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Preparation and Molecular Structure of a Heterobimetallic Acetylene Complex, $(\mu\text{-}C_6H_5C{\equiv}CC_6H_5)[(CO)_3Co{-}Ni(\eta^5\text{-}C_5H_5)]$

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The heterobimetallic acetylene complex μ-(diphenylacetylene)-(tricarbonylcobaltio)(η^5-cyclopentadienyl)nickel, $(\mu\text{-}C_6H_5C{\equiv}CC_6H_5)[(CO)_3Co{-}Ni(\eta^5\text{-}C_5H_5)]$, has been separated from the reactions of $(\mu\text{-}C_6H_5C{\equiv}CC_6H_5)[Ni_2(\eta^5\text{-}C_5H_5)_2]$ with $Co_2(CO)_8$, $(\mu\text{-}C_6H_5C{\equiv}CC_6H_5)[Co_2(CO)_6]$ with nickelocene, $(\mu\text{-}C_6H_5C{\equiv}CC_6H_5)[Co_2(CO)_6]$ with $(\mu\text{-}C_6H_5C{\equiv}CC_6H_5)[Ni_2(\eta^5\text{-}C_5H_5)_2]$ and $(\eta^5\text{-}C_5H_5)_2Ni_2(CO)_2$, and diphenylacetylene with $(\eta^5\text{-}C_5H_5)NiCo_3(CO)_9$. $(\mu\text{-}C_6H_5C{\equiv}CCH_3)[(CO)_3Co{-}Ni(\eta^5\text{-}C_5H_5)]$ has been prepared in similar fashion. The compounds have been characterized by mass spectrometry, infrared spectroscopy, and NMR studies. A single-crystal X-ray structure determination of the diphenylacetylene compound shows the acetylene bonded perpendicularly to the metal–metal bond. Crystals are orthorhombic, of space group *Pbca*, with unit cell dimensions $a = 15.799$ (4), $b = 21.460$ (5), and $c = 11.608$ (3) Å, with $Z = 8$. Refinement on F, using 3062 unique diffractometer data, converged to a final agreement factor $R = 0.040$. The Ni–Co bond distance is 2.3656 (8) Å, and the acetylene is distorted significantly from linearity (mean deviation 40.1 (1)°).

Introduction

There is a growing interest in the preparation of heterometallic cluster compounds. One possible approach to such species is to employ the interchangeability of cluster skeletal components, based upon the recognition of structural similarities between a series of related species. For example, common characteristics have been noted between the methinyltricobalt enneacarbonyl clusters $Co_3(CO)_9CR$ (R = alkyl, aryl, halogen) and the dicobalt acetylene compounds $Co_2(CO)_6(RC{\equiv}CR)$ (R = alkyl, aryl).[1] Other compounds such as the $[FeCo_3(CO)_{12}]^-$ anion,[2] $CpNiCo_3(CO)_9$,[3] $CpMCo_3(CO)_{11}$ (M = Mo, W),[4] and $Co_3(CO)_9PR$ (Cp = $\eta^5\text{-}C_5H_5$, R = phenyl, *tert*-butyl, $N(C_2H_5)_2$)[5,6] may be considered as derivatives of $Co_4(CO)_{12}$ in which a $Co(CO)_3$ unit has been replaced by $[Fe(CO)_3]^-$, CpNi, $CpM(CO)_2$, and PR, respectively. In a similar fashion the corresponding trinickel methinyl cluster Cp_3Ni_3CR (R = phenyl)[7] and the dinickel acetylene compound $(\eta^5\text{-}C_5H_5)_2Ni_2(DPA)$ (DPA = diphenylacetylene)[8-10] are known, although the tetranickel cluster required to complete the series has not been reported.[11]

Thus one is tempted to extend the array of compounds by combining such "equivalent" fragments as $Co(CO)_3$, CpNi, CR, etc. in a tetrahedral (or pseudotetrahedral) framework. As part of an investigation concerning the interchangeability of cluster skeletal components, we have examined a number of reactions which have led to the isolation of the previously unreported heterobimetallic acetylene complexes $CpNiCo(CO)_3(DPA)$ and $CpNiCo(CO)_3(PMA)$ (PMA = 1-phenylpropyne). We describe these studies herein and report the results of a three-dimensional X-ray structure analysis of the diphenylacetylene species.

Experimental Section

All manipulations were carried out under dry nitrogen gas. Solvents were reagent grade and were degassed before use. IR spectra in the carbonyl stretching region were recorded on a Beckman Acculab 4 spectrometer and were calibrated against polystyrene. NMR spectra in $CDCl_3$ were run on a Varian T60 spectrometer using Me_4Si as an internal reference. Mass spectra were obtained on a Varian Mat 311A mass spectrometer with an ionizing energy of 25 or 70 eV and an ionizing current of 1 mA. Diphenylacetylene was obtained from Aldrich Chemicals, Milwaukee, Wis. Octacarbonyldicobalt and nickelocene were obtained from Strem Chemicals Inc., Newburyport, Mass., and were used without further purification. Florisil was purchased from Fisher Scientific Co., Fair Lawn, N.J. $Cp_2Ni_2(CO)_2$,[9] $Cp_2Ni_2(DPA)$,[8,9] $Co_2(CO)_6(DPA)$,[12] and $CpNiCo_3(CO)_9$[3] were prepared by standard literature methods.

Reaction of $Cp_2Ni_2(DPA)$ with $Co_2(CO)_8$. Octacarbonyldicobalt (1.50 g, 4.39 mmol) was added to $Cp_2Ni_2(DPA)$ (1.80 g, 4.24 mmol) in 50 mL of hexanes and the mixture refluxed for $1^1/_2$ h. The solvent was removed in vacuo along with a small quantity of $CpCo(CO)_2$ (identified by IR). The dark residue was extracted with fresh hexane and chromatographed on Florisil. A small quantity of $CpCo(CO)_2$ (red-brown band) followed by $Co_4(CO)_{12}$ (brown band) was removed first by eluting with hexanes. Further elution gave a deep green solution. Removal of the solvent in vacuo followed by recrystallization from a small volume of hexanes afforded dark brown crystals of $CpNiCo(CO)_3(\mu\text{-}DPA)$ (~24% yield). The proton NMR spectrum ($CDCl_3$) exhibited a singlet at δ 5.25 (cyclopentadienyl protons) and a broad multiplet centered about δ 7.46 (phenyl protons).

Anal. Calcd for $C_{22}H_{15}CoNiO_3$: C, 59.38; H, 3.40; O, 10.79. Found: C, 59.98; H, 3.31; O, 10.96.

The reactions of $Cp_2Ni_2(CO)_2$ with $Co_2(CO)_6(DPA)$, $Cp_2Ni_2(DPA)$ with $Co_2(CO)_6(DPA)$, Cp_2Ni with $Co_2(CO)_6(DPA)$, and $CpNiCo_3(CO)_9$ with DPA were carried out in similar fashion. Mass spectral data are given in Table I (IR: ν(CO) 2060 (s), 2020 (w), 2010 (s) cm^{-1}).

Reaction of Cp_2Ni with $Co_2(CO)_6(PMA)$. Cp_2Ni (0.45 g, 2.39 mmol) was added to excess $Co_2(CO)_6(PMA)$ (prepared from $Co_2(CO)_8$ (5.0 g, 14.6 mmol) and PMA (2.2 g, 19.0 mmol)) in 35 mL of hexanes and the mixture refluxed for 20 h. Chromatography on Florisil yielded a deep green solution (hexanes). Removal of the solvent in vacuo afforded $CpNiCo(CO)_3(\mu\text{-}PMA)$ as a dark green oil in low yield (~12%). The proton NMR spectrum ($CDCl_3$) exhibited singlets at δ 2.73 (methyl protons) and 5.18 (cyclopentadienyl protons) and a broad multiplet centered about δ 7.50 (phenyl protons). Mass spectral data are given in Table I[13] (IR: ν(CO) 2080 (s), 2032 (w), 2004 (s) cm^{-1}).

Collection and Reduction of X-ray Data. Opaque brownish red crystals of μ-(diphenylacetylene)-(tricarbonylcobaltio)(η^5-cyclopentadienyl)nickel, $(\mu\text{-}C_6H_5C{\equiv}CC_6H_5)[(CO)_3Co{-}Ni(\eta^5\text{-}C_5H_5)]$, were recrystallized from hexane and mounted in glass capillaries. Orthorhombic symmetry was indicated by a photographic study using Weissenberg and precession cameras, and preliminary cell constants were obtained. Systematic absences k odd for $0kl$, l odd for $h0l$, and h odd for $hk0$ uniquely define the space group as *Pbca*, No. 61.[14] The

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Table II. Crystal Data and Experimental Conditions

$C_{22}H_{15}CoNiO_3$	fw 444.00
$a = 15.799(4)$ Å	space group *Pbca*, $Z = 8$
$b = 21.460(5)$ Å	d(obsd) = 1.4–1.5 g cm^{-3}
$c = 11.608(3)$ Å	d(calcd) = 1.50 g cm^{-3}

radiation	Mo Kα, monochromatized from graphite (λ(Kα_1) 0.709 26 Å)
receiving aperture	5.0 × 5.0 mm^2, 32 cm from crystal
scan	θ–2θ, 1° min^{-1} for $2\theta < 35°$, 2° min^{-1} for $2\theta > 35°$
scan range	1.2°, corrected for dispersion
background	stationary crystal, stationary counter at scan limits, 10 s for $2\theta < 35°$, 20 s for $2\theta > 35°$
index limits	$0 < h < 22$, $-1 < k < 28$, $0 < l < 15$

crystals are extremely soluble in and react with most liquids commonly used for density determination by the flotation method, though a value was finally obtained by using aqueous $ZnCl_2$, which suggested eight molecules per cell and no crystallographically imposed symmetry.

Intensity data were recorded from a crystal of approximate dimensions 0.26 × 0.20 × 0.16 mm, $V = 0.0075$ mm^3. Eight faces of the forms {100}, {010}, and {021} were identified, and the crystal was measured by using a filar micrometer eyepiece. The crystal was then transferred to a Picker FACS-1 diffractometer controlled by the Vanderbilt disk operating system.[15] Mo Kα radiation monochromatized from the 002 face of mosaic graphite was used to center 30 intense reflections at 24 °C. Cell constants and an orientation matrix were obtained from a least-squares refinement employing the angular settings.[16] ω scans of several intense, low-angle reflections had an average width at half-height of 0.08°, an acceptable value.[17] A total of 3991 observations were recorded over a period of 7 days by using the θ–2θ scan technique. Six standard reflections were monitored, $02\bar{1}$, 040, 021, 002, 200, and $0\bar{4}0$, but they showed only random fluctuations. There was little intensity beyond a 2θ value of 50°; however, the shell to 60° was surveyed[15] and yielded 309 observations. There was no change in ω scans after data collection was finished. Crystal data and the experimental conditions are summarized in Table II.

The raw data were corrected for background, the monochromator polarization, and Lorentz–polarization effects, and standard deviations were assigned as described earlier.[18] Ninety-eight equivalent reflections with k of -1 had also been collected as a test of crystal and electronic stability; the R factor for averaging was 0.015. An absorption correction was then applied to all data greater than zero by using the analytical method of de Meulenaer and Tompa;[19] transmission factors varied from 0.74 to 0.79. After this correction the R factor for averaging equivalent reflections was 0.013. In all, 3809 unique data were available, of which 2917 had $F^2 > 3\sigma(F^2)$ and were used in solution and preliminary refinement of the structure.

Structure Solution and Refinement. The Ni and Co atoms were located with the structure solution program MULTAN.[16] A difference Fourier synthesis phased by these atoms revealed the remaining 25 nonhydrogen atoms. Refinement of atomic parameters was carried out by full-matrix least-squares techniques on F, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, and the weighting factor w is defined as $4F_o^2/\sigma^2(F_o)^2$. Atomic scattering factors for neutral atoms were taken from ref 14 (Vol. IV), those for H were from Stewart et al.,[20] and anomalous dispersion contributions were included for Ni and Co as computed by Cromer and Liberman.[21] Two cycles with all 27 atoms assigned anisotropic thermal parameters gave agreement factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.048$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.052$.

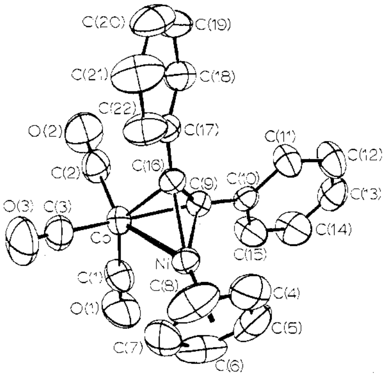

Figure 1. The atom numbering scheme used. Atoms are drawn as 50% probability thermal ellipsoids. H atoms have been omitted.

A difference Fourier synthesis phased by this model clearly showed all 15 H atoms with peak densities ranging from 0.49 (9) to 0.26 (9) e Å^{-3}. The 10 phenyl H atoms were included in idealized positions (C–H = 0.95 Å). An examination of the cyclopentadienyl H atoms showed all five were bent out of the C-atom plane toward the Ni atom, and we therefore attempted to refine their positional parameters. All H atoms were given isotropic thermal parameters 10% greater than that of the atom to which each was attached. Two cycles of refinement gave agreement factors $R_1 = 0.036$ and $R_2 = 0.035$, a significant improvement. As refinement progressed, the idealized positions of the phenyl H atoms were recalculated, and isotropic thermal parameters were varied for the cyclopentadienyl H atoms. The final cycles refined 264 variables, used 3062 unique data with $F^2 > 2\sigma(F_o^2)$, and converged at agreement factors $R_1 = 0.040$ and $R_2 = 0.043$. In the final cycle no shift exceeded 0.1σ, and the error on an observation of unit weight was 1.62 electrons. A statistical analysis of R_2 in terms of $|F_o|$, indices, $\lambda^{-1} \sin\theta$, and diffractometer setting angles χ and ϕ showed no unusual trends, and there was no evidence for secondary extinction. The largest peak in a difference Fourier synthesis was 0.27 (8) e Å^{-3}, at (0.084, 0.031, 0.230), and was of no chemical significance. Final atomic positional and thermal parameters are given in Table III, while phenyl H-atom parameters are listed in Table IV. Structure amplitudes, as $10|F_o|$ vs. $10|F_c|$ in electrons, have been deposited.[13]

Structure Description

The crystals are built up from discrete molecules, for the shortest intermolecular distances of approach are 2.74 Å, between O(3) and H1C(13), and 2.63 Å, between H1C(12) and H1C(15). Selected intramolecular distances and angles are given in Table V, while some weighted least-squares planes are reported in Table VI. Figure 1 shows the numbering scheme used for nonhydrogen atoms, while Figure 2 is a stereoview of the entire molecule. The halves of the heterometallic complex closely resemble the homonuclear species, and details of the metal–acetylene fragment for the three structures are compared in Table VII. The Ni–Co bond distance is closer to that found for the Ni–Ni bond, though comparison with the Co species is hampered by the incomplete refinement of that structure. The acetylene C atoms approach the Ni atom more closely (mean Ni–C = 1.911 (2) Å) than the Co atom (mean 1.972 (2) Å). In all three structures the C≡C bond distance is lengthened upon coordination, and the acetylene deviates significantly (35.8 (2)–42°) from linearity. The acetylene bond lies at 91.4 (2)° to the Ni–Co bond.

Dimensions within the $Co(CO)_3$ fragment are unexceptional, with mean values Co–C = 1.805 (3) Å and C–O = 1.126 (3) Å and a mean Co–C–O angle of 176.8 (3)°. Both phenyl rings are planar within experimental error. The mean C–C bond length in the phenyl rings is 1.377 (2) Å. The rings do not possess D_{6h} symmetry, for the mean angles are as follows at the indicated atom: C_1, 117.9 (3)°; *o*-C, 120.6 (2)°; *m*-C, 120.7 (2)°; *p*-C, 119.5 (3)°.

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(16) The computer programs used in this analysis include local modifications of the following: cell refinement and orientation matrix, PICKTT; full-matrix least squares by J. A. Ibers, NUCLS; structure solution, MULTAN, by P. Main, M. M. Woolfson, and G. Germain; functions and errors, ORFFE, by W. R. Busing, K. O. Martin, and H. A. Levy; molecular illustrations, C. K. Johnson's ORTEP; and Patterson and Fourier syntheses, A. Zalkin's FORDAP.

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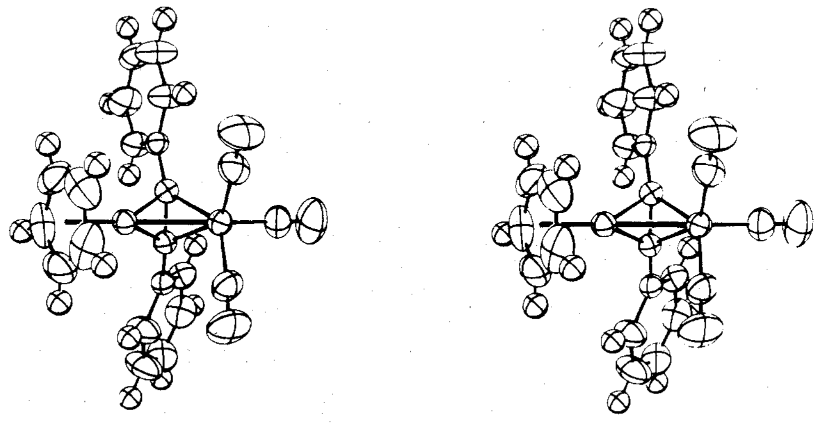

Figure 2. A stereoview of the molecule.

Table III. Atomic Positional and Thermal Parameters

atom	*x*	*y*	*z*	U_{11} or U^b	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	1339.3 (3)[a]	3649.5 (2)	1488.7 (4)	38.9 (2)	44.7 (2)	40.8 (2)	0.9 (2)	−1.3 (2)	−1.1 (2)
Co	2345.3 (3)	4426.4 (2)	1953.1 (4)	45.1 (3)	37.8 (2)	49.2 (3)	0.5 (2)	3.4 (2)	1.3 (2)
O(1)	3102 (3)	4479 (2)	−355 (3)	118 (3)	103 (3)	70 (2)	12 (3)	40 (2)	24 (2)
O(2)	3666 (3)	4907 (2)	3476 (4)	94 (3)	95 (3)	135 (4)	−20 (2)	−53 (3)	−7 (3)
O(3)	1019 (3)	5380 (2)	2015 (4)	99 (3)	70 (2)	143 (4)	40 (2)	−7 (3)	−4 (2)
C(1)	2821 (3)	4471 (2)	539 (4)	64 (3)	57 (2)	67 (3)	−2 (2)	11 (2)	15 (2)
C(2)	3155 (3)	4735 (2)	2870 (4)	60 (3)	52 (2)	79 (3)	−8 (2)	−7 (2)	3 (2)
C(3)	1544 (3)	5033 (2)	1987 (4)	67 (3)	48 (2)	75 (3)	7 (2)	−4 (2)	−4 (2)
C(4)	441 (4)	2969 (3)	1231 (5)	85 (4)	91 (4)	81 (4)	−46 (4)	−23 (3)	11 (3)
C(5)	1003 (4)	2938 (3)	338 (6)	79 (4)	83 (4)	97 (4)	13 (3)	−27 (3)	−44 (4)
C(6)	984 (4)	3490 (4)	−224 (5)	77 (4)	152 (7)	46 (3)	−29 (4)	−8 (3)	−3 (4)
C(7)	388 (5)	3868 (3)	302 (7)	97 (5)	73 (4)	118 (6)	7 (3)	−71 (5)	7 (4)
C(8)	35 (3)	3538 (4)	1192 (6)	44 (3)	134 (6)	93 (4)	−5 (3)	−7 (3)	−44 (4)
C(9)	2382 (2)	3532 (2)	2305 (3)	39 (2)	39 (2)	41 (2)	0 (1)	0 (2)	−2 (1)
C(10)	2965 (2)	3006 (2)	2214 (3)	36 (2)	42 (2)	41 (2)	2 (1)	−4 (1)	−7 (1)
C(11)	2976 (3)	2538 (2)	3034 (4)	64 (2)	51 (2)	63 (2)	9 (2)	13 (2)	11 (2)
C(12)	3494 (3)	2022 (2)	2894 (5)	85 (3)	52 (2)	93 (4)	21 (2)	3 (3)	16 (3)
C(13)	4011 (3)	1975 (2)	1967 (5)	60 (3)	58 (3)	87 (3)	21 (2)	−7 (3)	−16 (3)
C(14)	4016 (3)	2436 (3)	1166 (4)	85 (3)	93 (4)	70 (3)	37 (3)	23 (3)	−6 (3)
C(15)	3497 (3)	2949 (2)	1289 (4)	78 (3)	76 (3)	53 (3)	33 (3)	17 (2)	7 (2)
C(16)	1801 (2)	3801 (2)	2978 (3)	37 (2)	41 (2)	40 (2)	−1 (1)	0 (2)	−2 (1)
C(17)	1475 (2)	3841 (2)	4155 (3)	45 (2)	42 (2)	43 (2)	−4 (2)	4 (2)	−3 (1)
C(18)	1994 (3)	3716 (2)	5095 (4)	63 (3)	59 (2)	51 (2)	4 (2)	−4 (2)	−2 (2)
C(19)	1690 (4)	3769 (2)	6201 (4)	93 (4)	82 (3)	40 (2)	−6 (3)	−5 (2)	4 (2)
C(20)	873 (4)	3943 (3)	6401 (4)	90 (4)	100 (4)	46 (2)	−25 (3)	21 (3)	−12 (3)
C(21)	359 (3)	4075 (3)	5493 (5)	57 (3)	139 (5)	69 (3)	1 (3)	21 (3)	−15 (4)
C(22)	651 (3)	4026 (3)	4367 (4)	56 (3)	102 (4)	53 (2)	6 (3)	7 (2)	−10 (3)
H1C(4)	281 (38)	2633 (30)	1808 (54)	123 (22)					
H1C(5)	1349 (35)	2623 (28)	130 (49)	100 (20)					
H1C(6)	1294 (38)	3569 (29)	−725 (56)	82 (23)					
H1C(7)	279 (40)	4225 (30)	189 (53)	91 (24)					
H1C(8)	−316 (47)	3697 (34)	1711 (62)	146 (30)					

[a] Estimated standard deviations in this and other tables are given in parentheses and correspond to the least significant digits. Positional parameters have been multiplied by 10^4; thermal parameters by 10^3. [b] $U_{ij} = \beta_{ij}/(2\pi^2 a_i{}^* a_j{}^*)$ Å^2. The thermal ellipsoid is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table IV. Hydrogen Atom Parameters

atom	*x*	*y*	*z*	*B*, Å^2
H1C(11)[a]	2628[b]	2571	3697	5.15
H1C(12)	3488	1698	3454	6.63
H1C(13)	4366	1621	1876	5.98
H1C(14)	4381	2405	519	7.20
H1C(15)	3511	3268	722	5.99
H1C(18)	2564	3593	4972	4.98
H1C(19)	2055	3684	6831	6.23
H1C(20)	666	3970	7168	6.81
H1C(21)	−208	4203	5631	7.66
H1C(22)	284	4120	3742	6.12

[a] H1C(11) is bonded to C(11). [b] Positional parameters have been multiplied by 10^4.

The η^5-cyclopentadienyl ligand is also planar within experimental error. The mean C–C distance is 1.370 (4) Å, and the mean C–H distance is 0.88 (3) Å. The mean internal C–C–C angle is 108.0 (3)°, and the mean C–C–H angle is 126 (1)°. There is no indication of a systematic deviation of the H atoms from the plane of the C-atom framework, as has been reported in some previous electron-diffraction studies.[22-24]

Results and Discussion

The reaction of $Cp_2Ni_2(DPA)$ with $Co_2(CO)_8$ in refluxing hexane gives, after chromatography and removal of solvent, a dark brown solid (green solution) formulated $CpNi(DPA)Co(CO)_3$ on the basis of the elemental analysis and the mass spectrum. It is readily soluble in organic solvents and

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Table V. Selected Intramolecular Dimensions

	Bond Lengths, Å		
Ni–Co	2.3656 (8)	Co–C(9)	1.963 (3)
Ni–C(9)	1.917 (4)	Co–C(16)	1.989 (4)
Ni–C(16)	1.904 (4)	Co–C(1)	1.808 (5)
Ni–C(4)	2.059 (5)	Co–C(2)	1.791 (5)
Ni–C(5)	2.097 (5)	Co–C(3)	1.816 (4)
Ni–C(6)	2.094 (5)	C(1)–O(1)	1.130 (5)
Ni–C(7)	2.092 (5)	C(2)–O(2)	1.132 (5)
Ni–C(8)	2.103 (5)	C(3)–O(3)	1.116 (5)
C(9)–C(10)	1.461 (5)	C(9)–C(16)	1.337 (5)
C(16)–C(17)	1.462 (5)	C(4)–H1C(4)	1.01 (6)
C(4)–C(5)	1.367 (9)	C(5)–H1C(5)	0.90 (6)
C(5)–C(6)	1.352 (9)	C(6)–H1C(6)	0.78 (6)
C(6)–C(7)	1.384 (10)	C(7)–H1C(7)	0.80 (6)
C(7)–C(8)	1.371 (10)	C(8)–H1C(8)	0.89 (7)
C(8)–C(4)	1.381 (9)		
	Angles, Deg		
Ni–C(9)–Co	75.1 (1)	Co–C(1)–O(1)	177.3 (5)
Ni–C(9)–C(16)	69.0 (2)	Co–C(2)–O(2)	177.2 (5)
Ni–C(16)–Co	74.8 (1)	Co–C(3)–O(3)	176.1 (4)
Ni–C(16)–C(9)	70.0 (2)	C(1)–Co–C(2)	102.9 (2)
C(9)–Ni–C(16)	40.9 (1)	C(1)–Co–C(3)	105.7 (2)
C(9)–Co–C(16)	39.5 (1)	C(2)–Co–C(3)	102.7 (2)
C(16)–C(9)–C(10)	144.0 (3)	C(4)–C(5)–C(6)	108.0 (6)
C(9)–C(16)–C(17)	144.4 (3)	C(5)–C(6)–C(7)	108.4 (6)
		C(6)–C(7)–C(8)	107.9 (6)
		C(7)–C(8)–C(4)	107.0 (6)
		C(8)–C(4)–C(5)	107.7 (6)

Table VI. Weighted Least-Squares Planes

Plane A: $11.42x + 10.18y + 5.832z = 7.742$			
C(10)	−0.005 (3)[a]	C(13)	−0.003 (5)
C(11)	0.010 (5)	C(14)	0.004 (6)
C(12)	−0.006 (6)	C(15)	0.006 (6)
Plane B: $4.567x + 20.54y + 0.2709z = 8.678$			
C(17)	−0.004 (3)	C(20)	−0.008 (6)
C(18)	0.003 (4)	C(21)	0.005 (7)
C(19)	0.003 (5)	C(22)	0.006 (6)
Plane C: $11.13x + 7.871y + 7.052z = 3.680$			
C(4)	0.016 (5)	H1C(4)	−0.019
C(5)	−0.013 (5)	H1C(5)	−0.022
C(6)	0.004 (6)	H1C(6)	0.058
C(7)	0.009 (6)	H1C(7)	0.089
C(8)	−0.016 (5)	H1C(8)	0.085

[a] Distances from the plane are given in Å; atoms without esd's were not included in the calculation of the plane.

Table VII. Geometries of the M–M(DPA) Fragments

	Cp_2Ni_2-(DPA)[a]	$CpNiCo(CO)_3$-(DPA)[b]	$Co_2(CO)_6$-(DPA)[c]
M–M, Å	2.329 (4)	2.3656 (8)	2.47
M–C(acet), Å	1.89 (2)	1.905 (4)	2.01
	1.89 (2)	1.917 (4)	2.02
	1.90 (2)	1.963 (3)	1.93
	1.87 (2)	1.990 (4)	1.89
C≡C(acet), Å	1.35 (3)	1.337 (5)	1.46
			1.369[d]
C(acet)–C(phenyl), Å		1.461 (5)	
		1.462 (5)	
C–C≡C deg	137.8 (19)	144.0 (3)	137
	142.0 (19)	144.4 (3)	139

[a] Reference 10. [b] This work. [c] Reference 33. [d] Private communication reported in ref 34.

is apparently unaffected by atmospheric oxygen either in the solid state or in solution.

In its NMR spectrum, a singlet resonance due to the five equivalent cyclopentadienyl protons is observed, the chemical shift of which is similar to that of $CpNiCo_3(CO)_9$,[3] indicating that the cyclopentadienyl group remains bonded to the nickel atom. The phenyl protons on the acetylene display the typical broad multiplet. The mass spectrum of the complex shows the molecular ion $CpNi(DPA)Co(CO)_3^+$, together with ions formed by the loss of CO groups (Table I).

The infrared spectrum in the carbonyl region indicates the presence of terminal groups only.

The anticipated structure has been borne out by the single-crystal X-ray diffraction analysis, as shown in Figures 1 and 2.

It seems interesting that, while several other mixed binuclear carbonyls and their acetylene derivatives are known, both the compound presently under discussion and its parent carbonyl, $CpNiCo(CO)_5$, have not been reported, although the organophosphine compounds have been prepared.[25] This is especially surprising in view of the ease of formation and apparent stability of the cobalt–nickel–acetylene compound. Indeed, this product appears ubiquitous, being formed readily in all of the reactions

$$Cp_2Ni_2(DPA) + Co_2(CO)_8 \rightarrow \tag{1}$$

$$Cp_2Ni_2(CO)_2 + Co_2(CO)_6(DPA) \rightarrow \tag{2}$$

$$Cp_2Ni_2(DPA) + Co_2(CO)_6(DPA) \rightarrow \tag{3}$$

$$CpNiCo_3(CO)_9 + DPA \rightarrow \tag{4}$$

and even

$$Cp_2Ni + Co_2(CO)_6(DPA) \rightarrow \tag{5}$$

The formation of $CpNi(DPA)Co(CO)_3$ in reaction 3 is noteworthy since one other heterometallic compound shows a tendency toward disproportionation to its homometallic parents on reaction with diphenylacetylene,[26] reaction 6.

$$2Cp_2FeNi(CO)_3 + DPA \rightarrow Cp_2Fe_2(CO)_4 + Cp_2Ni_2(DPA) \tag{6}$$

Other heteronuclear complexes containing nickel include $Cp_2NiFe(CO)_3$,[26,27] $Cp_2Ni_2(DPA)Fe(CO)_3$,[27] $Cp_2Ni_2(DPA)Fe_2(CO)_6$,[27] $CpNi(CO)(PR_2)Fe(CO)_3$ (R = phenyl),[28] $Cp_3Ni_2Co(CO)_2$,[29,30] $[Ni_2Co_4(CO)_{14}]^{2-}$,[31] $CpNiFe(CO)_3(R_3PC_2H)$ (R = phenyl),[32] $CpNiCo_3(CO)_9$,[3] and $CpNiRu_3(CO)_9C_2(H)$-*t*-Bu.[35]

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Note Added in Proof Since the submission of this paper we have found a previous report of synthesis of the title compound by an alternative route: Muetterties, E. L.; Pretzer, W. R.; Thomas, M. G.; Beier, B. F; Thorn, D. L.: Day, V. W; Aderson, A. B. *J. Am. Chem. Soc.* **1978**, *100*, 2090.

Registry No. $CpNiCo(CO)_3(\mu$-DPA), 66752-82-7; $CpNiCo(CO)_3(\mu$-PMA), 72347-02-5; Cp_2Ni_2(DPA), 35828-66-1; $Co_2(CO)_8$, 10210-68-1; $Cp_2Ni_2(CO)_2$, 12170-92-2; $Co_2(CO)_6$(DPA), 14515-69-6; $CpNiCo_3(CO)_9$, 32761-41-4; Cp_2Ni, 1271-28-9; $Co_2(CO)_6$(PMA), 53556-74-4.

Supplementary Material Available: Table I, mass spectral data for $CpNiCo(CO)_3$(DPA) and $CpNiCo(CO)_3$(PMA), and a listing of structure amplitudes (9 pages). Ordering information is given on any current masthead page.

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