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Synthesis and Crystal Structure Analysis of $[Ni_2(CO)_2(\mu\text{-}C_3Cl_3)(\mu\text{-}Cl)]_2$, a Perchlorinated Organonickel Cluster Containing a Novel Bridging Propenyl Ligand

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Nickel tetracarbonyl reacts with tetrachlorocyclopropene to give orange-red crystals of a shock-sensitive material whose formulation is $[Ni_2(CO)_2(\mu\text{-}C_3Cl_3)(\mu\text{-}Cl)]_2$. The crystal and molecular structure of this complex has been determined by three-dimensional x-ray diffraction techniques. The crystals are triclinic, space group $P\bar{1}$, with two molecules in a unit cell of dimensions $a = 7.141$ (1) Å, $b = 10.637$ (2) Å, $c = 13.950$ (2) Å, $\alpha = 88.41$ (1)°, $\beta = 91.35(1)$°, and $\gamma = 104.58$ (1)°. The structure was solved by direct methods (MULTAN) and refined by full-matrix, anisotropic, least-squares analysis to a conventional R value of 0.048 for the 2304 independent observed ($I > 2\sigma(I)$) reflections. The molecular complex consists of a planar six-membered Ni_4Cl_2 ring. Within the ring, chlorine atoms bridge nonbonded pairs of nickel atoms while ring-opened trichloropropenyl ligands bridge bonded pairs of nickel atoms in a unique manner. The C_3Cl_3 fragments are planar and approximately orthogonal to the Ni_4Cl_2 plane; the dihedral angles between the Ni_4Cl_2 plane and the C_3Cl_3 planes measure 85 and 86°. The coordination sphere of each nickel atom is completed by a terminal carbonyl ligand. The average bond distances in the Ni_4Cl_2 unit are the following: Ni–Ni, 2.544 (1) and 2.528 (1) Å (C_3Cl_3 bridged); Ni–Ni, 3.686 (1) and 3.688 (1) Å (Cl bridged); Ni–Cl, 2.235 (2) and 2.236 (2) Å. In the C_3Cl_3 bridging unit the C–C distances average 1.396 (5) Å while the C–Cl distances are 1.715 (3) Å. The C_3Cl_3 unit bridges the bonded pair of nickel atoms with average Ni–C (terminal) distances of 1.961 (3) and 1.925 (4) Å; the Ni–C (central) distances average 2.293 (3) Å. Bond distances and angles suggest a high degree of electron delocalization throughout the entire molecule.

Introduction

Previous studies of the interaction of cyclopropenium cations, $C_3R_3^+$, with organometallic substrates have demonstrated a wide variety of different modes of coordination and reactivity for these species. Examples include: (1) η^3 coordination in $(\eta^3\text{-}C_3R_3)Ni(CO)X$ (R = alkyl, aryl; X = Cl, Br),[1,2] $(\eta^3\text{-}C_3R_3)Mo(CO)_2(CH_3CN)_2X$ ($R = C_6H_5$; X = Cl, Br),[3] and derivatives;[3,4] (2) carbon monoxide insertion leading to formation of a η^3-oxocyclobutenyl ligand as in $(\eta^3\text{-}C_3R_3CO)Co(CO)_3$, $(\eta^3\text{-}C_3R_3CO)Fe(CO)_2NO$ ($R = C_6H_5$, CH_3),[5] and $(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^3\text{-}C_3R_3CO)$ ($R = t\text{-}C_4H_9$);[6] (3) oxidative addition with ring cleavage to give a four-membered metallocycle as in $[Ir(CO)Cl\{P(CH_3)_3\}_2\{C_3(C_6H_5)_3\}][BF_4]$[7] and $[RhCl_2\{P(CH_3)_2(C_6H_5)\}_2\{C_3(C_6H_5)_3\}]$;[8] (4) electrophilic attack on ligands such as the cyclopentadienyl ring in $[(\eta^5\text{-}C_5H_5)M(CO)_3]^-$ to give $(\eta^5\text{-}C_5H_4R)M(CO)_3H$ ($R = c\text{-}C_3(t\text{-}C_4H_9)_3$, M = Mo, W);[6] (5) ring opening and oxygen insertion (presumably from methanolic solvent) leading to five-membered heterocyclic rings in $[Ru(NO)\{P(C_6H_5)_3\}_2\{OC_3(C_6H_5)_3\}][PF_6]$[9] and $[(\eta^6\text{-}C_6H_6)Ru\{P(C_6H_5)_3\}\{OC_3(C_6H_5)_3\}][PF_6]$;[10] and (6) asymmetric π coordination in the complex $[\{P(C_6H_5)_3\}_2Pt\{C_3(C_6H_5)_3\}][PF_6]$.[11]

The varied organometallic chemistry displayed by alkyl- and aryl-substituted cyclopropenium ions has led us to examine the interaction between reactive organometallic complexes and cyclopropenium ions which have been substituted with heteroatoms such as halogens. Tetrachlorocyclopropene, as prepared and characterized by West and co-workers,[12] is easily converted to the aromatic 2π 3C trichlorocyclopropenium ion in the presence of Lewis acids such as $AlCl_3$, $SbCl_5$, or $FeCl_3$. It has also been proposed[13] on the basis of anomalous NQR data that the ionized form $C_3Cl_3^+$, Cl^- may, in fact, contribute to the ground state of the C_3Cl_4 molecules. These facts, together with the known decomposition pathway of $Ni(CO)_4$ to generate strongly acidic species such as $Ni(CO)_3$ by stepwise loss of carbon monoxide as well as the known reactivity of $Ni(CO_4)$ toward allyl chloride[14] and cyclopropenium chloride[1-4] to generate π complexes, suggested that it may be possible to stabilize the $C_3Cl_3^+$ moiety through η^3 coordination to a nickel carbonyl fragment. We were unable to stabilize the cyclic cation in the manner desired but, fortunately, were able to stabilize the C_3Cl_3 species as a ring-opened propenyl ligand in a unique bonding configuration symmetrically bridging two metal atoms. This paper[15] describes the preparation and single-crystal x-ray crystallographic identification of the novel perchlorinated organometallic complex $[Ni_2(CO)_2(\mu\text{-}C_3Cl_3)(\mu\text{-}Cl)]_2$.

Experimental Section

Preparation of $[Ni_2(CO)_2(\mu\text{-}C_3Cl_3)(\mu\text{-}Cl)]_2$. Tetrachlorocyclopropene (0.18 g, 1.0 mmol), filtered through a plug of $NaHCO_3$ to remove possible HCl contamination, was syringed into a benzene solution containing excess nickel tetracarbonyl (approximately 0.20 mL) at 0 °C. The mixture was allowed to stand for 6–8 h during which time the solution darkened, carbon monoxide was evolved, and orange-red needle-shaped crystals were deposited. The reaction was carried out in an inert atmosphere (N_2), and CO evolution was monitored periodically. The reaction was complete when CO evolution ceased. The solvent was decanted from the reaction flask, and the crystals were washed several times with hexane and collected and dried on filter paper. It was discovered (the hard way!) that the crystalline product is shock sensitive so extreme caution should be used in its isolation;[16] yield 60–70% (isolated). The stoichiometry of the reaction, which is believed to be quantitative (no attempt was made to verify this fact), is summarized as

$$4Ni(CO)_4 + 2C_3Cl_4 \rightarrow [Ni_2(CO)_2(\mu\text{-}C_3Cl_3)(\mu\text{-}Cl)]_2 + 12CO$$

based on the results of the x-ray analysis of the product. Complete characterization of these air-stable crystals was precluded by their low solubility and shock sensitivity. A weak infrared spectrum, obtained in methylene chloride, showed absorptions typical of terminal carbonyl (2094, 2082 cm^{-1}) and C_3Cl_3 (1382, 1311, 790 cm^{-1})[12] groups. The crystals darken at 120 °C and decompose explosively at 138 °C. Anal.[17] Calcd for $Ni_4Cl_8C_{10}O_4$: Ni, 33.43; Cl, 40.37; C, 17.10; O, 9.11; H, 0.00. Found: Ni, 32.76; Cl, 39.26; C, 19.06; O, 8.92 (by difference); H, 0.05 (assumed to be absent). In view of the fact that the information in hand was not inconsistent with our preconceived ideas of the reaction pathway to generate the desired $[(\eta^3\text{-}C_3Cl_3)Ni(CO)Cl]_x$, x = 1 or 2, complex, a full x-ray crystallographic study was initiated.

X-Ray Data Collection and Reduction

Orange-red prismatic crystals of $[Ni_2(CO)_2(\mu\text{-}C_3Cl_3)(\mu\text{-}Cl)]_2$ were isolated directly from the reaction flask. Preliminary Weissenberg and precession photographs showed the space group to be either $P1$ or $P\bar{1}$ in the triclinic crystal system. Delaunay-reduced unit cell parameters of $a = 7.141$ (1) Å, $b = 10.637$ (2) Å, $c = 13.950$ (2) Å, $\alpha = 88.41$ (1)°, $\beta = 91.35$ (1)°, $\gamma = 104.58$ (1)°, and $V = 1025.0$ (2) Å^3 were obtained at 23 ± 1 °C by the autocentering of 15 random reflections followed by least-squares refinement of the angular settings. The density measured experimentally by flotation in a chloroform–bromoform mixed solvent system is 2.23 g cm^{-3} and agrees with the 2.27 g cm^{-3} value calculated for $Z = 2$ dimeric molecules of formulation $[Ni_2(CO)_2(\mu\text{-}C_3Cl_3)(\mu\text{-}Cl)]_2$, mol wt 702.5, per unit cell. $F(000) = 680$.

The crystal selected for data collection measured 0.148 × 0.274 × 0.570 mm. Intensity data were collected by the θ–2θ scan technique on a Syntex $P1$ autodiffractometer equipped with a graphite-monochromated Mo Kα radiation source. A variable scan rate of 4–24°/min was used. Stationary-crystal stationary-counter background counts were taken at each end of the symmetric scans which covered the range 2θ(Mo Kα) ± 0.8°; the ratio of total scan time to background counting time was 2.0. Three representative reflections which were monitored periodically throughout the data collection as a check on crystal and electronic stability showed no significant change.

Intensities and standard deviations on intensities were calculated using the formulas

$$I = S(C - RB)$$

$$\sigma(I) = [S^2(C + R^2B) + pI^2]^{1/2}$$

where S is the scan rate, C is the total integrated peak count, R is the ratio of scan time to background counting time, B is the total background count, and the parameter p is a factor introduced to downweight intense reflections. Here p was set to 0.07. The hemisphere of data collected in the region $0 < 2\theta(\text{Mo K}\alpha) < 45°$ totaled 2708 independent reflections of which 2304 had $I > 2\sigma(I)$ and were considered observed. The data were corrected for Lorentz and polarization effects in the usual way. An absorption correction was also applied in view of the shape of the crystal and the magnitude of the linear absorption coefficient of 46.33 cm^{-1};[18a] the transmission coefficients varied from 0.5803 ($7\bar{4}3$) to 0.3003 ($1\bar{2}1$).

Structure Determination and Refinement[19]

An initial choice of the centrosymmetric space group $P\bar{1}$ was suggested by an analysis of the statistical distribution of the normalized structure factor amplitudes calculated from a Wilson plot. Successful refinement of the structure confirmed this selection. The structure was solved with the multiple-solution tangent-formula program MULTAN, using 211 normalized structure factors with $3.48 > |E| > 1.65$. The three origin-specifying reflections and three additional reflections were automatically selected as the starting set by the program. With these as input, eight sets of phases for the data were derived from the Sayre relationship. The E map calculated from the phase set with the highest figure of merit (1.25) and lowest residual (13.3%) correctly located the positions of all four independent nickel atoms as well as one of the chlorine atoms. Least-squares analysis based on these five atoms converged after two cycles to give discrepancy indices of $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o| = 0.44$ and $R_2(F) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.50$, where w is a weighting factor defined as $w = 1/\sigma(F)$. Iterative difference-Fourier and isotropic least-squares analyses located the eight remaining independent atoms in the unit cell. Final isotropic least-squares refinement converged at $R_1(F) = 0.13$ and $R_2(F) = 0.16$. At this point anomalous dispersion corrections[18b] were applied to the nickel ($\Delta f' = 0.30$, $\Delta f'' = 1.1$) and chlorine ($\Delta f' = 0.10$, $\Delta f'' = 0.20$) scattering factors, temperature factors on all atoms were converted to anisotropic form, and the least-squares analysis was continued. After four cycles, the full-matrix, anisotropic least-squares refinement had converged to final residuals of $R_1(F) = 0.048$ and $R_2(F) = 0.061$.

During the final cycle of refinement, no parameter shifted by more than 0.16σ where σ refers to the estimated standard deviation of the parameter. In toto, 2304 observations were used in the final least-squares refinement of 235 parameters; this resulted in a data/parameter (overdetermination) ratio of 9.8. The final difference-Fourier analysis showed several peaks in the range 0.84–1.64 e/Å^3 (0.15–0.32 times the values of a typical carbon atom) at 1.0 Å or less from the nickel atoms. This residual electron density is attributed to anisotropic "ripples" in the heavy-atom scattering not totally accounted for by the thermal parameters.

The positional and thermal parameters from the output of the final least-squares cycle are given in Table I. Interatomic distances and angles are presented in Table II. Equations of weighted least-squares planes and distances of selected atoms from these planes are summarized in Table III. The table of observed and calculated structure factors from the final refinement is available.[20]

Results and Discussion

The structure consists of two dimeric molecules of formulation $[Ni_2(CO)_2(\mu\text{-}C_3Cl_3)(\mu\text{-}Cl)]_2$ per unit cell. Since each molecule is observed to lie on a crystallographic center of symmetry, two half-molecules constitute the independent unit. The packing of these molecules into the triclinic $P\bar{1}$ unit cell is shown in Figure 1. The crystal-packing forces acting on the two independent molecules, denoted I and II, are similar and result in comparable bond distances and angles for each; this fact is noted in Table II. The points of closest intermolecular contact are presented in Table II and suggest no unusual intermolecular interactions.

Table I. Final Atomic Parameters with Estimated Standard Deviations[a]

A. Positional Parameters

Atom	x	y	z	B, Å^2 [b]
Ni(1)	−0.23933 (12)	−0.41653 (9)	0.54545 (6)	3.13
Ni(2)	0.10062 (12)	−0.28360 (9)	0.51278 (6)	3.13
Ni(3)	−0.21943 (13)	0.11473 (10)	0.00243 (6)	3.59
Ni(4)	0.09720 (13)	0.18680 (9)	−0.08724 (6)	3.38
Cl(1)	−0.0990 (3)	−0.4648 (2)	0.3236 (1)	3.97
Cl(2)	−0.2304 (3)	−0.1755 (2)	0.3288 (1)	4.58
Cl(3)	−0.1962 (3)	−0.1016 (2)	0.5710 (1)	4.62
Cl(4)	−0.1668 (3)	−0.1080 (2)	−0.1546 (1)	4.85
Cl(5)	−0.3014 (3)	0.1467 (2)	−0.2735 (1)	5.24
Cl(6)	−0.1776 (4)	0.3965 (2)	−0.1124 (2)	5.62
Cl(7)	0.3418 (2)	−0.3681 (2)	0.4686 (1)	3.62
Cl(8)	0.3190 (3)	0.0714 (2)	−0.0864 (1)	4.22
C(1)	−0.1014 (9)	−0.3763 (7)	0.4243 (5)	3.02
C(2)	−0.1591 (9)	−0.2605 (7)	0.4227 (5)	3.08
C(3)	−0.1398 (10)	−0.2332 (7)	0.5209 (5)	3.39
C(4)	−0.1368 (10)	0.0456 (8)	−0.1126 (5)	3.64
C(5)	−0.1937 (9)	0.1438 (8)	−0.1629 (5)	3.45
C(6)	−0.1384 (11)	0.2441 (8)	−0.0971 (5)	4.20
CO(1)C	−0.3383 (11)	−0.4061 (8)	0.6627 (6)	4.24
CO(1)O	−0.3912 (12)	−0.3945 (8)	0.7348 (5)	7.85
CO(2)C	0.2389 (13)	−0.1796 (9)	0.6028 (7)	4.94
CO(2)O	0.3213 (12)	−0.1169 (8)	0.6611 (6)	8.71
CO(3)C	−0.2711 (16)	0.2196 (9)	0.0910 (6)	5.76
CO(3)O	−0.2975 (16)	0.2902 (9)	0.1452 (6)	10.47
CO(4)C	0.2617 (13)	0.3436 (10)	−0.0788 (6)	5.10
CO(4)O	0.3602 (12)	0.4458 (8)	−0.0796 (7)	8.59

B. Anisotropic Thermal Parameters[c]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni(1)	145 (2)	95 (1)	33 (1)	33 (1)	16 (1)	15 (1)
Ni(2)	143 (2)	87 (1)	38 (1)	29 (1)	5 (1)	11 (1)
Ni(3)	186 (2)	117 (1)	34 (1)	63 (1)	23 (1)	18 (1)
Ni(4)	162 (2)	104 (1)	35 (1)	44 (1)	12 (1)	13 (1)
Cl(1)	233 (5)	115 (2)	35 (1)	50 (3)	9 (2)	2 (1)
Cl(2)	246 (5)	139 (3)	47 (1)	89 (3)	−1 (2)	29 (1)
Cl(3)	260 (5)	107 (2)	61 (1)	62 (3)	27 (2)	−2 (1)
Cl(4)	295 (6)	118 (2)	49 (1)	42 (3)	0 (2)	−4 (1)
Cl(5)	216 (5)	197 (3)	42 (1)	63 (3)	−13 (2)	29 (1)
Cl(6)	361 (7)	139 (3)	67 (1)	132 (4)	55 (2)	36 (2)
Cl(7)	125 (4)	94 (2)	56 (1)	26 (2)	15 (2)	19 (1)
Cl(8)	168 (4)	134 (2)	52 (1)	64 (3)	33 (2)	33 (1)
C(1)	107 (14)	94 (8)	39 (4)	31 (9)	7 (6)	10 (4)
C(2)	143 (16)	88 (8)	35 (4)	27 (9)	13 (6)	25 (4)
C(3)	145 (16)	98 (8)	42 (4)	33 (9)	7 (6)	5 (4)
C(4)	151 (16)	128 (9)	32 (4)	30 (10)	6 (6)	14 (5)
C(5)	134 (15)	129 (9)	30 (4)	41 (10)	13 (6)	18 (5)
C(6)	226 (20)	118 (10)	47 (5)	70 (11)	39 (7)	31 (6)
CO(1)C	244 (21)	120 (10)	41 (5)	55 (11)	44 (8)	16 (5)
CO(1)O	489 (25)	221 (11)	63 (4)	78 (13)	95 (9)	7 (5)
CO(2)C	250 (22)	111 (10)	71 (6)	58 (12)	−19 (9)	1 (6)
CO(2)O	527 (28)	181 (10)	106 (6)	73 (14)	−101 (11)	−49 (6)
CO(3)C	456 (32)	120 (11)	52 (5)	97 (15)	45 (10)	32 (6)
CO(3)O	919 (46)	212 (12)	83 (5)	207 (20)	112 (13)	−7 (6)
CO(4)C	257 (23)	124 (11)	70 (6)	69 (14)	8 (9)	7 (6)
CO(4)O	390 (23)	134 (9)	154 (8)	18 (12)	−21 (10)	0 (7)

[a] Estimated standard deviations of the least significant figures are given in parentheses. [b] Overall isotropic B's equivalent to anisotropic β_{ij}'s in B. [c] Anisotropic temperature factors ($\beta_{ij} \times 10^4$) are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

The molecular complex $[Ni_2(CO)_2(\mu\text{-}C_3Cl_3)(\mu\text{-}Cl)]_2$, illustrated by ORTEP drawings in Figures 2 and 3, consists of

Table II. Interatomic Distances and Angles[a]

A. Bond Distances (Å)

Molecule I		Molecule II	
Ni(1)-Ni(2)	2.528 (1)	Ni(3)-Ni(4)	2.544 (1)
Ni(1)-Cl(7)′	2.235 (2)	Ni(3)-Cl(8)′	2.236 (2)
Ni(2)-Cl(7)	2.240 (2)	Ni(4)-Cl(8)	2.235 (2)
Ni(1)-C(1)	1.958 (6)	Ni(3)-C(4)	1.947 (7)
Ni(2)-C(1)	1.961 (6)	Ni(4)-C(4)	1.978 (7)
MID(1)[b]-C(1)	1.497 (7)	MID(2)[b]-C(4)	1.501 (7)
Ni(1)-C(2)	2.328 (7)	Ni(3)-C(5)	2.324 (7)
Ni(2)-C(2)	2.276 (7)	Ni(4)-C(5)	2.254 (7)
MID(1)-C(2)	1.924 (7)	MID(2)-C(5)	1.921 (7)
Ni(1)-C(3)	1.924 (7)	Ni(3)-C(6)	1.920 (8)
Ni(2)-C(3)	1.929 (7)	Ni(4)-C(6)	1.929 (8)
MID(1)-C(3)	1.454 (7)	MID(2)-C(6)	1.464 (8)
Ni(1)-CO(1)C	1.814 (8)	Ni(3)-CO(3)C	1.792 (10)
Ni(2)-CO(2)C	1.801 (9)	Ni(4)-CO(4)C	1.787 (10)
C(1)-C(2)	1.393 (10)	C(4)-C(5)	1.381 (11)
C(2)-C(3)	1.404 (9)	C(5)-C(6)	1.401 (11)
C(1)-Cl(1)	1.716 (7)	C(4)-Cl(4)	1.711 (8)
C(2)-Cl(2)	1.712 (7)	C(5)-Cl(5)	1.710 (7)
C(3)-Cl(3)	1.721 (7)	C(6)-Cl(6)	1.720 (8)
CO(1)C-CO(1)O	1.104 (11)	CO(3)C-CO(3)O	1.133 (13)
CO(2)C-CO(2)O	1.124 (13)	CO(4)C-CO(4)O	1.136 (13)

B. Bond Angles (deg)[a]

Molecule I		Molecule II	
Ni(1)-Ni(2)-Cl(7)	124.0 (1)	Ni(3)-Ni(4)-Cl(8)	123.1 (1)
Ni(2)-Ni(1)-Cl(7)′	125.0 (1)	Ni(4)-Ni(3)-Cl(8)′	125.7 (1)
Ni(2)-Cl(7)-Ni(1)′	110.9 (1)	Ni(4)-Cl(8)-Ni(3)′	111.2 (1)
Cl(7)′-Ni(1)-CO(1)C	97.4 (3)	Cl(8)′-Ni(3)-CO(3)C	96.9 (3)
Ni(2)-Ni(1)-CO(1)C	118.1 (3)	Ni(4)-Ni(3)-CO(3)C	118.5 (3)
Cl(7)-Ni(2)-CO(2)C	95.8 (3)	Cl(8)-Ni(4)-CO(4)C	97.1 (3)
Ni(1)-Ni(2)-CO(2)C	120.9 (3)	Ni(3)-Ni(4)-CO(4)C	124.6 (3)
Ni(2)-Ni(1)-C(1)	49.9 (2)	Ni(4)-Ni(3)-C(4)	50.1 (2)
Ni(2)-Ni(1)-C(2)	55.7 (2)	Ni(4)-Ni(3)-C(5)	55.0 (2)
Ni(2)-Ni(1)-C(3)	49.1 (2)	Ni(4)-Ni(3)-C(6)	48.8 (2)
Ni(1)-Ni(2)-C(1)	49.8 (2)	Ni(3)-Ni(4)-C(4)	49.1 (2)
Ni(1)-Ni(2)-C(2)	57.7 (2)	Ni(3)-Ni(4)-C(5)	57.6 (2)
Ni(1)-Ni(2)-C(3)	48.9 (2)	Ni(3)-Ni(4)-C(6)	48.5 (2)
Ni(1)-C(1)-Ni(2)	80.3 (2)	Ni(3)-C(4)-Ni(4)	80.8 (3)
Ni(1)-C(2)-Ni(2)	66.6 (2)	Ni(3)-C(5)-Ni(4)	67.5 (2)
Ni(1)-C(3)-Ni(2)	82.0 (3)	Ni(3)-C(6)-Ni(4)	82.7 (3)
Ni(1)-C(1)-Cl(1)	132.8 (4)	Ni(3)-C(4)-Cl(4)	133.7 (4)
Ni(2)-C(1)-Cl(1)	133.7 (4)	Ni(4)-C(4)-Cl(4)	132.0 (4)
MID(1)-C(1)-Cl(1)	153.6 (5)	MID(2)-C(4)-Cl(4)	152.4 (5)
Ni(1)-C(2)-Cl(2)	149.4 (4)	Ni(3)-C(5)-Cl(5)	149.7 (4)
Ni(2)-C(2)-Cl(2)	144.0 (4)	Ni(4)-C(5)-Cl(5)	142.6 (4)
MID(1)-C(2)-Cl(2)	177.5 (4)	MID(2)-C(5)-Cl(5)	175.6 (5)
Ni(1)-C(3)-Cl(3)	130.8 (4)	Ni(3)-C(6)-Cl(6)	130.6 (5)
Ni(2)-C(3)-Cl(3)	132.0 (4)	Ni(4)-C(6)-Cl(6)	131.5 (5)
MID(1)-C(3)-Cl(3)	151.2 (5)	MID(2)-C(6)-Cl(6)	150.8 (5)
Ni(1)-C(1)-C(2)	86.3 (4)	Ni(3)-C(4)-C(5)	86.8 (5)
Ni(2)-C(1)-C(2)	83.6 (4)	Ni(4)-C(4)-C(5)	82.2 (5)
MID(1)-C(1)-C(2)	83.4 (4)	MID(2)-C(4)-C(5)	83.5 (5)
Ni(1)-C(3)-C(2)	87.3 (4)	Ni(3)-C(6)-C(5)	87.4 (5)
Ni(2)-C(3)-C(2)	84.6 (4)	Ni(4)-C(6)-C(5)	83.6 (5)
MID(1)-C(3)-C(2)	84.6 (5)	MID(2)-C(6)-C(5)	84.2 (5)
Cl(1)-C(1)-C(2)	122.9 (5)	Cl(4)-C(4)-C(5)	123.8 (5)
C(1)-C(2)-C(3)	99.4 (6)	C(4)-C(5)-C(6)	100.0 (6)
C(1)-C(2)-Cl(2)	130.4 (5)	C(4)-C(5)-Cl(5)	131.3 (6)
C(3)-C(2)-Cl(2)	130.2 (5)	C(6)-C(5)-Cl(5)	128.7 (6)
C(2)-C(3)-Cl(3)	124.2 (5)	C(5)-C(6)-Cl(6)	124.9 (6)
Ni(1)-CO(1)-C-CO(1)O	176.5 (8)	Ni(3)-CO(3)C-CO(3)O	176.9 (10)
Ni(2)-CO(2)C-CO(2)O	177.8 (9)	Ni(4)-CO(4)C-CO(4)O	174.9 (9)

C. Selected Nonbonding Intramolecular Distances (Å)[a]

Molecule I		Molecule II	
Ni(1)· · ·Ni(1)′	4.453 (2)	Ni(3)· · ·Ni(3)′	4.433 (2)
Ni(1)· · ·Ni(2)′	3.686 (1)	Ni(3)· · ·Ni(4)′	3.688 (1)
Ni(1)· · ·Cl(7)	4.212 (2)	Ni(3)· · ·Cl(8)	4.205 (2)
Ni(2)· · ·Ni(2)′	4.486 (2)	Ni(4)· · ·Ni(4)′	4.527 (2)
Cl(7)· · ·Cl(7)′	5.064 (2)	Cl(8)· · ·Cl(8)′	5.070 (2)

Table II (*Continued*)

Molecule I		Molecule II	
Cl(7)· · ·C(1)	3.191	Cl(8)· · ·C(4)	3.210
Cl(7)′· · ·C(1)	3.180	Cl(8)′· · ·C(4)	3.180
Cl(1)· · ·Cl(2)	3.479	Cl(4)· · ·Cl(5)	3.464
Cl(2)· · ·Cl(3)	3.439	Cl(5)· · ·Cl(6)	3.456
C(1)· · ·C(3)	2.132	C(4)· · ·C(6)	2.132
C(3)· · ·CO(1)C	2.815	C(6)· · ·CO(3)C	2.793
C(3)· · ·CO(2)C	2.839	C(6)· · ·CO(4)C	2.794
Cl(7)′· · ·CO(1)C	3.055	Cl(8)′· · ·CO(3)C	3.030
Cl(7)· · ·CO(2)C	3.014	Cl(8)· · ·CO(4)C	3.030
D. Intermolecular Nonbonding Distances (Å) of Closest Contact			
Cl(1)· · ·Cl(6)	3.541	Cl(6)· · ·CO(3)C	3.347
Cl(2)· · ·Cl(5)	3.500	Cl(6)· · ·CO(4)C	3.344
Cl(2)· · ·CO(2)O	3.340	Cl(6)· · ·CO(4)O	3.513
Cl(3)· · ·CO(1)C	3.367	CO(1)O· · ·CO(3)O	3.293
Cl(3)· · ·CO(2)C	3.428	CO(1)O· · ·CO(4)O	3.347
Cl(4)· · ·CO(1)O	3.452	CO(2)O· · ·CO(3)O	3.211
Cl(5)· · ·CO(2)O	3.490	CO(4)O· · ·CO(4)O	3.004

[a] The prime notation denotes the centrosymmetrically related atom. [b] MID(1) and MID(2) refer to the midpoints between the pairs of nickel atoms in the two independent molecular units, i.e., between Ni(1) and Ni(2) and between Ni(3) and Ni(4), respectively.

Table III. Equations of Weighted Least-Squares Planes and Distances (Å) of Atoms from These Planes[a]

A. Plane through Ni(1), Ni(2), Cl(7), Ni(1)′, Ni(2)′, and Cl(7)′
$0.2355X - 0.1587Y + 0.9588Z - 7.4696 = 0$

Ni(1)	0.004	Ni(1)′	−0.004
Ni(2)	−0.004	Ni(2)′	0.004
Cl(7)	0.015	Cl(7)′	−0.015
C(1)	−1.405	CO(1)C	1.351
C(2)	−1.732	CO(2)C	1.279
C(3)	−0.441		

B. Plane through Ni(3), Ni(4), Cl(8), Ni(3)′, Ni(4)′, and Cl(8)′
$0.4276X + 0.3884Y + 0.8163Z + 0.0000 = 0$

Ni(3)	0.007	Ni(3)′	−0.007
Ni(4)	−0.006	Ni(4)′	0.006
Cl(8)	0.030	Cl(8)′	−0.030
C(4)	−1.408	CO(3)C	1.335
C(5)	−1.705	CO(4)C	1.109
C(6)	−0.413		

C. Plane through C(1), C(2), C(3), Cl(1), Cl(2), and Cl(3)
$-0.9562X - 0.2674Y + 0.1189Z - 2.4921 = 0$

C(1)	−0.043	Cl(1)	0.014
C(2)	−0.022	Cl(2)	0.005
C(3)	−0.043	Cl(3)	0.017
Ni(1)	1.132	Ni(2)	−1.387

D. Plane through C(4), C(5), C(6), Cl(4), Cl(5), and Cl(6)
$-0.9141X - 0.0573Y + 0.4014Z - 0.1952 = 0$

C(4)	−0.025	Cl(4)	0.012
C(5)	−0.023	Cl(5)	0.004
C(6)	−0.046	Cl(6)	0.016
Ni(3)	1.113	Ni(4)	−1.418

[a] The least-squares planes are of the form $AX + BY + CZ + D = 0$. Atoms are weighted by the reciprocals of their variances. X, Y, and Z are coordinates (Å) in an orthogonal system relative to the crystal axes a, b, and c, respectively.

a six-membered Ni_4Cl_2 ring which is planar to within 0.02 Å in molecule I and to within 0.03 Å in molecule II (Table III). Chlorine atoms bridge nonbonded pairs of nickel atoms while ring-opened trichloropropenyl ligands bridge the bonded pairs of nickel atoms Ni(1)–Ni(2) and Ni(3)–Ni(4).[21] These C_3Cl_3 ring-opened units are planar to within 0.04 and 0.05 Å, respectively, in molecules I and II and are approximately orthogonal to the Ni_4Cl_2 planes as can be seen in Figure 3. The dihedral angles between the best planes of the Ni_4Cl_2 and C_3Cl_3 fragments measure 86 and 85°. The coordination sphere of each nickel atom is completed by a terminal linear carbonyl ligand which is bent away from the C_3Cl_3 bridging group.

A crude electron count[22] demonstrates that each nickel atom in the cluster is short of the number of electrons required for a closed-shell electronic configuration. Under sterically favorable conditions this deficiency can be remedied by the formation of multiple bonds between metal atoms. However, this is not a general observation since many complexes can be

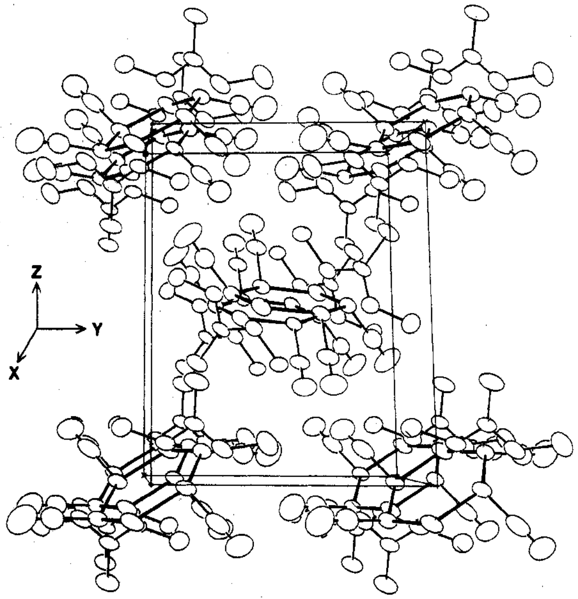

Figure 1. Packing diagram for the triclinic $P\bar{1}$ unit cell of $[Ni_2(CO)_2(\mu\text{-}C_3Cl_3)(\mu\text{-}Cl)]_2$.

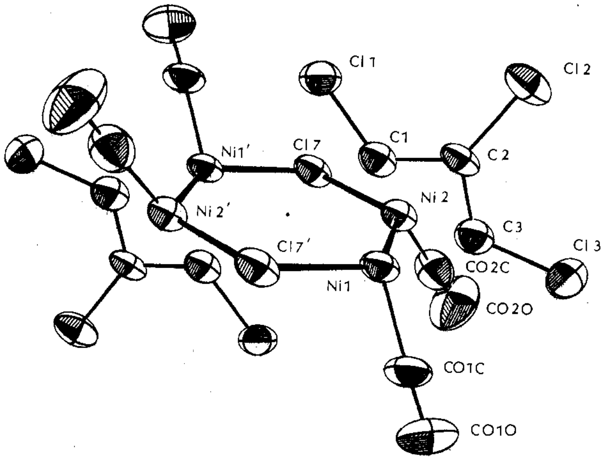

Figure 2. Perspective view of the molecular structure of $[Ni_2(CO)_2(\mu\text{-}C_3Cl_3)(\mu\text{-}Cl)]_2$ showing geometry and atomic numbering.

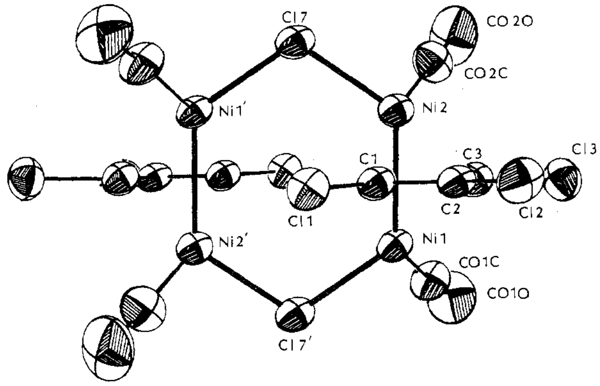

Figure 3. Alternate view of the $[Ni_2(CO)_2(\mu\text{-}C_3Cl_3)(\mu\text{-}Cl)]_2$ cluster displaying the orthogonality of the C_3Cl_3 and Ni_4Cl_2 fragments.

Table IV. Acetylene- and Propenyl-Bridged Binuclear Complexes of Iron, Cobalt, and Nickel[a]

Complex	M-M, Å	C-C, Å	M-C, Å	Ref
$(\eta^5\text{-}C_5H_5)_2Ni_2(\mu\text{-}C_2H_2)$	2.345 (3)	1.341 (6)	1.884 (4)	25
$(\eta^5\text{-}C_5H_5)_2Ni_2(\mu\text{-}C_2Ph_2)$	2.329 (4)	1.35 (3)	1.89 (2)	26
$(\eta^5\text{-}C_5H_5)NiFe(CO)_3(\mu\text{-}Ph_3PCCH)$	2.420 (4)	1.37 (3)	1.93 (2)	27
$(\eta^5\text{-}C_5H_5)_2Ni_2(\mu\text{-}Ph_2P\text{-}(O)CCCF_3)$	2.365 (1)	1.353 (9)	1.897 (3)	28
$Fe_2(CO)_6(\mu\text{-}C_2\text{-}t\text{-}Bu_2)$	2.316 (1)	1.31 (1)	2.09 (1)	29
$Fe_2(CO)_4(\mu\text{-}C_2\text{-}t\text{-}Bu_2)_2$	2.215	1.283	2.05, 2.11	30
$Co_2(CO)_6(\mu\text{-}C_2Ph_2)$	2.47	1.369	1.91, 2.02	31
$Co_2(CO)_6(\mu\text{-}C_2\text{-}t\text{-}Bu_2)$	2.463 (1)	1.335 (6)	1.996 (4)	29
$(COD)_2Ni_2(\mu\text{-}C_2Ph_2)$	2.617 (2)	1.39 (1)	1.927 (6)	32
$(\eta^5\text{-}C_5Ph_5)(\eta^4\text{-}C_4Ph_4)\text{-}Ni_2(\mu\text{-}C_3Ph_3)$	2.459	1.37, 1.45	1.99, 2.11, 2.44	33
$[Ni_2(CO)_2(\mu\text{-}C_3Cl_3)(\mu\text{-}Cl)]_2$	2.544 (1) 2.528 (1)	1.396 (5)	1.961 (4) 1.925 (4)	This work

[a] Pauling[24] lists the single-bond metallic radii of iron, cobalt, and nickel, respectively, as 1.165, 1.162, and 1.154 Å.

cited where short metal–metal bonds are expected for electronic reasons but not observed due to other factors, the most important of which are steric effects. Examination of some structural data on acetylene-bridged iron, cobalt, and nickel complexes,[23] summarized in Table IV, demonstrates that the metal–metal bond distances vary over a wide range (2.21–2.62 Å) and that, in general, the variation is dependent upon the steric requirements of both the bridging and the terminal ligands. Cotton and co-workers[34] have estimated that the Ni–Ni separation to be expected in sterically favorable situations should be in the range 2.32–2.36 Å for a single bond. In the $[Ni_2(CO)_2(\mu\text{-}C_3Cl_3)(\mu\text{-}Cl)]_2$ complex the Ni–Ni bond lengths measure 2.544 (1) and 2.528 (1) Å.[35] These long metal–metal bonds can be explained by the steric requirements of the ligands coordinated to the nickel atoms.

At one terminus of the bridging C_3Cl_3 moiety, C(1) has short nonbonded intramolecular contacts of 3.19 and 3.18 Å with the bridging chlorine atoms Cl(7) and Cl(7)′, while at the other end, C(3) has very short nonbonded contacts of 2.82 and 2.84 Å with the carbonyl carbon atoms CO(1)C and CO(2)C. Similar close contacts are noted in Table II for molecule II. These contacts are approximately 0.25 and 0.50 Å shorter than the sum of the van der Waals radii[36] of C⋯Cl (3.45 Å) and C⋯C (3.30 Å) and no doubt restrict the closeness of approach of the two nickel atoms.

Other pertinent bond distances and angles in the planar $[Ni_2(CO)_2(\mu\text{-}Cl)]_2$ fragments of the molecules are summarized in Table II and presented in Figure 4 where average values are noted. The bridging chlorine atoms Cl(7), Cl(7)′, Cl(8), and Cl(8)′[21] link nonbonded pairs of nickel atoms separated by 3.686 (1) and 3.687 (1) Å. The four independent Ni–Cl bonds which average 2.237 (1) Å (range 2.235–2.240 Å) are significantly shorter than those found in the complex $[(\eta^4\text{-}C_4Ph_4)NiCl(\mu\text{-}Cl)]_2$[37] where they are observed to be 2.343 (3) and 2.349 (3) Å. These short Ni–Cl bonds suggest some π delocalization perhaps significant enough to account for the planarity of the Ni_4Cl_2 unit. The carbonyl ligands are well-behaved with approximately linear Ni–C–O angles of 175–178°. The carbonyl ligands do not lie in the Ni_4Cl_2 plane but are bent away from the bridging C_3Cl_3 group by steric interactions between C(3) and CO(1)C and CO(2)C and between C(6) and CO(3)C and CO(4)C[21] such that the dihedral angles between the Ni_4Cl_2 plane and the CO vectors are about 60°.

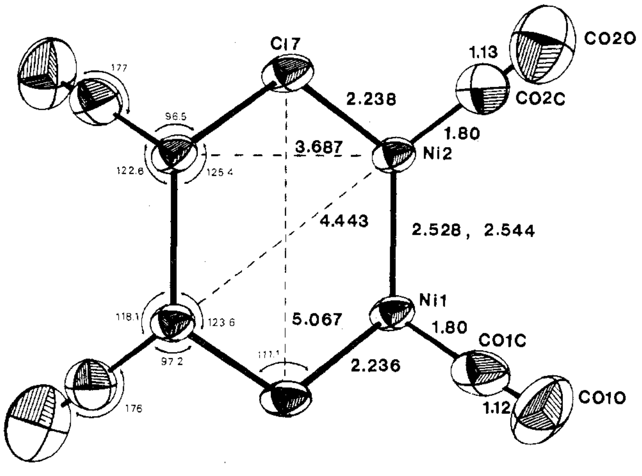

Figure 4. Close-up view of the $[Ni_2(CO)_2(\mu\text{-}Cl)]_2$ fragment with average bond distances and angles indicated.

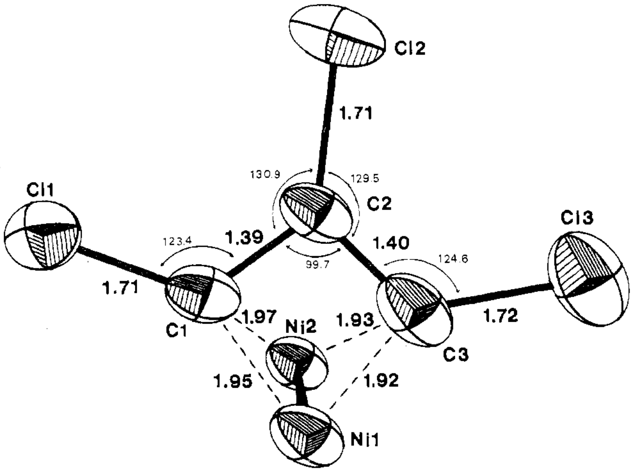

Figure 5. Close-up view of the $Ni_2(\mu\text{-}C_3Cl_3)$ fragment with average bond distances and angles indicated.

Examination of the bond length data within the $Ni_2(\mu\text{-}C_3Cl_3)$ fragments, listed in Table II and indicated on Figure 5 as average values, demonstrates that the ring-opened trichloropropenyl moieties symmetrically bridge the bonded pairs of nickel atoms, retain a high degree of electron delocalization and bond multiplicity, and, in general, closely resemble bridging acetylenic units in their disposition with respect to the bridged metal atoms. The Ni–C distances which measure 1.961 (3) Å (four values; range 1.947–1.978 Å) for Ni–C(1,4), 2.293 (3) Å (four values; range 2.254–2.328 Å) for Ni–C(2,5), and 1.925 (4) Å (four values; 1.920–1.929 Å) for Ni–C(3,6) indicate a highly symmetric bridging configuration for the novel C_3Cl_3 group. A slight degree of asymmetry exists between the two ends of the propenyl ligand with C(3,6) being on average 0.03 Å closer to the nickel atoms. The terminal carbon, C(1,3,4,6),[21] to nickel distances compare favorably

Table V. Comparative Data for $Ni_2(\mu\text{-}C_3R_3)$ Complexes (R = Cl, Ph)

R	Ni-Ni, Å	Ni-C(terminal), Å	Ni-C(central), Å	C-C, Å
Ph	2.459	1.94, 1.96, 2.01, 2.03	2.11, 2.44	1.37, 1.45
Cl(I)	2.528	1.92, 1.96, 1.93, 1.96	2.28, 2.33	1.39, 1.40
Cl(II)	2.544	1.92, 1.95, 1.93, 1.98	2.25, 2.32	1.38, 1.40

with the M–C bond lengths (1.88–2.11 Å) observed in the acetylene-bridged complexes listed in Table IV. Within the C_3Cl_3 unit, the C–C bond lengths average 1.396 (5) Å (4 values; range 1.381–1.404 Å) and may be favorably compared to the C–C distances in acetylene complexes (1.28–1.39 Å),[25–32,38] allyl complexes (1.35–1.42 Å),[39] and propenyl and cyclopropenyl complexes (1.37–1.47 Å).[4,5,7–11,40] The chelating C(1)···C(3) and C(4)···C(6) distances both measure 2.132 Å and agree with values obtained for complexes containing terminal propenyl ligands, e.g., 2.15 Å in $[Ir(CO)Cl(PMe_3)_2(C_3Ph_3)]^+$,[7] 2.17 Å in $[RhCl_2(PMe_2Ph)_2(C_3Ph_3)]$,[8] and 2.06 and 2.10 Å in [{*endo*- and [{*exo*-$C_4Ph_4(OEt)$}Pd-$(\mu\text{-}Cl)]_2$[40a] complexes, respectively. The C–Cl bond lengths which average 1.715 (3) Å (six values; range 1.710–1.721 Å) are significantly shorter than the sum of the covalent radii (1.76 Å) and are typical of C–Cl distances found in many chloro-substituted olefins.[41]

The symmetric disposition of the bridging C_3Cl_3 ligand in the $[Ni_2(CO)_2(\mu\text{-}C_3Cl_3)(\mu\text{-}Cl)]_2$ complex may be contrasted to the asymmetric nature of the bridging C_3Ph_3 group in the recently reported $[(\eta^4\text{-}C_4Ph_4)(\eta^5\text{-}C_5Ph_5)Ni_2](\mu\text{-}C_3Ph_3)$ complex.[33] Data related to the C_3R_3 (R = Cl, Ph) bridging groups are compared in Table V. In the phenyl complex the C_3Ph_3 group leans toward the nickel atom coordinated to the cyclobutadiene ligand which is electron deficient relative to the nickel atom coordinated to the cyclopentadienyl ligand. This asymmetry is particularly noted by the difference between the central carbon to nickel distances: 2.11 vs. 2.44 Å. The Ni–C(terminal) distances also reflect this shortening in favor of the cyclobutadiene nickel atom (1.95 vs. 2.02 Å). In the chloro complex, each of the C_3Cl_3 units does have a slight, but significant, tilt in favor of one of the nickel atoms. This tilt is reflected in the two independent molecules by 85 and 86° dihedral angles between the Ni_4Cl_2 and C_3Cl_3 planes and by the difference of 0.05 and 0.07 Å in the Ni(1,2)–C(3) and Ni(3,4)–C(5) bond distances. Since there is no apparent electronic reason for this observation, it is attributed to crystal-packing effects.

The accumulation of data enumerated above, viz., the short C–C and C–Cl bond distances and the planarity of the C_3Cl_3 moiety and its orthogonality to the Ni–Ni bond, are indicative of a completely delocalized $Ni_2(\mu\text{-}C_3Cl_3)$ fragment. One aspect of the bonding can be explained in terms of the modified Dewar–Chatt–Duncanson model[42] used to describe the bonding in dinuclear acetylene-bridged complexes where the C–C vector of the acetylene triple bond (and consequently the π-electron cloud) is orthogonal to the M–M vector. In the $[Ni_2(CO)_2(\mu\text{-}C_3Cl_3)(\mu\text{-}Cl)]_2$ complex the open three-carbon propenyl fragment C(1,2,3) with its π cloud is also positioned orthogonally to the Ni–Ni vector. However, this bonding rationale is not totally satisfactory since opening of the strained cyclopropenium ion results in a three-carbon fragment which possesses considerable electron density on the terminal carbon atoms C(1,3) and C(4,6). A more in-depth molecular-orbital analysis is required to rationalize fully all aspects of the delocalized $Ni_2(\mu\text{-}C_3Cl_3)$ bonding.

The preparation and isolation of this novel perchlorinated propenyl cluster complex extend our current ideas of the mode of coordination of cyclopropenyl and propenyl species from those involving only one metal atom as enumerated previously to binuclear and possibly polynuclear types of metal interactions. The oxidative addition adducts $[Ir(CO)Cl(PMe_3)_2(C_3Ph_3)]^{+}$[7] and $RhCl_2(PMe_2Ph)_2(C_3Ph_3)$[8] where four-membered metallocycles are formed serve as examples of mononuclear precursors to the binuclear complex reported here. It also suggests that the use of halo-substituted C_3X_4 and $C_3X_3^+$ species may prove a fruitful synthetic approach into perhalogenated organometallic complexes. We are currently pursuing synthetic work to probe the utility of these ideas.

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Registry No. Nickel tetracarbonyl, 13463-39-3; tetrachlorocyclopropene, 6262-42-6; $[Ni_2(CO)_2(\mu\text{-}C_3Cl_3)(\mu\text{-}Cl)]_2$, 64297-36-5.

Supplementary Material Available: Listing of the structure factors for the title compound (10 pages). Ordering information is given on any current masthead page.

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(16) Extreme care should be exercised in the isolation of this material as it can detonate upon touch when it is dry. We at first thought the shock sensitivity was due to the presence of pyrophoric nickel intermixed with the crystalline product but close examination of single crystals conclusively demonstrates that the shock sensitivity is an intrinsic property of the material.
(17) Analysis was performed by Galbraith Laboratories, Inc., Knoxville, Tenn. 37921.
(18) (a) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1968, p 163; (b) *ibid.*, p 215.
(19) The computer programs used in the analysis and refinement of the data include: FAME, generation of normalized structure factors and calculation of Wilson plot; MULTAN, multiple-solution tangent-formula program by J. P. Declercq, G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **29**, 231 (1973); SFLS5, full-matrix least-squares refinement program; FORDAP, Fourier summation program; DISTAN, bond distance and angle program; MGEOM, error analysis and least-squares planes calculations; and ORTEP II, crystal structure illustrations.
(20) Supplementary material.
(21) The numbering system employed for molecule I is shown in Figure 2. The relationship between the atoms in molecules I and II is Ni(1):Ni(3), Ni(2):Ni(4), Cl(7):Cl(8), C(1,2,3):C(4,5,6), and Cl(1,2,3):Cl(4,5,6). The respective carbonyl groups are labeled according to the numbers of the nickel atoms to which they are attached; e.g., CO(3)C and CO(3)O comprise the carbonyl group bonded to Ni(3). The primed notation indicates the atom in either molecule centrosymmetrically related to the unprimed one.
(22) If one considers all the ligands as neutral, μ-Cl as a three-electron donor, Ni–Ni as single bonds, and $\mu\text{-}C_3Cl_3$ as a five-electron donor (one electron each for "σ bonds" to C(1) and C(3) and three from the propenyl π system), the total number of electrons available is 28. The total number of electrons required to attain the closed-shell electronic configuration for each nickel atom in the cluster is 32.
(23) Due to the unique nature of the propenyl bridging ligand, no analogous complexes, with the exception of the $(\eta^5\text{-}C_5Ph_5)(\eta^4\text{-}C_4Ph_4)Ni_2(\mu\text{-}C_3Ph_3)$ complex (see text) are available for comparison. Consequently, structurally similar μ-acetylene complexes have been employed for comparative purposes.
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Crystal Structure at −35 °C of (π-Cyclopentadienyl)(bis(diphenylphosphino)ethane)(acetonitrile)iron Tetraphenylborate and Evidence for Cationic Iron–Methylene Complexes

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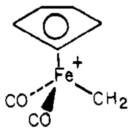
$(\pi\text{-}C_5H_5)[((C_6H_5)_2PCH_2)_2](CH_3OCH_2)Fe$ and $(\pi\text{-}C_5H_5)((C_6H_5)_3P)(CH_3OCH_2)Fe(CO)$ have been synthesized and their abilities to transfer CH_2 to cyclohexene have been examined. The structure of the compound $\{(\pi\text{-}C_5H_5)[((C_6H_5)_2PCH_2)_2]Fe(NCCH_3)\}B(C_6H_5)_4$, resulting from the acid treatment of the diphosphine complex has been determined by single-crystal x-ray diffraction techniques with intensity data gathered at −35 °C. Crystals form as deep red irregular blocks in monoclinic space group Cc with $a = 23.542\ (8)$ Å, $b = 11.494\ (3)$ Å, $c = 18.774\ (4)$ Å, $\beta = 112.26\ (2)$ Å. The calculated density of 1.248 g cm^{-3} for four formula weights of $\{(C_5H_5)[((C_6H_5)_2PCH_2)_2]Fe(NCCH_3)\}B(C_6H_5)_4$ per unit cell agrees with the measured value of 1.24 g cm^{-3}. Iron is bonded to the C_5H_5 ring in a symmetric π manner, to the two phosphorus atoms of the diphosphine ligand—thereby forming a five-membered chelate ring—and to the nitrogen atom of the CH_3CN molecule. The angle at the N atom of the Fe–N–C linkage is 171.9 (5)°. Four of the atoms of the $\overline{C{-}P{-}Fe{-}P{-}C}$ ring are essentially coplanar; one carbon atom lies ~0.7 Å from this plane, so that the ring has an envelope conformation. Full-matrix least-squares refinement of the structure has converged with an R index (on $|F|$) of 0.059 for the 4963 symmetry-independent reflections within the Mo Kα shell defined by $4 < 2\theta < 55°$ which have $I_o/\sigma(I_o) > 2.0$.

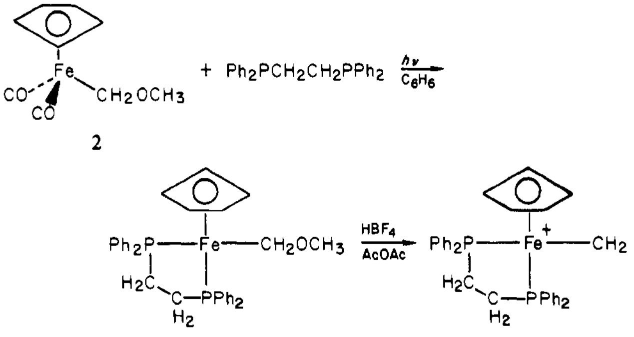
Introduction

Although transition-metal–methylene complexes have long been postulated as reaction intermediates, the first successful preparation and characterization of such a complex, $(\pi\text{-}C_5H_5)_2Ta(CH_3)(CH_2)$, was not reported until 1975.[1,2] Earlier, however, considerable evidence for the existence of the transitory iron–methylene complex **1** had been obtained in these laboratories.[3] In an attempt to isolate such a species, the two CO molecules of **1** were replaced with the chelating ligand bis(diphenylphosphino)ethane (dppe) in accordance with Scheme I. Compound **2** was prepared as previously reported.[3] It was hoped that the additional electron density (in comparison to that of **2**) at Fe resulting from its coordination with the strongly electron-donating/weakly electron-withdrawing diphosphine ligand[4] might be transferred to the CH_2 moiety, thereby stabilizing cation **4**.



1

Scheme I



Treatment of the orange-red compound **3** with acid, as shown, gave a very dark solution, which upon addition of ether afforded a light brown precipitate **5** (subsequently found to liberate ethylene in both the dissolved and the solid states[5]). However, neither the ^1H nor the ^{13}C NMR spectrum (see Experimental Section) provided support for the formulation of the product as **4**. Thus, to establish the nature of the product of these reactions a single-crystal x-ray diffraction study has been carried out.

In addition to the diphosphine complex **3**, the corresponding (π-cyclopentadienyl)(triphenylphosphine)(methoxymethyl)iron carbonyl complex **6** was prepared by photolysis of **2** with

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