

dimension of its cavity to the size of the cation. The conformational changes are drastic upon complexation: anti forms pass to gauche forms and anti clinal forms pass to anti forms. The mean values of the torsion angles about the C-C and C-O bonds in the lead complex are respectively equal to 59 and 167° (Table IV).

Registry No. $C_{18}H_{36}N_2O_6 \cdot Pb(SCN)_2$, 51567-34-1.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036 Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-2094.

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Transition Metal σ -Acyls. II.¹ Crystallographic Determination of the Molecular Structure of $(\pi-C_5H_5)Ni[C_5H_5(Me_2C_2O)_2]$, Including the Location and Refinement of All Hydrogen Atoms

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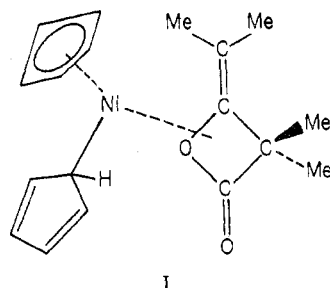
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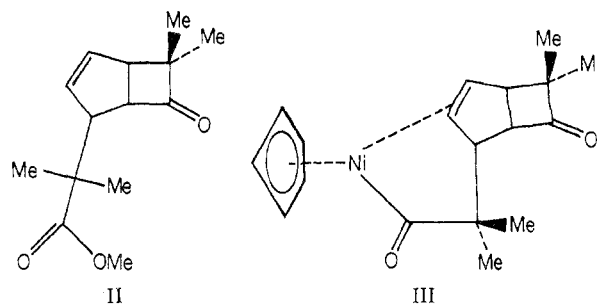
The reaction of bis(π -cyclopentadienyl)nickel with dimethylketene has previously been shown to produce a complex of stoichiometry $(C_5H_5)_2(Me_2C_2O)_2Ni$. A single-crystal X-ray diffraction study of this complex shows it to be (*pentahapto*-cyclopentadienyl)-1,3',4'-*trihapto*[2-methyl-2-(6',6'-dimethylbicyclo[3.2.0]hept-3'-en-7'-on-2'-yl)propionyl]nickel(II). The complex crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ [C_i^1 ; No. 2] with $a = 9.0048$ (16) Å, $b = 15.5241$ (33) Å, $c = 6.0445$ (12) Å, $\alpha = 94.17$ (2)°, $\beta = 109.94$ (1)°, $\gamma = 94.04$ (2)°, and $Z = 2$. Observed and calculated densities are 1.378 (5) and 1.386 g cm⁻³, respectively. All atoms, including hydrogen atoms, were accurately located from an analysis based on 2794 symmetry-independent reflections (representing data complete to $2\theta = 50^\circ$, using Mo K α radiation) collected with a Picker FACS-1 automated diffractometer. Final discrepancy indices are $R_F = 3.04\%$ and $R_{wF} = 3.05\%$. The nickel atom is bonded to a π -cyclopentadienyl ligand [Ni-C = 2.066 (2)-2.172 (2) Å], an olefin [Ni-C = 2.004 (2) and 2.024 (2) Å], and a σ -acyl residue [Ni-C = 1.895 (2) Å].

Introduction

The reaction of bis(π -cyclopentadienyl)nickel(II) with dimethylketene ($Me_2C=C=O$) was originally reported by Sato, Ichibori, and Sato in 1971.² On the basis of infrared and ¹H nmr spectroscopy, the product of this reaction (which has the stoichiometry $(C_5H_5)_2(Me_2C_2O)_2Ni$ or $C_{18}H_{22}O_2Ni$) was assigned a structure in which a four-membered lactone ring was bonded to the nickel atom *via* π electrons (see I).



However, degradation of this complex with ceric ammonium nitrate in methanol produces a good yield of the bicyclic species II.³ A more reasonable structure for the complex $C_{18}H_{22}O_2Ni$, in which the bicyclic fragment of II is retained, is shown in III.



In order to determine unambiguously the molecular geometry of the complex $C_{18}H_{22}O_2Ni$, we have undertaken a three-dimensional X-ray diffraction study. Our results, which confirm the correctness of structure III, are reported below.

Collection and Treatment of the X-Ray Diffraction Data

Orange crystals of the complex were provided by Dr. D. A. Young of Tennessee Eastman Co. The material was recrystallized from methanol under an inert atmosphere.

The crystal chosen for the X-ray diffraction study was an approximately rectangular plate between {100} faces, 0.066 mm apart and bounded by {010}, 0.137 mm apart, and {001}, 0.780 mm apart. The crystal was placed within a lightly greased 0.2-mm diameter thin-walled Lindemann glass capillary, which was then flushed with nitrogen, flame sealed, fixed into a brass pin with melted paraffin wax, and transferred to a eucentric goniometer.

Preliminary $hk(0-1)$ Weissenberg photographs, a c -axis rotation photograph, $(0-1)kl$ and $h(0-1)l$ precession photographs, and a and b cone-axis photographs gave approximate unit cell dimensions, indicated only C_i (1) Laue symmetry, and showed no systematic absences. These conditions are compatible only with the triclinic space groups $P1[C_i^1$; No. 1] or $P\bar{1}[C_i^1$; No. 2].

The crystal was transferred to a Picker FACS-1 computer-con-

(1) Part I: M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **7**, 953 (1968).

(2) M. Sato, K. Ichibori, and F. Sato, *J. Organometal Chem.*, **26**, 267 (1971).

(3) Personal communication from Dr. D. A. Young, Tennessee Eastman Co.

trolled diffractometer, was accurately centered, and was orientated so as to place c^* precisely coincident with the instrumental Φ axis. The apparatus and experimental technique have been described previously.⁴ Details specific to the present analysis are as follows.

Under "high-resolution conditions,"¹⁴ the 2θ , ω , and χ settings of the resolved Mo $K\alpha_1$ peaks (λ 0.709300 Å)⁵ of 12 high-angle ($2\theta = 41$ – 51°) reflections which were well dispersed in reciprocal space were determined automatically.⁶ These values were used in a least-squares refinement of cell and orientation parameters. The resulting unit cell parameters (at $21.8 \pm 0.5^\circ$) and estimated standard deviations are $a = 9.0048$ (16) Å, $b = 15.5241$ (33) Å, $c = 6.0445$ (12) Å, $\cos \alpha = -0.0727$ (3), $\cos \beta = -0.3410$ (2), and $\cos \gamma = -0.0705$ (3). The derived angles are $\alpha = 94.17$ (2°), $\beta = 109.94$ (1°), and $\gamma = 94.04$ (2°). The unit cell volume is 788.1 Å³. The observed density (ρ -obsd) = 1.378 (5) g cm⁻³, by neutral buoyancy in KI-H₂O) is in agreement with the value calculated for mol wt 329.085 and $Z = 2$ (ρ (calcd) = 1.386 g cm⁻³).

A takeoff angle of 3.0° was used in the collection of intensity data; molybdenum radiation was filtered through a niobium β filter (47% transmission of Mo $K\alpha$ radiation) at the detector aperture (6 mm \times 6 mm, 330 mm from the crystal).

Intensity data for reflections in the hemisphere defined by $\pm h$, $\pm k$, $+l$ were collected by executing a coupled θ (crystal)– 2θ (counter) scan from 0.5° in 2θ below the Mo $K\alpha_1$ peak to 0.5° in 2θ above the Mo $K\alpha_2$ peak, the scan rate being 1.0° /min. Stationary-background counts, each of 20-sec duration, were recorded at the two extremes of the scan for reflections in the range $0^\circ < 2\theta \leq 45^\circ$; the counting time was increased to 40 sec for the (weaker) reflections in the range $45^\circ < 2\theta \leq 50^\circ$.

Three strong reflections, in approximately mutually orthogonal directions in reciprocal space, were measured after each batch of 48 reflections in order to monitor crystal and electronic stability. The three standard reflections exhibited root-mean-square fluctuations about their average values of 0.66, 1.49, and 0.88%.

The integrated intensity of a reflection, I , and its estimated standard deviation, $\sigma(I)$, were calculated *via* the equations⁴

$$I = [(C + 4.5) - (t_C/t_B)(B_1 + B_2 + 9.0)]$$

$$\sigma(I) = [(C + 4.5) + (t_C/t_B)^2(B_1 + B_2 + 9.0) + 24.75 + p^2 I^2]^{1/2}$$

The "ignorance factor" (p)⁷ was set equal to 0.02 and numerical terms arise from the statistics involved in the truncation of the last digit of C , B_1 , and B_2 , which occurs on the punched-tape output from the Picker FACS-1 system. Any negative I was reset to zero.⁸

All data were corrected for Lorentz, polarization, and absorption⁹ effects. With $\mu(\text{Mo } K\alpha) = 12.3$ cm⁻¹, maximum and minimum transmission factors were 0.929 and 0.835, respectively. The validity of the absorption correction was confirmed by processing data from the strong axial 001 reflection which had been measured, by a θ – 2θ scan, at $\chi = 90^\circ$ and at 10° intervals from $\phi = 0^\circ$ to $\phi = 350^\circ$. The observed variation in intensity ($\pm 9.3\%$ from the mean) was thereby essentially eliminated.

In all, a total of 3289 reflections with $2\theta \leq 50^\circ$ were measured, of which 206 were standards and 584 were symmetry-related $hk0$ and $\bar{h}k0$ pairs. Duplicated reflections were averaged, thereby yielding a final data set of 2794 symmetry-independent reflections.

Although approximately 11% of the data had $I < 3\sigma(I)$, no reflections were rejected on the grounds of being "not significantly above background."

Unscaled structure factor amplitudes, F , and their standard deviations $\sigma(F)$, were calculated from the expressions $F = (I/Lp)^{1/2}$ and

(4) M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **12**, 525 (1973).

(5) J. A. Bearden, *Rev. Mod. Phys.*, **39**, 78 (1967); see, especially, Table II on p 82.

(6) Diffractometer routines, *i.e.*, crystal orientation, centering of reflections, least-squares refinement of cell parameters, and θ – 2θ scan routines were performed using programs written by Busing and Levy and adapted by Picker Corp. to the PDP 8/I which forms an integral part of the FACS-1 system: W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **22**, 457 (1967).

(7) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967); see also W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).

(8) Data reduction was performed using the Fortran IV program RDUS, by B. G. DeBoer.

(9) Absorption corrections were made by the Fortran IV program DRAB, by B. G. DeBoer.

$\sigma(F) = (\sigma(I)/Lp)^{1/2}$ for $\sigma(I) \geq I$ and $\sigma(F) = [F - \{F^2 - (\sigma(I)/Lp)\}^{1/2}]$ for $\sigma(I) < I$. The Lorentz-polarization correction, Lp , is given by $(1 + \cos^2 2\theta)/(2 \sin 2\theta)$.

Solution and Refinement of the Structure

All computations were performed on an IBM 370/158 computer at the Computer Center, University of Illinois at Chicago Circle. Programs used in determining the structure were as follows: FORDAP (Fourier Synthesis, by A. Zalkin), LSHF (a much-modified version of C. T. Prewitt's SFLSS, by B. G. DeBoer), STAN1 (distances and angles, with their estimated standard deviations, by B. G. DeBoer), PLOD (least-squares planes, by B. G. DeBoer), ORTEP (thermal ellipsoid drawings, by C. K. Johnson).

Scattering factors for nickel, oxygen, and carbon were taken from the compilation of Cromer and Waber,¹⁰ both the real and imaginary components of anomalous dispersion were included, using the values of Cromer and Liberman.¹¹ For hydrogen, the "best floated spherical H atom" values of Stewart, Davidson, and Simpson¹² were used. The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w(hkl) = \sigma^{-2}(hkl)$.

Discrepancy indices used within the text are defined as

$$R_F = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \times 100 (\%)$$

$$R_{wF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right]^{1/2} \times 100 (\%)$$

The analysis was begun under the assumption that the true space group was the (statistically more probable¹³) centrosymmetric $P\bar{1}$. The successful solution of the structure confirms this assumption.

The position of the nickel atom ($x = 0.05$, $y = 0.22$, $z = 0.25$) was quickly determined from a three-dimensional Patterson map. A Fourier synthesis, phased by this atom, yielded the positions of the remaining 20 nonhydrogen atoms. Four cycles of full-matrix least-squares refinement of a scale factor along with positional and isotropic thermal parameters for all nonhydrogen atoms (85 parameters in all) led to convergence with $R_F = 10.81\%$ and $R_{wF} = 12.44\%$. Two further cycles now using anisotropic thermal parameters for the 21 nonhydrogen atoms (190 parameters) led to $R_F = 6.10\%$ and $R_{wF} = 7.65\%$. A difference-Fourier synthesis now led to the unambiguous location of all 22 hydrogen atoms with peak heights ranging from 0.70 to 0.32 e Å⁻³. Two cycles of refinement, with hydrogen atom positional and thermal parameters also included (278 variable parameters), led to $R_F = 3.62\%$ and $R_{wF} = 3.83\%$. At this stage the low-angle data were corrected for the "β-filter effect"¹⁴ and a secondary extinction correction was found to be required. A further four cycles of full-matrix least-squares refinement [scale factor, secondary extinction parameter, positional parameters for all atoms, anisotropic thermal parameters for nonhydrogen atoms, isotropic thermal parameters for hydrogen atoms—279 parameters in all] led to final convergence with $R_F = 3.04\%$ and $R_{wF} = 3.05\%$. Final shifts of parameters were $(\Delta/\sigma) < 0.03$ for all parameters of nonhydrogen atoms and $(\Delta/\sigma) < 0.06$ for all hydrogen atom parameters.

[A reviewer has claimed that there is "no justification for the refinement of the H positions. . . [and that] . . . it is clearly better to put things into the model that you know to greater precision than you can determine in the experiment. . . the H atoms of the π -cyclopentadienyl ring, at least."]

Our defense is as follows. (i) Placing hydrogen atoms in idealized positions, while perfectly reasonable, can often obscure certain features of chemical interest. Thus, in the present structure, the hydrogen atoms of the π -cyclopentadienyl system are not coplanar with

(10) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(11) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

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

(13) W. Nowacki, T. Matsumoto, and A. Edenharter, *Acta Crystallogr.*, **22**, 935 (1967).

(14) At small values of 2θ , the constant 2θ offset at which the low-angle background (B_1) is measured places the counter in a wave-length region which is strongly absorbed by the niobium β filter. This results in an anomalously low value for B_1 and an erroneously large value for F_o . The method of correction is outlined in ref 4.

Table I. Final Positional and Isotropic Thermal Parameters for $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}[\text{C}_5\text{H}_5(\text{Me}_2\text{C}_2\text{O})_2]$ with Estimated Standard Deviations^{a,b}

Atom	x	y	z	B, Å ²
Ni	0.051115 (26)	0.216563 (15)	0.250808 (43)	2.85
O(1)	-0.48795 (18)	0.37800 (10)	0.08151 (33)	5.16
O(2)	-0.06728 (18)	0.11674 (12)	-0.18053 (28)	5.42
C(1)	-0.31667 (21)	0.28724 (12)	-0.06582 (36)	3.02
C(2)	-0.28907 (21)	0.21913 (12)	0.11062 (35)	3.00
C(3)	-0.13847 (22)	0.25973 (12)	0.30813 (35)	3.07
C(4)	-0.06173 (22)	0.32553 (12)	0.22831 (36)	3.14
C(5)	-0.15881 (21)	0.34680 (12)	-0.01255 (35)	2.99
C(6)	-0.25113 (22)	0.42993 (12)	-0.01531 (36)	3.30
C(7)	-0.38314 (21)	0.36803 (12)	0.00609 (36)	3.43
C(8)	-0.26070 (21)	0.13041 (12)	0.01085 (36)	3.17
C(9)	-0.09599 (21)	0.14697 (12)	-0.01451 (34)	3.10
C(10)	-0.24493 (32)	0.06461 (15)	0.19340 (49)	4.51
C(11)	-0.38804 (27)	0.09457 (16)	-0.22458 (49)	4.41
C(12)	-0.18413 (30)	0.50419 (15)	0.17791 (51)	4.45
C(13)	-0.30346 (36)	0.46282 (19)	-0.25945 (48)	4.95
CP(1)	0.20267 (29)	0.12130 (19)	0.35134 (57)	5.54
CP(2)	0.26797 (32)	0.17905 (29)	0.24260 (56)	6.59
CP(3)	0.30165 (28)	0.25897 (23)	0.37744 (77)	7.13
CP(4)	0.25479 (31)	0.24598 (20)	0.57523 (57)	6.08
CP(5)	0.19827 (28)	0.16075 (18)	0.55590 (49)	5.02
H(1)	-0.3674 (24)	0.2667 (13)	-0.2203 (39)	3.49 (46)
H(2)	-0.3747 (24)	0.2117 (12)	0.1691 (36)	3.25 (43)
H(3)	-0.1179 (25)	0.2524 (13)	0.4781 (41)	3.40 (48)
H(4)	0.0200 (24)	0.3692 (13)	0.3329 (37)	3.36 (43)
H(5)	-0.1070 (23)	0.3433 (12)	-0.1338 (36)	3.16 (42)
H(10A)	-0.2128 (29)	0.0077 (17)	0.1360 (46)	5.90 (63)
H(10B)	-0.3478 (33)	0.0558 (16)	0.2133 (46)	5.52 (60)
H(10C)	-0.1631 (29)	0.0879 (15)	0.3550 (45)	4.79 (54)
H(11A)	-0.3853 (29)	0.1295 (16)	-0.3607 (48)	5.53 (63)
H(11B)	-0.4870 (35)	0.0986 (18)	-0.2091 (51)	6.83 (73)
H(11C)	-0.3736 (29)	0.0365 (17)	-0.2612 (46)	5.43 (60)
H(12A)	-0.2666 (31)	0.5462 (16)	0.1669 (47)	6.15 (65)
H(12B)	-0.0926 (32)	0.5352 (17)	0.1540 (49)	6.13 (66)
H(12C)	-0.1552 (29)	0.4846 (15)	0.3402 (50)	5.24 (60)
H(13A)	-0.3463 (28)	0.4158 (16)	-0.3811 (45)	4.72 (57)
H(13B)	-0.2152 (36)	0.4934 (18)	-0.2897 (53)	6.87 (76)
H(13C)	-0.3912 (31)	0.5052 (17)	-0.2700 (48)	6.56 (67)
HP(1)	0.1621 (38)	0.0618 (21)	0.2863 (60)	8.21 (82)
HP(2)	0.2863 (42)	0.1691 (24)	0.1106 (71)	10.20 (98)
HP(3)	0.3354 (39)	0.3088 (21)	0.3539 (62)	8.32 (91)
HP(4)	0.2538 (34)	0.2839 (18)	0.6761 (53)	6.34 (76)
HP(5)	0.1499 (35)	0.1307 (18)	0.6582 (55)	7.09 (76)

^a Estimated standard deviations, shown in parentheses, are right adjusted to the last digit of the preceding number and are derived from the inverse of the final least-squares matrix. ^b For nonhydrogen atoms, "equivalent isotropic temperature factors" are listed. They correspond to a mean-square displacement which is the average of the mean-square displacements along the three principal axes of the anisotropic vibration ellipsoid.

the five-membered carbocyclic ring but are, on average, displaced toward the nickel atom (*vide infra*). (ii) Hydrogen atoms of the methyl groups are indeterminate from the viewpoint of calculation; their positions can only be determined *via* difference-Fourier and/or least-squares refinement techniques. (iii) Information on *idealized* positions can, in the final analysis, only be obtained as the result of experiments in which they are optimized. This article represents only one report in a prolonged series in which we will attempt to determine idealized positions for hydrogen atoms in a wide variety of chemical systems.]

The final value for the secondary extinction parameter, c , was $0.1099 (67) \times 10^{-3} \text{ mm}^{-1} \text{ e}^{-2}$, where this parameter enters the equation for the corrected structure factor in the form^{15,16}

$$F_{c,\text{cor}} = F_{c,\text{uncor}}(1 + c\beta F_{c,\text{uncor}}^2)^{-1/4}$$

and

$$\beta = \left(\frac{1 + \cos^4 2\theta}{(\sin 2\theta)(1 + \cos^2 2\theta)} \right) \left(\frac{-d \ln T}{d\mu} \right)$$

The final standard deviation in an observation of unit weight,

(15) W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139 (1963); **23**, 558 (1967).

(16) A. C. Larson in "Crystallographic Computing," F. R. Ahmed, Ed., Munksgaard, Copenhagen, 1970, p 291 ff.

$\Sigma w(|F_o| - |F_c|)^2 / (m - n)^{1/2}$, was 1.71, where the number of data (m) was 2794 and the number of parameters (n) was 279 ($m/n = 10.0$). The function $\Sigma w(|F_o| - |F_c|)^2$ showed no significant dependence on either $\sin \theta$ or $|F_o|$, thus indicating a valid weighting scheme.

The correctness of the structure was confirmed by means of a final difference-Fourier synthesis, on which the greatest feature was a peak of height $0.29 \text{ e} \text{ \AA}^{-3}$, within the $\pi\text{-C}_5\text{H}_5$ ring.

A final test was run using only data with $I > 3\sigma(I)$. Convergence was reached with $R_F = 2.51\%$ and $R_{wF} = 2.99\%$. The final parameters were all within 1.0σ of the previous values, but all esd's were higher (by ~6-8%). These results were discarded.

A table of observed and calculated structure factor amplitudes is available.¹⁷ Positional parameters are given in Table I. Anisotropic thermal parameters are listed in Table II.

The Molecular Structure

The crystals consist of discrete molecular units of $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}[\text{C}_5\text{H}_5(\text{Me}_2\text{C}_2\text{O})_2]$ which are separated by normal van der Waals distances. There are no abnormally short intermolecular contacts. The packing of molecules within the unit cell is shown in Figure 1.

Interatomic distances with their estimated standard deviations (esd's) are shown in Table III; bond angles (with esd's) are collected in Table IV. The labeling of atoms within the

(17) See paragraph at end of paper regarding supplementary material.

Table II. Anisotropic Thermal Parameters with Esd's for $(\pi\text{-C}_5\text{H}_5)\text{Ni}[\text{C}_5\text{H}_5(\text{Me}_2\text{C}_2\text{O})_2]^{a,b}$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U \rangle^c$		
Ni	2.213 (11)	3.061 (12)	2.879 (12)	0.304 (7)	0.350 (8)	0.487 (8)	0.160	0.195	0.211
O(1)	3.87 (7)	4.80 (7)	7.55 (10)	1.07 (6)	2.86 (7)	0.43 (7)	0.190	0.252	0.310
O(2)	3.99 (7)	7.97 (10)	4.02 (7)	0.03 (7)	1.58 (6)	-1.44 (7)	0.201	0.224	0.339
C(1)	2.38 (7)	3.17 (8)	3.02 (9)	0.32 (6)	0.35 (7)	0.05 (7)	0.166	0.197	0.220
C(2)	2.48 (7)	3.13 (8)	3.48 (9)	0.11 (6)	1.21 (7)	0.20 (7)	0.172	0.199	0.212
C(3)	3.05 (8)	3.27 (8)	2.71 (8)	0.54 (6)	0.77 (7)	0.11 (6)	0.183	0.192	0.215
C(4)	2.58 (7)	2.85 (8)	3.44 (9)	0.12 (6)	0.43 (7)	0.04 (7)	0.173	0.193	0.228
C(5)	2.62 (7)	2.99 (8)	3.38 (9)	0.50 (6)	0.99 (7)	0.57 (7)	0.178	0.194	0.210
C(6)	3.12 (8)	3.04 (8)	3.63 (9)	0.68 (6)	0.92 (7)	0.55 (7)	0.182	0.208	0.222
C(7)	2.50 (8)	3.60 (8)	3.63 (9)	0.70 (6)	0.29 (7)	0.34 (7)	0.165	0.213	0.240
C(8)	2.66 (7)	2.83 (7)	3.76 (9)	0.05 (6)	0.88 (7)	0.14 (7)	0.179	0.195	0.224
C(9)	2.80 (8)	3.28 (8)	3.05 (8)	0.51 (6)	0.74 (7)	0.41 (7)	0.181	0.204	0.208
C(10)	4.89 (11)	3.43 (10)	5.48 (13)	-0.16 (8)	2.12 (11)	1.07 (9)	0.189	0.255	0.266
C(11)	3.17 (9)	3.54 (10)	5.37 (13)	-0.10 (8)	0.35 (9)	-0.79 (9)	0.180	0.220	0.295
C(12)	4.14 (10)	3.20 (9)	5.46 (13)	0.46 (8)	1.03 (10)	-0.05 (9)	0.199	0.226	0.280
C(13)	5.62 (13)	5.03 (13)	4.41 (12)	2.05 (11)	1.48 (11)	1.76 (11)	0.193	0.256	0.292
CP(1)	3.51 (10)	5.18 (13)	6.75 (16)	1.80 (9)	0.13 (11)	-0.07 (12)	0.179	0.254	0.337
CP(2)	3.18 (11)	12.38 (28)	4.45 (14)	2.96 (14)	1.08 (10)	1.56 (16)	0.176	0.242	0.401
CP(3)	2.29 (9)	7.09 (18)	10.29 (26)	-0.63 (10)	-0.61 (12)	5.00 (19)	0.162	0.221	0.442
CP(4)	4.00 (11)	6.32 (16)	5.28 (14)	1.93 (11)	-1.56 (11)	-1.86 (13)	0.168	0.232	0.386
CP(5)	3.60 (10)	6.46 (15)	4.98 (13)	1.81 (10)	0.81 (9)	2.69 (12)	0.171	0.251	0.314

^a These anisotropic thermal parameters are analogous to the usual form of the isotropic parameter and have units of \AA^2 . They enter the expression for the structure factor in the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.
^b Esd's were obtained from the inverse of the final least-squares matrix. ^c These values correspond to the root-mean-square amplitudes of vibration (in \AA) of the atom along the three principal axes (minor, median, major, respectively) of its vibration ellipsoid. For relative orientations, see the figures.

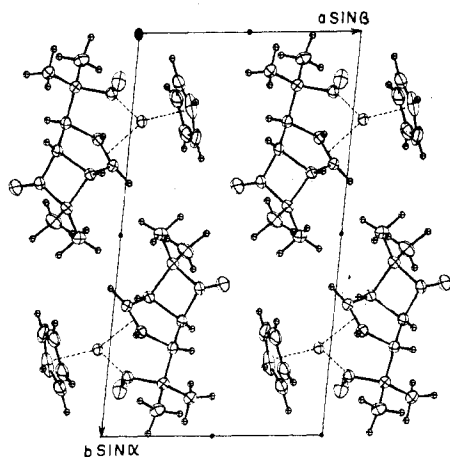


Figure 1. Packing of $(\pi\text{-C}_5\text{H}_5)\text{Ni}[\text{C}_5\text{H}_5(\text{Me}_2\text{C}_2\text{O})_2]$ molecules within the unit cell, as viewed down c .

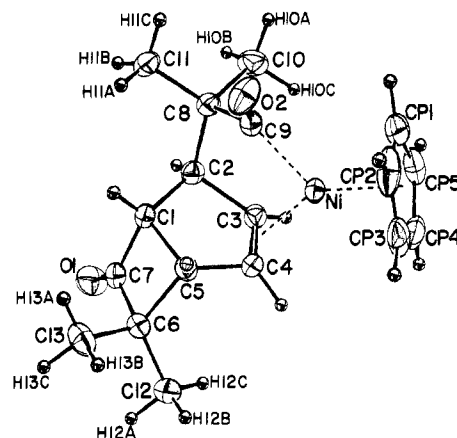


Figure 2. Molecular geometry and labeling of atoms for $(\pi\text{-C}_5\text{H}_5)\text{Ni}[\text{C}_5\text{H}_5(\text{Me}_2\text{C}_2\text{O})_2]$.

$(\pi\text{-C}_5\text{H}_5)\text{Ni}[\text{C}_5\text{H}_5(\text{Me}_2\text{C}_2\text{O})_2]$ molecule is shown in Figure 2. [Hydrogen atoms of the π -cyclopentadienyl system, which are not labeled on this figure, are numbered similarly to their attached carbon atoms; thus, HP(1) is linked to CP(1) etc.] As can clearly be seen, the overall structure of the molecule is that suggested by structure III (*quod vide*). The molecule is thus properly named as (*pentahapto* cyclopentadienyl)-1,3',4'-*trihapto* {2-methyl-2-(6',6'-dimethylbicyclo[3.2.0]-hept-3'-en-7'-on-2'-yl)propionyl}nickel(II).

The coordination environment of the nickel atom is shown in Figure 3. The formally d^8 Ni(II) atom is in a quasipentacoordinate environment and may be regarded as attaining the appropriate 18 outer electron ("noble gas") configuration *via* the donation of two electrons from an olefinic residue (C(3)-C(4)), two electrons from the σ -acyl group (C bonded at C(9)) and six electrons from the formally tridentate π -cyclopentadienyl anion. Angles around the nickel atom are "centroid"-Ni-C(9) = 126.68° , "centroid"-Ni-midpt [C(3)-C(4)] = 139.49° , and midpt [C(3)-C(4)]-Ni-C(9) = 92.97° . [Here "centroid" is the center of gravity of the five carbon

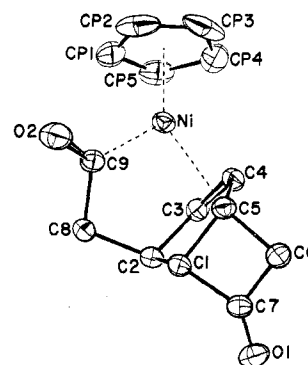


Figure 3. The coordination geometry of the nickel atom.

atoms of the π -cyclopentadienyl system, defined by atoms CP(1) through CP(5).]

Individual nickel-carbon distances for the π -cyclopentadienyl system vary significantly from Ni-CP(1) = $2.066(2)$ \AA to Ni-CP(4) = $2.172(2)$ \AA , the mean of the five independent values being 2.128 \AA . The Ni-"centroid" distance is $1.776(2)$ \AA .

Table III. Intramolecular Distances (in Å) for $(\pi\text{-C}_5\text{H}_5)\text{Ni}[\text{C}_5\text{H}_5(\text{Me}_2\text{C}_2\text{O})_2]$, with Estimated Standard Deviations^{a,b}

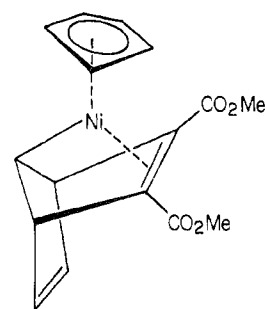
Atoms	Dist	Atoms	Dist
(A) Nickel–Carbon Distances			
Ni–C(9)	1.895 (2)	Ni–CP(1)	2.066 (2)
		Ni–CP(2)	2.092 (3)
Ni–C(3)	2.004 (2)	Ni–CP(3)	2.156 (2)
Ni–C(4)	2.024 (2)	Ni–CP(4)	2.172 (2)
		Ni–CP(5)	2.153 (2)
Ni–midpt ^c	1.888 (2)	Ni–centroid ^c	1.776 (2)
(B) Carbon···Carbon Contacts (<3.5 Å) between Ligands			
CP(1)···C(9)	2.916 (3)	CP(4)···C(4)	3.293 (3)
CP(2)···C(9)	3.096 (3)	CP(4)···C(3)	3.384 (3)
CP(3)···C(4)	3.345 (3)	CP(5)···C(3)	3.420 (3)
(C) Carbon–Carbon Distances within the $[\text{C}_5\text{H}_5(\text{Me}_2\text{C}_2\text{O})_2]$ Ligand			
C(1)–C(2)	1.529 (3)	C(5)–C(6)	1.582 (2)
C(1)–C(5)	1.562 (2)	C(6)–C(7)	1.522 (3)
C(1)–C(7)	1.525 (3)	C(6)–C(12)	1.511 (3)
C(2)–C(3)	1.526 (3)	C(6)–C(13)	1.526 (3)
C(2)–C(8)	1.536 (3)	C(8)–C(9)	1.548 (3)
C(3)–C(4)	1.398 (3)	C(8)–C(10)	1.536 (3)
C(4)–C(5)	1.495 (3)	C(8)–C(11)	1.527 (3)
(D) Carbon–Carbon Distances within the $\pi\text{-C}_5\text{H}_5$ Ligand			
CP(1)–CP(2)	1.363 (5)	CP(4)–CP(5)	1.366 (4)
CP(2)–CP(3)	1.388 (5)	CP(5)–CP(1)	1.354 (4)
CP(3)–CP(4)	1.420 (5)		
(E) Carbon–Oxygen Distances			
C(7)–O(1)	1.194 (2)	C(9)–O(2)	1.191 (2)
(F) Carbon–Hydrogen Distances within the $[\text{C}_5\text{H}_5(\text{Me}_2\text{C}_2\text{O})_2]$ Ligand			
C(1)–H(1)	0.91 (2)	C(11)–H(11B)	0.93 (3)
C(2)–H(2)	0.96 (2)	C(11)–H(11C)	0.94 (3)
C(3)–H(3)	1.00 (2)	C(12)–H(12A)	1.01 (3)
C(4)–H(4)	0.98 (2)	C(12)–H(12B)	0.98 (3)
C(5)–H(5)	0.99 (2)	C(12)–H(12C)	1.00 (3)
C(10)–H(10A)	1.02 (3)	C(13)–H(13A)	0.95 (3)
C(10)–H(10B)	0.98 (3)	C(13)–H(13B)	0.97 (3)
C(10)–H(10C)	1.02 (2)	C(13)–H(13C)	1.05 (3)
C(11)–H(11A)	1.02 (3)		
(G) Carbon–Hydrogen Distances within the $\pi\text{-C}_5\text{H}_5$ Ligand			
CP(1)–HP(1)	0.97 (3)	CP(4)–HP(4)	0.82 (3)
CP(2)–HP(2)	0.87 (4)	CP(5)–HP(5)	0.99 (3)
CP(3)–HP(3)	0.85 (3)		

^a Esd's are calculated by considering all elements of the positional covariance matrix of the last cycle of refinement. The calculation was performed using the Fortran IV program STAN1, by B. G. DeBoer. Contributions from errors in the unit cell dimensions are included. ^b No distances have been corrected for the effects of thermal motion. ^c "midpt" is the midpoint of the C(3)–C(4) olefinic bond; "centroid" is the centroid of the π -cyclopentadienyl system.

Atom C(9) [the acyl carbon atom] lies below the CP(1)–CP(2) bond such that the contacts CP(1)···C(9) and CP(2)···C(9) are 2.916 (3) and 3.096 (3) Å, respectively. The olefinic group C(3)–C(4) lies below atom CP(4), with CP(3)···C(4) = 3.345 (3) Å, CP(4)···C(4) = 3.293 (3) Å, CP(4)···C(3) = 3.384 (3) Å, and CP(5)···C(3) = 3.420 (3) Å.

The nickel(II) atom is more or less symmetrically linked to the two olefinic carbon atoms, with Ni–C(3) = 2.004 (2) Å and Ni–C(4) = 2.024 (2) Å. The distance of the nickel atom from the midpoint of C(3)–C(4) is 1.888 (2) Å.

The nickel–(substituted propionyl) linkage, Ni–C(9), is 1.895 (2) Å. This distance is, as expected, substantially lower than the nickel–carbon (sp^3) distance of 1.965 (12) Å reported by Dahl and Wei¹⁸ for $(\pi\text{-C}_5\text{H}_5)\text{Ni}[\text{C}_5\text{H}_5\text{C}_2(\text{CO}_2\text{Me})_2]$, IV (see Discussion). Other distances within this



IV

species are also comparable with those in the $(\pi\text{-C}_5\text{H}_5)\text{Ni}[\text{C}_5\text{H}_5(\text{Me}_2\text{C}_2\text{O})_2]$ molecule—viz., Ni–C(π -cyclopentadienyl) = 2.091 (14)–2.191 (16) Å (average 2.130 Å), Ni–C(olefin) = 1.965 (12)–1.975 (13) Å (average 1.970 Å), and Ni–(midpt of olefin) = 1.831 (11) Å.

The π -Cyclopentadienyl Ring. The five carbon atoms of this carbocyclic ring have a root-mean-square deviation of 0.011 Å from their least-squares plane (see Table V). Since the esd's on carbon atom positions are ~ 0.0028 – 0.0037 Å, the deviations are on the borderline of statistical significance at the 3σ level.

Individual carbon–carbon bond distances range from CP(5)–CP(1) = 1.354 (4) to 1.420 (5) Å; the mean of the five independent values is 1.378 ± 0.027 Å.¹⁹ This mean value is significantly lower than the accepted C–C(π -cyclopentadienyl) distance of ~ 1.43 Å.²⁰ However, this reduction is regarded as a systematic error due to libration of the π -cyclopentadienyl ring about the metal···centroid axis. In keeping with this, Figures 2 and 3 show clearly that the major axes of the vibration ellipsoids of atoms CP(1)–CP(5) are tangential to an imaginary circle described through these atoms.

Angles within the carbocyclic ring range from CP(2)–CP(3)–CP(4) = 105.75 (26°) to CP(5)–CP(1)–CP(2) = 109.57 (29°), the mean value being 107.99° (cf. 108.00° for an ideally planar pentagon).

The nickel atom lies 1.774 Å from the plane of the π -cyclopentadienyl ring. The individual displacements of hydrogen atoms range from $+0.02$ to -0.09 Å, the mean of the five values being -0.05 Å (i.e., the mean direction of displacement is toward the nickel atom).

Carbon–hydrogen distances range from CP(4)–HP(4) = 0.82 (3) Å to CP(5)–HP(5) = 0.99 (3) Å, the average bond length being 0.90 ± 0.07 Å.¹⁹ As has been noted elsewhere,¹² X-ray crystallographically determined carbon–hydrogen distances are expected to be reduced from the true internuclear separation of 1.08 Å, because the centroid of the electron density around hydrogen is not coincident with the nuclear position and is displaced along the H→C vector. [The normally observed C–H distance is ~ 0.95 Å.²¹]

The C–C–H angles, which are not affected by any systematic errors, range from HP(3)–CP(3)–CP(4) = 122.1 (25°) to HP(3)–CP(3)–CP(2) = 132.0 (25°), the mean value being 125.9° . [The external half-angle for a regular planar pentagon is precisely 126° .]

Finally, it should be noted that the plane of the π -cyclopentadienyl ring makes an angle of 96.68° with the plane defined by Ni, C(9), and midpt[C(3)–C(4)]—see Table V.

(19) Esd's on average bond lengths etc. are calculated using the scatter formula, viz., $\sigma = [\sum(x_i - \bar{x})^2 / (N - 1)]^{1/2}$, where x_i is the i th observation and \bar{x} is the mean of N such observations. They are distinguished by being preceded by "±."

(20) M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, **12**, 1650 (1973); see, particularly, p 1655 and ref 22–30 of this article.

(21) M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973).

Table IV. Interatomic Angles (in deg) for $(\pi\text{-C}_5\text{H}_5)\text{Ni}[\text{C}_5\text{H}_5(\text{Me}_2\text{C}_2\text{O})_2]^a$

Atoms	Angle	Atoms	Angle
(A) Angles Involving the Nickel Atom			
centroid-Ni-C(9) ^b	126.68	Ni-C(9)-C(8)	112.03 (13)
centroid-Ni-midpt	139.49	Ni-C(9)-O(2)	125.29 (15)
midpt-Ni-C(9)	92.97		
(B) C-C-C Angles within the $[\text{C}_5\text{H}_5(\text{Me}_2\text{C}_2\text{O})_2]$ Ligand			
C(2)-C(1)-C(5)	109.13 (15)	C(5)-C(6)-C(12)	120.30 (17)
C(2)-C(1)-C(7)	114.34 (17)	C(5)-C(6)-C(13)	111.02 (15)
C(5)-C(1)-C(7)	86.18 (14)	C(7)-C(6)-C(12)	116.31 (19)
C(1)-C(2)-C(3)	101.93 (15)	C(7)-C(6)-C(13)	110.04 (18)
C(1)-C(2)-C(8)	113.55 (17)	C(12)-C(6)-C(13)	111.12 (16)
C(3)-C(2)-C(8)	109.94 (15)	C(1)-C(7)-C(6)	93.75 (15)
C(2)-C(3)-C(4)	110.65 (17)	C(2)-C(8)-C(9)	103.89 (14)
C(3)-C(4)-C(5)	112.55 (16)	C(2)-C(8)-C(10)	110.05 (18)
C(1)-C(5)-C(4)	102.13 (15)	C(2)-C(8)-C(11)	113.94 (17)
C(1)-C(5)-C(6)	90.03 (14)	C(9)-C(8)-C(10)	107.11 (17)
C(4)-C(5)-C(6)	114.89 (16)	C(9)-C(8)-C(11)	111.50 (18)
C(5)-C(6)-C(7)	85.58 (13)	C(10)-C(8)-C(12)	110.01 (18)
(C) C-C-O Angles			
C(1)-C(7)-O(1)	132.66 (19)	C(8)-C(9)-O(2)	122.67 (18)
C(6)-C(7)-O(1)	132.94 (19)		
(D) C-C-C Angles within the $\pi\text{-C}_5\text{H}_5$ Ligand			
CP(5)-CP(1)-CP(2)	109.57 (29)	CP(3)-CP(4)-CP(5)	108.01 (29)
CP(1)-CP(2)-CP(3)	108.34 (29)	CP(4)-CP(5)-CP(1)	108.26 (29)
CP(2)-CP(3)-CP(4)	105.75 (26)		
(E) H-C-C Angles Involving Methine Hydrogens			
H(1)-C(1)-C(2)	115.6 (13)	H(3)-C(3)-C(4)	124.3 (12)
H(1)-C(1)-C(5)	115.5 (13)	H(4)-C(4)-C(3)	123.8 (12)
H(1)-C(1)-C(7)	112.6 (13)	H(4)-C(4)-C(5)	118.9 (12)
H(2)-C(2)-C(1)	111.7 (12)	H(5)-C(5)-C(1)	117.1 (11)
H(2)-C(2)-C(3)	110.4 (12)	H(5)-C(5)-C(4)	116.0 (11)
H(2)-C(2)-C(8)	109.2 (12)	H(5)-C(5)-C(6)	113.5 (11)
H(3)-C(3)-C(2)	122.7 (12)		
(F) Angles within Methyl Groups			
C(8)-C(10)-H(10A)	110.3 (15)	H(10A)-C(10)-H(10B)	111.3 (20)
C(8)-C(10)-H(10B)	107.0 (15)	H(10A)-C(10)-H(10C)	109.2 (19)
C(8)-C(10)-H(10C)	111.7 (13)	H(10B)-C(10)-H(10C)	107.4 (20)
C(8)-C(11)-H(11A)	112.5 (14)	H(11A)-C(11)-H(11B)	107.1 (22)
C(8)-C(11)-H(11B)	107.9 (18)	H(11A)-C(11)-H(11C)	109.0 (22)
C(8)-C(11)-H(11C)	109.3 (16)	H(11B)-C(11)-H(11C)	111.0 (22)
C(6)-C(12)-H(12A)	109.8 (15)	H(12A)-C(12)-H(12B)	108.2 (21)
C(6)-C(12)-H(12B)	108.4 (16)	H(12A)-C(12)-H(12C)	105.9 (21)
C(6)-C(12)-H(12C)	112.7 (14)	H(12B)-C(12)-H(12C)	111.7 (21)
C(6)-C(13)-H(13A)	110.9 (15)	H(13A)-C(13)-H(13B)	107.1 (23)
C(6)-C(13)-H(13B)	111.8 (18)	H(13A)-C(13)-H(13C)	109.0 (20)
C(6)-C(13)-H(13C)	108.8 (15)	H(13B)-C(13)-H(13C)	109.1 (22)
(G) H-C-C Angles within the $\pi\text{-C}_5\text{H}_5$ Ligand			
HP(1)-CP(1)-CP(5)	126.1 (21)	HP(3)-CP(3)-CP(4)	122.1 (25)
HP(1)-CP(1)-CP(2)	124.2 (21)	HP(4)-CP(4)-CP(3)	125.8 (21)
HP(2)-CP(2)-CP(1)	127.3 (26)	HP(4)-CP(4)-CP(5)	125.9 (22)
HP(2)-CP(2)-CP(3)	124.4 (26)	HP(5)-CP(5)-CP(4)	129.1 (17)
HP(3)-CP(3)-CP(2)	132.0 (25)	HP(5)-CP(5)-CP(1)	122.4 (17)

^a See footnote a to Table III. ^b See footnote c to Table III.

The $[\text{C}_5\text{H}_5(\text{Me}_2\text{C}_2\text{O})_2]$ Ligand. The overall configuration of this ligand is shown clearly in Figure 2. The major portion of this system is defined by a bicyclo[3.2.0]heptenone skeleton, but the ligand as a whole is best named as a disubstituted σ -propionyl group, viz., as the 2-methyl-2-(6',6'-dimethylbicyclo[3.2.0]hept-3'-en-7'-on-2'-yl)propionyl ligand. For the purposes of subsequent discussion, the numbering system of Figure 2 will be used. Atoms C(1)-C(5) define a cyclopentene ring in which the $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^3)$ distances are $\text{C}(1)\text{-C}(2) = 1.529$ (3) Å and $\text{C}(1)\text{-C}(5) = 1.562$ (2) Å [average 1.546 Å], the $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^2)$ distances are $\text{C}(2)\text{-C}(3) = 1.526$ (3) Å and $\text{C}(5)\text{-C}(4) = 1.495$ (3) Å [average 1.511 Å], and the metal-coordinated olefinic linkage, $\text{C}(3)\text{-C}(4)$, is 1.398 (3) Å. Extension of this last bond from the value of 1.335 ± 0.005 Å²² found for uncoordinated olefinic linkages

is, of course, expected and is in keeping with the recognized mode of interaction of an olefin with a transition metal, which involves $\text{d}\text{-}\pi^*$ metal \rightarrow olefin back-donation.²³ Manojlovic-Muir, Muir, and Ibers²⁴ have compiled a list of C=C distances in metal-bonded olefins, which confirms this tendency; however, it should be emphasized that the esd's on these reported olefinic distances are sometimes an order of magnitude greater than that of 0.003 Å calculated for the present compound.

Angles within the cyclopentene ring are $\text{C}(5)\text{-C}(1)\text{-C}(2) = 109.13$ (15)°, $\text{C}(1)\text{-C}(2)\text{-C}(3) = 101.93$ (15)°, $\text{C}(2)\text{-C}(3)\text{-C}(4) = 110.65$ (17)°, $\text{C}(3)\text{-C}(4)\text{-C}(5) = 112.55$ (16)°, and $\text{C}(4)\text{-C}(5)\text{-C}(1) = 102.13$ (15)°; the largest two angles are

(23) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(24) L. Manojlovic-Muir, K. W. Muir, and J. A. Ibers, *Discuss. Faraday Soc.*, 47, 84 (1969); see, especially, Table 3 on pp 88-89.

Table V. Least-Squares Planes^{a, b} within the (π -C₅H₅)Ni[C₅H₅(Me₂C₂O)₂] Molecule

Atom	Dev, Å	Atom	Dev, Å
Plane I: $0.7911X - 0.3492Y + 0.5022Z = 1.3089$			
CP(1)*	-0.013	HP(1)	-0.07
CP(2)*	0.007	HP(2)	0.02
CP(3)*	0.001	HP(3)	-0.05
CP(4)*	-0.009	HP(4)	-0.09
CP(5)*	0.014	HP(5)	-0.04
		Ni	-1.774
		C(3)	-3.321
		C(4)	-3.222
		C(9)	-2.828
Plane II: $-0.5086X - 0.6063Y + 0.6113Z = -1.5012$			
Ni*	0.000	midpt[C(3)-C(4)]*	0.000
C(9)*	0.000		
Plane III: $0.0623X + 0.0495Y + 0.9968Z = 0.1137$			
C(5)*	0.000	C(7)*	0.000
C(6)*	0.000		
Plane IV: $-0.0233X - 0.3183Y + 0.9477Z = -1.7823$			
C(5)*	0.000	C(7)*	0.000
C(1)*	0.000		
Plane V: $-0.1696X - 0.0922Y + 0.9812Z = -0.3380$			
C(1)*	0.000	C(6)*	0.000
C(5)*	0.000		
Plane VI: $0.2218X - 0.1770Y + 0.9589Z = -1.7871$			
C(1)*	0.000	C(6)*	0.000
C(7)*	0.000		
Dihedral Angles, Deg			
I-II	96.68		
III-IV	21.95		
V-VI	23.14		

^a All planes are given in cartesian coordinates such that $X = xa \sin \gamma + [zc(\cos \beta - \cos \alpha \cos \gamma)/\sin \gamma]$, $Y = yb + xa \cos \gamma + zc \cos \alpha$, and $Z = zc[(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)/\sin^2 \gamma]^{1/2}$. This corresponds to defining the mutually orthogonal directions as $b \times c^*$, b , and c^* . ^b The plane is derived using unit weights for atoms marked with an asterisk and zero weight for all other atoms.

centered on the two unsaturated carbon atoms. The slight nonplanarity of the cyclopentene ring may be seen in Figure 3.

The cyclobutanone ring, defined by atoms C(1), C(5), C(6), and C(7), is severely distorted from planarity. Principal dihedral angles [see Table V] are [C(5)-C(6)-C(7)]-[C(7)-C(1)-C(5)] = 21.95° and [C(1)-C(5)-C(6)]-[C(6)-C(7)-C(1)] = 23.14°.

Distances within the four-membered ring are C(1)-C(5) = 1.562 (2) Å, C(5)-C(6) = 1.582 (2) Å, C(6)-C(7) = 1.522 (3) Å, and C(7)-C(1) = 1.525 (3) Å [average 1.548 Å]; angles within this highly strained framework are C(7)-C(1)-C(5) = 86.18 (14)°, C(1)-C(5)-C(6) = 90.03 (14)°, C(5)-C(6)-C(7) = 85.58 (13)°, and C(6)-C(7)-C(1) = 93.75° [average 88.89°].

The carbonyl fragment of the σ -acyl group and the keto group of the cyclobutanone residue have essentially indistinguishable carbon-oxygen distances, with C(9)-O(2) = 1.191 (2) Å and C(7)-O(1) = 1.194 (2) Å.

The four methyl groups all have the expected geometry, with C-CH₃ distances varying from C(6)-C(12) = 1.511 (3) Å to C(8)-C(10) = 1.536 (3) Å, averaging 1.525 ± 0.010 Å.¹⁹

Carbon-hydrogen distances immediately surrounding the bicyclo[3.2.0]heptenonyl moiety range from C(1)-H(1) = 0.91 (2) Å to C(3)-H(3) = 1.00 (2) Å, averaging 0.97 ± 0.03 Å.¹⁹

Hydrogen atoms of the methyl groups are also well defined, with C-H distances ranging from C(11)-H(11B) = 0.93 (3)

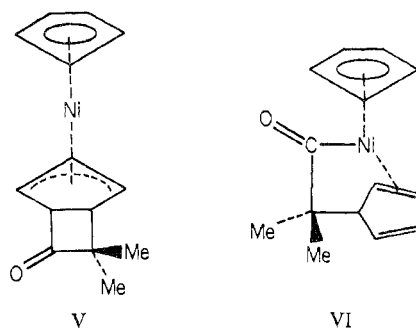
Å to C(13)-H(13C) = 1.05 (3) Å. The average of the 12 independent values is 0.99 ± 0.04 Å.¹⁹ The hydrogen atoms complete regular tetrahedra about the methyl carbon atoms; angles thus defined fall in the ranges C-C-H = 107.0 (15)-112.7 (14)° and H-C-H = 105.9 (21)-111.7 (21)°.

Discussion

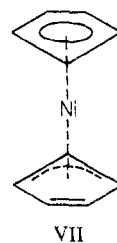
The discussion will be involved with two principal topics: (1) the formation of the (π -C₅H₅)Ni[C₅H₅(Me₂C₂O)₂] molecule and (2) some comments on the nickel-(σ -acyl) linkage. These are considered below in order.

Formation of the Molecule. There is no *direct* information on the mechanism of the reaction of nickelocene with dimethylketene. However, the stoichiometry of the derived product shows that two molecules of dimethylketene have reacted with one molecule of nickelocene. Using the numbering scheme of Figure 2, one dimethylketene moiety participates in a [2 + 2] cycloaddition reaction with the C(1)-C(5) bond, while the other dimethylketene fragment forms a bridge between the nickel atom and C(2).

The two newly arrived dimethylketene fragments take up positions which are mutually trans relative to the plane of the cyclopentene ring. It seems unlikely that the two additions occur simultaneously, so the first step in the reaction could involve the formation of either V or VI.



One is tempted toward favoring V as the intermediate, since there is ample evidence²⁵ that nickelocene often reacts as though it had the structure VII.



The Nickel-(σ -Acyl) Linkage. For some years we have been interested in attempting to determine the degree to which unsaturation or highly electronegative substituents at an α -carbon atom can influence a (transition metal)-carbon bond distance.²⁶

A gross case of contraction in metal-carbon bond length (relative to that of a linkage of unit bond order) does, of course, occur in transition metal carbonyls. Thus, for example, a Mo-CO distance may be as short as ~1.95 Å, a value which is reduced by more than 0.4 Å from the characteristic molybdenum-alkyl distance of ~2.38 Å.²⁷ The explanation for this contraction is, of course, provided by

(25) M. R. Churchill and R. Mason, *Advan. Organometal Chem.*, **5**, 93 (1967); see, especially, Figure 26, p 119.

(26) M. R. Churchill, *Perspect. Struct. Chem.*, **3**, 91 (1970).

(27) P. H. Bird and M. R. Churchill, *Inorg. Chem.*, **7**, 349 (1968).

Table VI. Selected Nickel-Carbon Distances (Å)

Molecule	Bond	Bond length	Ref
(a) Pseudo Five-Coordinate Species			
$(\pi\text{-C}_5\text{H}_5)\text{Ni}[\text{C}_5\text{H}_5\text{C}_2(\text{CO}_2\text{Me})_2]$	Ni-C(sp ³)	1.964 (12) ^a	18
$(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{PPh}_3)(\sigma\text{-CF}_3)$	Ni-CF ₃ {	1.949 (29)	31
		1.947 (34)	
$(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{PPh}_3)(\sigma\text{-C}_6\text{F}_5)$	Ni-($\sigma\text{-C}_6\text{F}_5$)	1.914 (14)	32
$(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{PPh}_3)(\sigma\text{-C}_6\text{H}_5)$	Ni-($\sigma\text{-C}_6\text{H}_5$)	1.904 (7)	33
$(\pi\text{-C}_5\text{H}_5)\text{Ni}[\text{C}_5\text{H}_5(\text{Me}_2\text{C}_2\text{O})_2]$	Ni-CO-R	1.895 (2)	This work
(b) Square-Planar Species			
<i>trans</i> -(PPh ₂ Me) ₂ Ni($\sigma\text{-C}_6\text{Cl}_5$)($\sigma\text{-C}_6\text{F}_5$)	Ni-($\sigma\text{-C}_6\text{F}_5$) [trans to C ₆ Cl ₅]	1.978 (10)	35
<i>trans</i> -(PPh ₂ Me) ₂ Ni($\sigma\text{-C}_6\text{F}_5$) ₂	Ni-($\sigma\text{-C}_6\text{F}_5$) [trans to C ₆ F ₅]	1.939 (3)	36
<i>trans</i> -(PPh ₂ Me) ₂ Ni($\sigma\text{-C}_6\text{F}_5$)Br	Ni-($\sigma\text{-C}_6\text{F}_5$) [trans to Br]	1.880 (4)	37
<i>trans</i> -(PPh ₂ Me) ₂ Ni($\sigma\text{-C}_6\text{Cl}_5$)($\sigma\text{-C}_6\text{F}_5$)	Ni-($\sigma\text{-C}_6\text{Cl}_5$)	1.905 (10)	35
<i>trans</i> -(PEt ₃) ₂ Ni($\sigma\text{-C}\equiv\text{CPh}$) ₂	Ni-($\sigma\text{-C}\equiv\text{CPh}$) {	1.87 (1)	b
		1.847 (11)	c

^a The C(sp³)-Ni-(midpt of olefin) angle in this species is only 69.0°, as opposed to values of 90–100° for L-Ni-C in the other species. This distance, therefore, may well be reduced from a normal Ni-C(sp³) single-bond length, since the molecule might contain a "bent bond." ^b G. R. Davies, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc. A*, 1750 (1967). ^c W. A. Spofford, P. D. Garfagna, and E. L. Amma, *Inorg. Chem.*, 6, 1553 (1967); see, also, *Erratum, ibid.*, 7, 2677 (1968).

the postulation of d- π^* back-donation from the metal to the carbonyl ligand; such a postulate is backed convincingly by a self-consistent pattern of physical observations including, *inter alia*, a reduction in the frequency of C=O stretches, relative to that found in molecular CO.

Our research work has been confined to cases in which smaller, more subtle effects are in play, and we have reported structural data on a number of σ -perfluoroalkyls,^{28–31} σ -aryls,^{32–37} and σ -vinyls.^{38–39} In those cases where a direct comparison with a corresponding σ -alkyl bond length is possible [*i.e.*, in the $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{R}$ and $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{R}$ families], each of the above bond types is found to be contracted by ~ 0.1 Å from a bond of unit bond order.

The available data on nickel-carbon distances are compiled in Table VI. There are indications that the single observed Ni-C(sp³) bond distance may be atypical due to strain in the molecule. We feel that this value is a *lower limit* for a nickel-alkyl bond length in a $(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{L})\text{R}$ molecule (L = neutral monodentate ligand, R = alkyl group). Nevertheless, we see that the observed nickel-(σ -acyl) distance of 1.895 (2) Å in $(\pi\text{-C}_5\text{H}_5)\text{Ni}[\text{C}_5\text{H}_5(\text{Me}_2\text{C}_2\text{O})_2]$ is very similar to the nickel-(σ -aryl) distances of 1.904 (7) and 1.914 (14) Å in $(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{PPh}_3)(\sigma\text{-C}_6\text{H}_5)$ ³³ and $(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{PPh}_3)(\sigma\text{-C}_6\text{F}_5)$ ³² and is contracted significantly (by 0.069 ± 0.012 Å or $\sim 6\sigma$) from the Ni-C(sp³) distance of 1.964 (12) Å in $(\pi\text{-C}_5\text{H}_5)\text{Ni}[\text{C}_5\text{H}_5\text{C}_2(\text{CO}_2\text{Me})_2]$.

(28) M. R. Churchill, *Inorg. Chem.*, 4, 1734 (1965).

(29) M. R. Churchill, *Inorg. Chem.*, 6, 185 (1967).

(30) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, 6, 1213 (1967).

(31) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 161 (1970).

(32) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 2970 (1968).

(33) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 266 (1969).

(34) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 1110 (1969).

(35) M. R. Churchill and M. V. Veidis, *J. Chem. Soc. A*, 3463 (1971).

(36) M. R. Churchill and M. V. Veidis, *J. Chem. Soc., Dalton Trans.*, 670 (1972).

(37) M. R. Churchill, K. L. Kalra, and M. V. Veidis, *Inorg. Chem.*, 12, 1656 (1973).

(38) M. R. Churchill and J. Wormald, *Inorg. Chem.*, 8, 1936 (1969).

(39) M. R. Churchill and J. Wormald, *J. Amer. Chem. Soc.*, 93, 354 (1971).

We note, at this point, that comparison of the Mo-CO-Me distance of 2.264 (14) Å in $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{PPh}_3)(\text{COMe})$ ¹ with the "best available"⁴⁰ Mo-Me distance of 2.383 (10) Å (in $[(\text{azulene})\text{Mo}(\text{CO})_3\text{Me}]_2$ ²⁷) yields a difference of 0.119 ± 0.017 Å or $\sim 7\sigma$. It is not clear, at this time, whether the greater contraction for the molybdenum-(σ -acyl) linkage is a true difference or an artifact of choosing the Ni-C(sp³) distance of 1.964 (12) Å in $(\pi\text{-C}_5\text{H}_5)\text{Ni}[\text{C}_5\text{H}_5\text{C}_2(\text{CO}_2\text{Me})_2]$ as a base line, when a normal Ni-C(sp³) distance would be longer than this value.

Finally, we note that contraction of a metal-(σ -acyl) linkage from a M-C(sp²) linkage of unit bond order is expected as a result of the metal-carbon σ bond being accompanied by some d- π^* back-donation. Such a scheme can conveniently be represented by the valence bond resonance hybrids VIII and IX.



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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-2098.

(40) Based on the value with the lowest esd.