −1.693 V for $n = 5$ (relative to a Ag/Ag^+ reference electrode). For a 100-mV/s scan rate the corresponding peak-to-peak separations, $|E_{p,c} - E_{p,a}|$, were 70, 85, and 85 mV, respectively. Evidence for the chemical reversibility of the above one-electron process for each of three $CoNi_2$ compounds is given by the ratio between the cathodic and anodic peak currents, $i_{p,c}/i_{p,a}$, being unity as well as by the peak-to-peak separations being reasonably close to the theoretical value of 59 mV.

These electrochemical data are consistent with the pentamethylcyclopentadienyl $CoNi_2$ molecule ($n = 5$) having the highest negative $E_{1/2}$ value and hence being the most difficult one in the $(\eta^5\text{-}C_5H_{5-n}Me_n)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ series ($n = 0, 1, 5$) to reduce or conversely its monoanion being the easiest one to oxidize to the neutral parent. Of particular note is the observation that one-fifth of the 168-mV separation (viz., 34 mV) between the determined $E_{1/2}$ values for $n = 0$ and $n = 5$ is equivalent to the 33-mV separation between the $E_{1/2}$ values for $n = 0$ and $n = 1$. This indication of a relatively linear correlation between the $E_{1/2}$ value and the number of methyl substituents n on the cobalt-coordinated $C_5H_{5-n}Me_n$ ring is not surprising in light of an early investigation by Furlani[38] on the quasi-reversible polarographic behavior of the methyl-substituted (arene)chromium compounds, $Cr(C_6H_{6-n}Me_n)_2$ (denoted as [Cr] with $n = 0$–3, 6); Furlani[38] found that the introduction of methyl groups into the benzene rings results in a negative shift of the $[Cr]^0/[Cr]^+$ couple with the $E_{1/2}$ values being linearly related to the number of methyl groups per ring (for $n = 0$–3). He attributed this correlation to an additive effect of the strong electron-releasing methyl substituents, which lead to increased electron density at the chromium atom and therefore to a higher energy of the redox orbital.[39–41]

In the case of the $(\eta^5\text{-}C_5H_{5-n}Me_n)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ series, the fact that a sequential substitution of n methyl groups for hydrogen atoms gives rise to an indicated change in the $E_{1/2}$ value of ca. −33 mV per methyl group for a one-electron reduction process may likewise be rationalized from similar electronic considerations which primarily involve an additivity of ligand effects. These arguments are consistent with the notion that for

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[37] These electrochemical measurements have led to the isolation and crystallization of the $[(\eta^5\text{-}C_5Me_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2]^-$ monoanion whose structure is presently being investigated by an X-ray diffraction analysis (Maj, J. J.; Dahl, L. F., unpublished research).

[38] Furlani, C. *Ric. Sci.* **1966**, *36*, 989–992.

[39] Extensive electrochemical studies correlating the oxidation potentials with Hammett substituent constants for various substituent groups in the ligands have been carried out on other arenechromium(0) complexes containing electronegative substituents[40] as well as on a number of substituted ferrocenes.[41]

[40] Treichel, P. M.; Essenmacher, G. P.; Efner, H. F.; Klabunde, K. J., *Inorg. Chim. Acta*, in press.

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this series of closely related metal clusters, an *n* methyl substitution in place of a hydrogen atom on a cyclopentadienyl ring gives rise to a relatively constant charge donation to the trimetal core thereby electrostatically destabilizing the LUMO (which is mainly of antibonding trimetal orbital character). The greater instability of the LUMO (to which the electron is added upon formation of the monoanion) is then deemed to be responsible for the increased difficulty of reduction upon methyl substitution of the cyclopentadienyl ligands in this series. This observation may allow one to tailor the electrochemical properties of similar compounds by suitable choice of substituents on the cyclopentadienyl ligands.

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Supplementary Material Available: Three tables listing the observed and calculated structure factor amplitudes for $(\eta^5\text{-}C_5H_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$, $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$, and $(\eta^5\text{-}C_5Me_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$, (16 pages). Ordering information is given on any current masthead page.

Bis[bis(*F*-methyl)sulfimide], *N*-Chlorobis(*F*-methyl)sulfimide, and *N*-Fluorobis(*F*-methyl)sulfimide

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Abstract: The first member of a new class of stable sulfimides, bis[bis(*F*-methyl)sulfimide], $(CF_3)_2S{=}NN{=}S(CF_3)_2$, results from the photolysis of $(CF_3)_2S{=}NCl$. The latter is prepared by reacting $(CF_3)_2S{=}NH$ with ClF in the presence of CsF. Under similar conditions, $(CF_3)_2S{=}NH$ reacts with SF_4 to give $(CF_3)_2S{=}NF$.

The simplest *N*-halo sulfur difluoride imides, $XN{=}SF_2$ (X = F, Cl, Br, I), have been synthesized via the mercurial $Hg(NSF_2)_2$ in reaction with the respective halogen under mild conditions[1] or from the appropriate *N*-halogen hexamethyl disilazanes and SF_4.[1] The chloro compound is also formed when NSF is treated with chlorine in the presence of CsF.[2] However, the formal parent sulfimide, $HN{=}SF_2$ has not been prepared. Earlier we reported the synthesis of bis(*F*-methyl)sulfimide, $(CF_3)_2S{=}NH$[3,4] and some nucleophilic reactions of its lithium derivative.[3,5] It now has been possible to synthesize the fluoro and chloro analogues of $(CF_3)_2S{=}NH$ as well as the bis[bis(*F*-methyl)sulfimide] $(CF_3)_2S{=}NN{=}S(CF_3)_2$.

Results and Discussion

When a primary amine is added to a mixture of NH_3 and $(CF_3)_2SF_2$, bis(*F*-methyl)sulfimide, $(CF_3)_2S{=}NH$, is formed in 50%–60% yield (eq 1).[3,4] It is stable in Pyrex glass under ambient

$$(CF_3)_2SF_2 + NH_3 \xrightarrow{PhCH_2NH_2} (CF_3)_2S{=}NH \qquad (1)$$

conditions for extended periods. Although the lithiated salt $LiN{=}S(CF_3)_2$ behaves as a useful transfer reagent for the $(CF_3)_2S{=}N\text{-}$ moiety, prior to this report the parent imine has not been used successfully as a precursor to new $(CF_3)_2S{=}N$ containing compounds.

At first glance, it is somewhat surprising that when an equimolar mixture of ClF and $(CF_3)_2S{=}NH$ in the presence of CsF is allowed to warm from −78 to 25 °C over a 12-h period, the product is the slightly yellow *N*-chloro imide, viz.

$$(CF_3)_2S{=}NH + ClF \xrightarrow[CsF]{-78\text{ to }25\ ^\circ C} \underset{70\%}{(CF_3)_2S{=}NCl} \qquad (2)$$

rather than a saturated derivative or molecules of decomposition. The carbon analogue $(CF_3)_2C{=}NCl$ is synthesized similarly although saturation of the $>C{=}N$ bond occurs if the reaction temperature is allowed to approach 25 °C.[6] In a qualitative comparative study of the relative ease of saturating the double bond in $CF_3SF_3{=}NCF_3$ and $CF_3SF_4N{=}CFCF_3$, it was found that ClF did not saturate at a temperature lower than 50 and 70 °C, respectively.[7] In the presence of CsF, saturation occurred at or below 25 °C. Thus, as would be expected, the polarity of the $S^{IV}{-}N$ bond in $(CF_3)_2S{=}NCl$ is much reduced over that of the $S^{VI}{-}N$ bond in $CF_3SF_3{=}NCF_3$, and addition does not occur. The new chloro imide is stable for a few hours in Pyrex glass at 25 °C and decomposes to the volatile $(CF_3)_2S$ and other unidentified material. In the mass spectrum, an intense molecular ion is observed where the appropriate $^{35}Cl{-}^{37}Cl$ isotope ratio is present. Preliminary electron diffraction studies indicate that the bond angles and bond distances in $(CF_3)_2S{=}NCl$ differ markedly from those of $F_2S{=}NCl$. These data will be published upon completion of the study.

As is typical of compounds which contain positive halogen atoms, i.e., O–Cl or >NCl, photolysis, even through Pyrex glass, results in the generation of chlorine and a second compound which contains an O—O or >N—N< bond. Such is the case for $(CF_3)_2S{=}NCl$ (eq 3). The novel bis[bis(*F*-methyl)sulfimide],

$$(CF_3)_2S{=}NCl \xrightarrow[Pyrex]{UV} \underset{50\%}{(CF_3)_2S{=}N{-}N{=}S(CF_3)_2} + Cl_2 \qquad (3)$$

which is a colorless liquid, is stable in Pyrex glass for indefinite periods. Although a molecule ion is not observed in the mass spectrum, determination of molecular weight with use of PVT

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