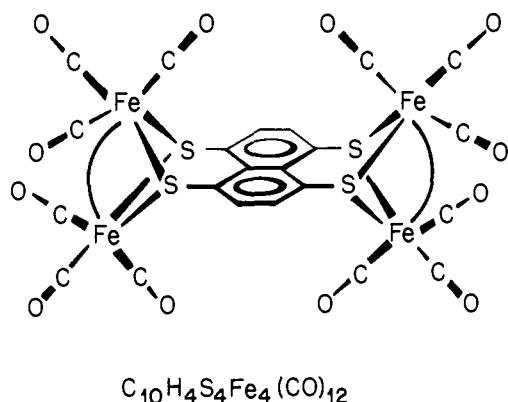


1330 (sh), 1192 (m), and 818 (w)  $\text{cm}^{-1}$ ) as well as FeCO (580 (m) and 562 (m)  $\text{cm}^{-1}$ ) bands. The intensity pattern in the carbonyl region closely resembles that observed in  $\text{Fe}_2(\text{CO})_6\text{S}_2$ .<sup>6a</sup> The electronic spectrum of **3** in dichloromethane solution is consistent with the presence of both the coordinated TTN ( $\lambda_{\text{max}}$  262 nm ( $\epsilon$   $2.15 \times 10^4$ ), 370 (sh,  $1.29 \times 10^4$ ), 400 (sh,  $1.35 \times 10^4$ ), 422 ( $1.43 \times 10^4$ ))<sup>2</sup> and the  $\text{Fe}_2(\text{CO})_6(\text{SR})_2$  moieties ( $\lambda_{\text{max}}$  338 nm ( $\epsilon$   $1.44 \times 10^4$ ), 472 (sh,  $1.23 \times 10^4$ )).<sup>6b</sup> Structure III with two  $\text{Fe}_2(\text{CO})_6$  groups bridged by the TTN ligand can readily be assigned to **3**.



The present "tetrathiolene" systems differ from the normal dithiolenes in the following ways. First, the bridging TTN ligand is capable of accommodating up to a total of four valence electrons. Thus, upon coordination to transition metal complexes via oxidative addition of both S-S bonds, the ligand may exist as formally a neutral entity, mono-, di-, tri-, or tetraanion.<sup>7</sup> This charge-buffering ability is qualitatively similar to two dithiolenes combined.<sup>8a</sup> Second, though each of the two chelating rings  $\text{C}_3\text{S}_2$  contains an "odd" number of  $\pi$  orbitals, yet the ligand as a whole exhibits unusual charge delocalization ability<sup>7</sup> similar to "even" dithiolenes such as  $\text{S}_2\text{C}_2\text{R}_2$ <sup>8a</sup> but in sharp contrast to "odd" dithiolenes such as  $\text{SacSac}$ <sup>8b</sup> which behaves "normally". Third, the reaction of  $\text{Co}_2(\text{CO})_8$  with TTN does not lead to complete elimination of carbonyls as in the case of the reaction of  $\text{Co}_2(\text{CO})_8$  with the dithiolene ligand  $\text{S}_2\text{C}_2(\text{CF}_3)_2$  to give the dimeric  $\text{Co}_2(\text{S}_2\text{C}_2(\text{CF}_3)_2)_4$ .<sup>8c</sup> Fourth, the presumed polymerization of  $(\text{TTN Ni})_x$  (**1**) rather than the formation of  $\text{TTN Ni}_2(\text{CO})_4$  or  $(\text{TTN})_2\text{Ni}$  (cf.  $\text{Ni}(\text{CO})_4 + 2\text{S}_2\text{C}_2(\text{CF}_3)_2 \rightarrow \text{Ni}[\text{S}_2\text{C}_2(\text{CF}_3)_2]_2 + 4\text{CO}$ )<sup>8d</sup> is quite surprising. On the other hand, **1** is probably analogous to the polymeric  $[\text{Ni}(\text{SR})_2]_x$  ( $\text{R} = \text{Et}, \text{Ph}$ ) compounds formed by the reaction of  $\text{Ni}(\text{CO})_4$  with disulfides.<sup>5c</sup>

The most intriguing physical property of **1** and **2** is their electrical conductivity. Figure 1 shows the temperature ( $T$ ) dependence of the powder resistance ( $R$ ) of **1** and **2** which can be characterized by the relation

$$\ln \frac{R}{R_0} = \left( \frac{T}{T_0} \right)^{-1/2} \quad (1)$$

where  $T_0$  is the square of the slope of  $\ln R$  vs.  $T^{-1/2}$  and is inversely proportional to the density of localized states.<sup>9,10</sup> Plots of this type have been observed for a number of known one-dimensional systems<sup>9</sup> and taken as evidence for one-dimensional hopping conductivity between localized states. This theory has been questioned recently by Mott.<sup>10</sup> Nevertheless, this type of plot may be used to characterize the conductivity of these materials. The  $T_0$  values of  $1.7 \times 10^5$  K observed for both **1** and **2** are, however, significantly higher than that generally observed for one-dimensional conductors or semiconductors (range:  $0.5 \sim 5 \times 10^4$  K).<sup>9</sup>

In conclusion, TTN is a highly versatile tetradentate ligand which can be used in synthesizing new coordination compounds with unusual physical or structural properties. Its reaction

chemistry, however, is quite different from the well-known dithiolene systems. We believe that both **1** and **2** are first examples of a new class of organometallic compounds which possess interesting electrical conductivity behavior. We are actively pursuing the reactions of other transition metal complexes with tetrathionaphthalene, tetrathiotetracene, and their analogues.

**Acknowledgments.** We thank C. M. Antosh for the conductivity, C. R. Sprinkle for the molecular weight, and J. E. Bernardini for the x-ray powder pattern measurements. We are also grateful to J. Marshall, M. L. Kaplan, and D. J. Freed for technical assistance.

## References and Notes

- (1) (a) U. T. Muller-Westenhoff and F. Heinrich in "Extended Interactions Between Metal Ions", American Chemical Society Symposium Series 5, Interrante, Ed., 1974, p 396. (b) For the first attempt to join two metal complexes via a tetradentate  $\pi$  ligand, see the excellent work by S. W. Kaiser, R. B. Saillant, W. M. Butler, and P. G. Rasmussen, *Inorg. Chem.*, **15**, 2681, 2688 (1976).
- (2) For the synthesis of TTN, see F. Wudl, B. Miller, and D. E. Schaffer, *J. Am. Chem. Soc.*, **98**, 252 (1976).
- (3) Stoichiometry was established by microanalysis performed by Midwest Microlab, Ltd., Indianapolis, Ind., and Galbraith Laboratories, Knoxville, Tenn. Calcd for  $(\text{C}_{10}\text{H}_4\text{S}_4\text{Ni})_x$  (**1**): C, 38.61; H, 1.30. Found: C, 38.35; H, 1.80. Calcd for  $[\text{C}_{10}\text{H}_4\text{S}_4\text{Co}_2(\text{CO})_2]_x$  (**2**): C, 33.81; H, 0.95. Found: C, 32.82; H, 1.26. Calcd for  $\text{C}_{10}\text{H}_4\text{S}_4\text{Fe}_4(\text{CO})_{12}$  (**3**): C, 32.38; H, 0.50. Found: C, 32.48; H, 0.85.
- (4) The four strongest bands in the IR spectrum (Csl) of free TTN occur at 1537 (s), 1360 (s), 1378 (sh), 1182 (vs), and 795 (vs)  $\text{cm}^{-1}$ .
- (5) (a) K. A. Jensen, *Z. Anorg. Chem.*, **252**, 227 (1944); (b) F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1549 (1935); (c) R. G. Hayter and F. S. Humiec, *J. Inorg. Nucl. Chem.*, **26**, 807 (1964).
- (6) (a) W. M. Scovell and T. G. Spiro, *Inorg. Chem.*, **13**, 304 (1974); (b) E. Bayer, H. Eckstein, H. Hagenmaier, D. Josef, J. Koch, P. Krauss, A. Roder, and P. Schretzmann, *Eur. J. Biochem.*, **8**, 33 (1969).
- (7) TTN  $\text{Pt}_2(\text{PPh}_3)_4$  (B. K. Teo, F. Wudl, J. Marshall, and A. Kruger, *J. Am. Chem. Soc.*, **99**, 2349 (1977)) undergoes four reversible oxidations to give the mono-, di-, tri- and tetracations.
- (8) (a) G. N. Schrauzer, *Acc. Chem. Res.*, **2**, 72 (1969), and references cited therein; (b) R. L. Martin and I. M. Stewart, *Nature*, **210**, 522 (1966); (c) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **3**, 814 (1964); (d) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *ibid.*, **2**, 1227 (1963).
- (9) (a) J. P. Ferraris, D. O. Cowan, V. Walalka, and J. A. Perlestein, *J. Am. Chem. Soc.*, **95**, 948 (1973); (b) T. W. Thomas et al., *J. Chem. Soc.*, 2050 (1972); (c) A. P. Ginsberg et al., *Inorg. Chem.*, **15**, 514 (1976); (d) V. K. S. Shante, C. M. Varma, and A. N. Bloch, *Phys. Rev. B*, **8**, 4885 (1973).
- (10) N. Mott, "Metal-Insulator Transitions", Taylor and Francis, London, 1974, Chapters 4 and 6.

Boon-Keng Teo,\* F. Wudl, J. J. Hauser, A. Kruger  
Bell Laboratories, Murray Hill, New Jersey 07974

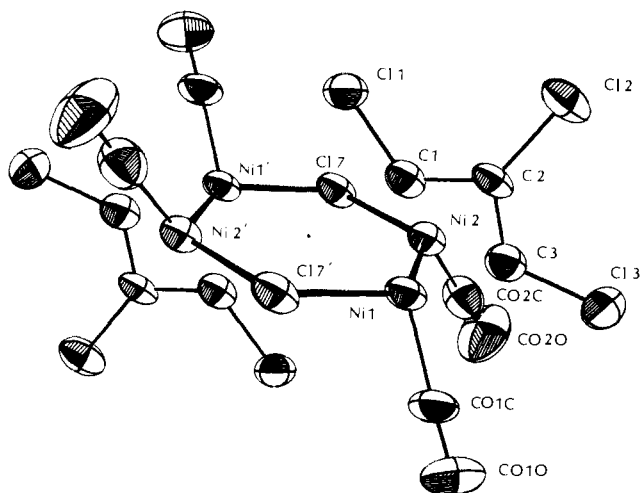
Received December 2, 1976

## Synthesis and Structure of a Novel Perchlorinated Organonickel Complex Containing a Bridging Trichloropropenyl Ligand

Sir:

Previous studies of the interaction of cyclopropenium cations,  $\text{C}_3\text{R}_3^+$ , with organometallic substrates have demonstrated a wide variety of different modes of coordination and reactivity for these species. Examples include trihapto coordination,<sup>1-4</sup> carbon monoxide insertion leading to formation of a *trihapto*oxocyclobutenyl ligand,<sup>5,6</sup> oxidative addition with ring cleavage,<sup>7</sup> electrophilic attack on ligands such as the cyclopentadienyl ring,<sup>6</sup> ring opening and oxygen insertion,<sup>8,9</sup> and asymmetric  $\pi$  coordination.<sup>10</sup> Here we wish to report a completely different mode of coordination exhibited by these aromatic but highly strained  $2\pi$  3C ring systems.

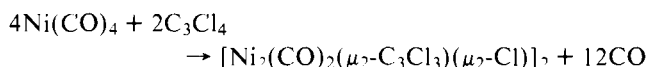
Tetrachlorocyclopropene, as prepared and characterized by West and coworkers,<sup>11</sup> is easily converted to the aromatic  $2\pi$  3C trichlorocyclopropenium ion in the presence of Lewis acids such as  $\text{AlCl}_3$ ,  $\text{SbCl}_5$ , or  $\text{FeCl}_3$ . This fact together with the known reactivity of  $\text{Ni}(\text{CO})_4$  toward allyl chloride<sup>12</sup> and



**Figure 1.** Molecular configuration of the  $[\text{Ni}_2(\text{CO})_2(\mu_2\text{-C}_3\text{Cl}_3)(\mu_2\text{-Cl})]_2$  cluster.

triphenylcyclopropenium chloride<sup>1-4</sup> to generate  $\pi$  complexes suggested that it may be possible to stabilize the  $\text{C}_3\text{Cl}_3^+$  moiety through trihapto coordination to a nickel carbonyl fragment. We were unable to realize this desired result, but, fortunately, were able to stabilize the  $\text{C}_3\text{Cl}_3$  species as a ring-opened propenyl ligand in a unique bonding configuration bridging two metal atoms. This communication describes the preparation and single-crystal x-ray crystallographic identification of the novel perchlorinated organometallic complex  $[\text{Ni}_2(\text{CO})_2(\mu_2\text{-C}_3\text{Cl}_3)(\mu_2\text{-Cl})]_2$ .

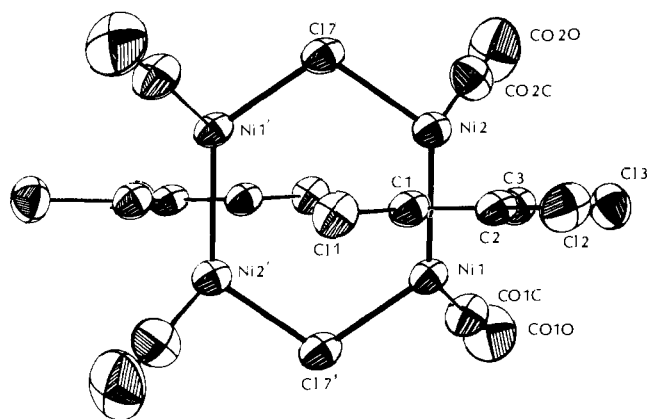
Nickel tetracarbonyl reacts with  $\text{C}_3\text{Cl}_4$  in a wide variety of different solvents (benzene, paraffins, ether, cyclohexene) to generate in high yield (60–70% isolated) a red-orange crystalline material which is insoluble in all solvents with which it does not react. The reaction can be summarized as



based upon the x-ray analysis of the product. Complete characterization of this air stable molecule was precluded by its low solubility and extreme shock sensitivity.<sup>13</sup> Needle-shaped crystals suitable for single-crystal x-ray work were isolated directly from the reaction mixture when benzene was used as the solvent.

The results of the solid-state structural investigation<sup>14</sup> are shown in two representative views of the  $[\text{Ni}_2(\text{CO})_2(\mu_2\text{-C}_3\text{Cl}_3)(\mu_2\text{-Cl})]_2$  cluster (Figures 1 and 2). The centrosymmetric unit cell contains two formula units and, since each formula unit is found to lie on a crystallographic center of inversion, two half-molecules comprise the independent unit.<sup>15</sup> The  $[\text{Ni}_2(\text{CO})_2(\mu_2\text{-C}_3\text{Cl}_3)(\mu_2\text{-Cl})]_2$  complex consists of a six-membered  $\text{Ni}_4\text{Cl}_2$  ring which is planar in each case to within a maximum deviation of 0.03 Å from the least-squares best plane through the six atoms. Chlorine atoms bridge non-bonded pairs of nickel atoms,  $\text{Ni}(1)\cdots\text{Ni}(2)'$  and  $\text{Ni}(2)\cdots\text{Ni}(1)'$ , while, symmetrically disposed in a unique position bridging the bonded pair of nickel atoms,  $\text{Ni}(1)\text{—Ni}(2)$ , lies a trichloropropenyl ligand. This  $\text{C}_3\text{Cl}_3$  ring-opened species is planar to within a maximum deviation of 0.05 Å and is orthogonal to the  $\text{Ni}_4\text{Cl}_2$  plane as can be seen in Figure 2. The coordination sphere of each nickel atom is completed by a terminal carbonyl ligand which is bent away from the  $\text{C}_3\text{Cl}_3$  bridging group.

Examination of the bond lengths within the  $\text{Ni}_4\text{Cl}_2$  ring gives no indication of extremely short, multiply-bonded, nickel atoms even though a crude electron count demonstrates that the nickel atoms are electron deficient. The independent  $\text{Ni—Ni}$  bonds bridged by the trichloropropenyl ligands are 2.528 (1) and 2.544 (1) Å<sup>16</sup> and are long when compared with those of



**Figure 2.** Alternate view of the  $[\text{Ni}_2(\text{CO})_2(\mu_2\text{-C}_3\text{Cl}_3)(\mu_2\text{-Cl})]_2$  cluster displaying the orthogonality of the  $\text{C}_3\text{Cl}_3$  and  $\text{Ni}_4\text{Cl}_2$  fragments.

some hydrocarbon-bridged nickel complexes, e.g., 2.36 Å in  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\mu_2\text{-CO})]_2$ ,<sup>17</sup> 2.338 (7) Å in  $\text{Ni}_4(\text{CN-}t\text{-Bu})_7$ ,<sup>18</sup> 2.329 (4) Å in  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}_2(\mu_2\text{-C}_2\text{Ph}_2)]$ ,<sup>19</sup> 2.265 (1) Å in  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}_2(\mu_2\text{-Ph}_2\text{P}(\text{O})\text{C}\equiv\text{CCF}_3)]$ ,<sup>20</sup> and 2.345 (3) Å in  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}_2(\mu_2\text{-C}_2\text{H}_2)]$ ,<sup>21</sup> but more reasonable when compared with those of others, e.g., 2.617 (2) Å in  $[(1,5\text{-COD})_2\text{Ni}_2(\mu_2\text{-C}_2\text{Ph}_2)]$ ,<sup>22</sup> 2.47 Å in  $[(\text{CO})_3\text{Co}]_2(\mu_2\text{-C}_2\text{Ph}_2)$ ,<sup>23,24</sup> 2.463 (1) Å in  $[(\text{CO})_3\text{Co}]_2(\mu_2\text{-C}_2\text{-}t\text{-Bu}_2)$ ,<sup>24,26</sup> and 2.540 (1) Å in  $[\text{Ni}(\mu_2\text{-C}_5\text{H}_7)]_2$ .<sup>27</sup> The  $\text{Ni—Ni}$  separation in nickel metal measures 2.492 Å.<sup>28</sup> The  $\text{M—M}$  separations in bridged binuclear organometallic complexes are observed to vary over a wide range and to be dependent upon the steric requirements of both the bridging and terminal ligands. Cotton and co-workers<sup>29</sup> have estimated the  $\text{Ni—Ni}$  separation in bridged complexes of this type to be in the range 2.32–2.36 Å for a single bond when bridged in a sterically favorable manner. In the case of the  $\text{C}_3\text{Cl}_3$  bridged pair of nickel atoms, very short interatomic  $\text{C}\cdots\text{C}$  contacts of 2.79–2.84 Å are found between  $\text{C}(3)$  and the carbonyl carbon atoms  $\text{CO}(1)$  C and  $\text{CO}(2)$  C. These short nonbonded contacts, when compared with the sum of the van der Waals radii of carbon of >3.30 Å,<sup>30</sup> no doubt restrict the closeness of approach of the two nickel atoms. The chlorine-bridged pair of nickel atoms are separated by non-bonded distances of 3.687 (1) Å while the  $\text{Ni—Cl}$  bond measures 2.237 (1) Å (four values, range 2.235–2.240). The average bond angles within the ring are 111.1 (1)° for  $\text{Ni}(1)'\text{—Cl}(7)\text{—Ni}(2)$ , 123.6 (1)° for  $\text{Ni}(1)\text{—Ni}(2)\text{—Cl}(7)$ , and 125.4 (1)° for the  $\text{Ni}(2)\text{—Ni}(1)\text{—Cl}(7)'$  angle.

The trichloropropenyl ligand is planar and symmetrically bridges the bonded pair of nickel atoms such that its plane is approximately orthogonal to the  $\text{Ni}_4\text{Cl}_2$  plane.<sup>31</sup> The  $\text{Ni—C}$  distances which measure 1.961 (3) (four values, range 1.947–1.978) for  $\text{Ni—C}(1)$ , 2.293 (3) (four values, range 2.254–2.328) for  $\text{Ni—C}(2)$ , and 1.925 (4) Å (four values, range 1.920–1.929) for  $\text{Ni—C}(3)$  indicate a slight degree of asymmetry between the two ends of the propenyl ligand with  $\text{C}(3)$  being on average  $\sim 0.03$  Å closer to the nickel atoms. The terminal  $\text{C}(1,3)\text{—Ni}$  distances compare quite favorably with the 1.90–2.00 Å  $\text{Ni—C}$  bond lengths observed in acetylene-bridged nickel complexes<sup>19–23,26</sup>

The  $\text{C—C}$  and  $\text{C—Cl}$  bond lengths within the trichloropropenyl bridging ligand suggest a high degree of electron delocalization.  $\text{C—C}$  bond lengths average 1.396 (5) Å (four values, range 1.381–1.404) and may be compared with  $\text{C—C}$  distances in acetylene bridged complexes (1.35–1.40),<sup>19–23,26,32</sup> allyl complexes (1.35–1.48),<sup>33</sup> and propenyl, cyclopropenyl, and cyclobutenyl complexes (1.37–1.48).<sup>4,5,7–10,34</sup> The  $\text{C}(1)\text{—C}(2)\text{—C}(3)$  bond angle spans 99.7 (6)°. The chelating  $\text{C}(1)\cdots\text{C}(3)$  distance measures 2.132 Å and agrees with previously observed values obtained for complexes containing terminal propenyl ligands, viz., 2.15 Å in  $[\text{Ir}(\text{CO})\text{Cl—}$

$[P(\text{Me})_3]_2[\text{C}_3(\text{C}_6\text{H}_5)_3]^+7$  and 2.06 and 2.10 Å in the  $[[\text{endo-}[\text{exo-C}_4(\text{C}_6\text{H}_5)_4(\text{OC}_2\text{H}_5)]\text{Pd}(\mu_2\text{-Cl})]_2$  complexes, respectively.<sup>34a</sup> The C—Cl bond lengths which average 1.715 (3) Å (six values, range 1.710–1.721) are typical of C—Cl distances found in many chloro-substituted olefins.<sup>35</sup>

The short C—C and C—Cl bond distances, the planarity of the  $\text{C}_3\text{Cl}_3$  moiety, and its orthogonality to the Ni—Ni bond, are indicative of a completely delocalized  $\text{Ni}_2(\mu_2\text{-C}_3\text{Cl}_3)$  fragment. One aspect of the bonding can be explained in terms of the modified Dewar–Chatt–Duncanson model<sup>36</sup> used to describe the bonding in dinuclear acetylene bridged complexes where the C—C vector of the acetylene triple bond (and consequently the  $\pi$  electron cloud) is orthogonal to the M—M vector. In the  $[\text{Ni}_2(\text{CO})_2(\mu_2\text{-C}_3\text{Cl}_3)(\mu_2\text{-Cl})_2]$  complex the open three-carbon propenyl fragment C(1,2,3) with its  $\pi$  cloud is also positioned orthogonal 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) and C(3). A more in-depth molecular orbital analysis is required to rationalize fully all aspects of the delocalized  $\text{Ni}_2(\mu_2\text{-C}_3\text{Cl}_3)$  bonding.

The preparation and isolation of this novel perchlorinated propenyl cluster complex extends 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 adduct  $[\text{Ir}(\text{CO})\text{Cl}[\text{P}(\text{CH}_3)_3]_2[\text{C}_3(\text{C}_6\text{H}_5)_3]^+7$  where a four-membered iridocycle is formed serves as an example of a mononuclear precursor to the binuclear complex reported here. It also suggests that the use of halosubstituted  $\text{C}_3\text{X}_4$  and  $\text{C}_3\text{X}_3^+$  species may prove a fruitful synthetic approach into perhalogenated organometallic complexes. We are currently pursuing synthetic work to probe the utility of these ideas.

**Acknowledgments.** This research was generously supported by the National Science Foundation (Grant No. MPS-74-06348 A01). The x-ray data were collected by Molecular Structure Corporation, College Station, Texas. The use of the IBM 370-145 computer at the Center for Computing and Data Processing Services at the University of Maine, Orono, is gratefully acknowledged.

## References and Notes

- E. W. Gowling and S. F. A. Kettle, *Inorg. Chem.*, **3**, 604 (1964).
- W. K. Olander and T. L. Brown, *J. Am. Chem. Soc.*, **94**, 2139 (1972).
- R. G. Hayter, *J. Organomet. Chem.*, **13**, P1 (1968).
- (a) M. D. Rausch, R. M. Tuggle, and D. L. Weaver, *J. Am. Chem. Soc.*, **92**, 4981 (1970); (b) R. M. Tuggle and D. L. Weaver, *Inorg. Chem.*, **10**, 1504 (1971); (c) R. M. Tuggle and D. L. Weaver, *ibid.*, **10**, 2599 (1971); (d) P. S. Welcker and L. J. Todd, *ibid.*, **9**, 286 (1970).
- (a) C. E. Coffey, *J. Am. Chem. Soc.*, **84**, 118 (1962); (b) R. B. King and A. Efraty, *J. Organomet. Chem.*, **24**, 241 (1970); (c) J. Potenza, R. Johnson, D. Mastropaulo, and A. Efraty, *ibid.*, **64**, C13 (1974).
- M. Green and R. P. Hughes, *J. Chem. Soc., Chem. Commun.*, 862 (1976).
- R. M. Tuggle and D. L. Weaver, *Inorg. Chem.*, **11**, 2237 (1972).
- G. M. Macjunas, Ph.D. Dissertation, Carnegie–Mellon University, 1975.
- M. D. McClure, Ph.D. Dissertation, Carnegie–Mellon University, 1975.
- M. D. McClure and D. L. Weaver, *J. Organomet. Chem.*, **54**, C59 (1973).
- R. West, *Acc. Chem. Res.*, **3**, 130 (1970), and references contained therein.
- (a) E. O. Fischer and G. Burger, *Z. Naturforsch., Teil B*, **16**, 77 (1961); (b) E. O. Fischer and G. Burger, *Chem. Ber.*, **94**, 2409 (1961).
- 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.
- $[\text{Ni}_2(\text{CO})_2(\mu_2\text{-C}_3\text{Cl}_3)(\mu_2\text{-Cl})_2]$ : triclinic; P1; Delaunay reduced cell parameters are  $a = 7.141$  (1),  $b = 10.637$  (2),  $c = 13.950$  (2) Å,  $\alpha = 88.41$  (1),  $\beta = 91.35$  (1),  $\gamma = 104.58$  (1)°;  $V = 1025.0$  Å<sup>3</sup>;  $\rho_{\text{obsd}} = 2.23$  vs.  $\rho_{\text{calcd}} = 2.28$  g/cm<sup>3</sup> for  $Z = 2$ . The centrosymmetric P1 space group was suggested by the statistical distribution of the normalized structure factors calculated from a Wilson plot. The structure was solved by MULTAN and refined by full anisotropic least-squares analysis to  $R_1(\text{F}) = 4.8\%$  and  $R_2(\text{F}) = 6.1\%$  for the 2304 independent reflections with  $I > 2\sigma(I)$ .
- These two molecules are similar and minor variation in the bond distances and bond angles for the most part are attributable to slightly different crystal packing forces. Differences where significant are noted; otherwise average bond distances and angles for the two independent half-molecules are reported.
- The 0.016 Å difference between the two crystallographically independent Ni—Ni distances more than likely indicates that the ESDs of 0.001 Å noted are underestimates. Since the two molecular units are chemically equivalent, one may independently derive the magnitude of the likely errors by direct comparison of the chemically equivalent bonds. Such a procedure suggests that the true uncertainty in the Ni—Ni distance is  $\sim 0.005$  Å.
- A. A. Hock and O. S. Mills, "Advances in the Chemistry of Coordination Compounds", S. Kirschner, Ed., MacMillan, New York, N.Y., 1961, p 647.
- V. W. Day, R. O. Day, J. S. Kristoff, F. J. Hirsekorn, and E. L. Muetterties, *J. Am. Chem. Soc.*, **97**, 2571 (1975).
- O. S. Mills and B. W. Shaw, *J. Organomet. Chem.*, **11**, 595 (1968).
- R. J. Restivo, G. Ferguson, T. W. Ng, and A. J. Carty, *Inorg. Chem.*, **16**, 172 (1977).
- Y. Wang and P. Coppens, *Inorg. Chem.*, **15**, 1122 (1976).
- V. W. Day, S. S. Abdel-Meguid, S. Dabestani, M. G. Thomas, W. R. Pretzer, and E. L. Muetterties, *J. Am. Chem. Soc.*, **98**, 8289 (1976).
- W. G. Sly, *J. Am. Chem. Soc.*, **81**, 18 (1959).
- Dimeric tricarbonyl cobalt and cyclopentadienyl nickel complexes containing bridging acetylene ligands are electronically equivalent. The single-bond covalent radii<sup>25</sup> differ only by 0.01 Å: 1.16 for cobalt vs. 1.15 Å for nickel.
- L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N.Y., 1960.
- F. A. Cotton, J. D. Jamerson, and B. R. Stults, *J. Am. Chem. Soc.*, **98**, 1774 (1976).
- C. Kruger, *Angew. Chem., Int. Ed. Engl.*, **8**, 678 (1969).
- W. B. Pearson, "Lattice Spacings and Structures of Metals and Alloys," Pergamon Press, London, 1957.
- R. D. Adams, F. A. Cotton, and R. A. Rusholme, *J. Coord. Chem.*, **1**, 275 (1971).
- A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
- The dihedral angle between the best planes of the  $\text{Ni}_4\text{Cl}_2$  and  $\text{C}_3\text{Cl}_3$  fragments measure 85 and 86°, respectively for the two independent half-molecules.
- R. S. Dickson and P. J. Fraser, *Adv. Organomet. Chem.*, **12**, 323 (1974).
- (a) R. Uttech and H. Dietrich, *Z. Krist.*, **122**, 60 (1965); (b) G. D. Andreeti, G. Bocelli, and P. Sgarabotto, *Cryst. Struct. Commun.*, **3**, 109 (1974); (c) T. S. Cameron and C. K. Prout, *Acta Crystallogr.*, **B28**, 2021 (1972); (d) B. Barnett, B. Bussemeier, P. Heimbach, P. W. Jolly, C. Kruger, I. T. Katchenko, and G. Wilke, *Tetrahedron Lett.*, 1457 (1972).
- (a) L. F. Dahl and W. E. Oberhansli, *Inorg. Chem.*, **4**, 629 (1965); (b) L. F. Dahl and W. Oberhansli, *ibid.*, **4**, 150 (1965); (c) R. F. Bryan, *J. Am. Chem. Soc.*, **86**, 733 (1964).
- Tables of Interatomic Distances and Configuration in Molecules and Ions. Special Publication No. 11, Chemical Society, London, 1958.
- (a) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **C71**, (1951); (b) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

R. G. Posey, G. P. Khare, P. D. Frisch\*

Department of Chemistry, University of Maine  
Orono, Maine 04473

Received March 11, 1977

## Sterically Hindered Isomers of Retinal from Direct Irradiation of the All-Trans Isomer. Isolation of 7-cis-Retinal<sup>1</sup>

Sir:

Wald, Hubbard, and Brown established that the all important 11-cis-retinal can be obtained by direct irradiation of the all-trans isomer in a dilute ethanol solution.<sup>2</sup> In a steady-state mixture, the amount of 11-cis was estimated to reach 25% of the combined isomer composition. They further showed in a simple and elegant experiment that from the photolysate all-trans, 13-cis, and 11-cis isomers can be isolated by fractional recrystallization.<sup>2b</sup> To the vision researchers this procedure remains the most direct route to small amounts of pure 11-cis-retinal.

The mechanistic details of the photoreaction have since been examined in great detail, but much confusion still exists. The product mixtures have been analyzed by UV spectroscopy,<sup>3-5</sup> thin layer chromatography (TLC),<sup>4</sup> and more recently by high pressure liquid chromatography (HPLC),<sup>6</sup> quantum yields determined under direct and sensitized irradiation condi-