$[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$, depending on the nature of the isothiocyanate molecule itself. The first mode observed for the so-called activated isothiocyanates EtOC(O)NCS and PhC(O)NCS involves formation of 1:1 adducts in which the isothiocyanate ligand bridges the metal, bound by carbon to one and by sulfur to the other metal center. The ethoxycarbonyl isothiocyanate adduct, in turn, reacts further with a variety of heteroallenes yielding unusual condensation products that have resulted from C–N bond formation by nucleophilic attack of the nitrogen atom of the coordinated EtOC(O)NCS ligand at carbon of the incoming heteroallene molecule. In addition, these condensation reactions are accompanied by a 1,3 shift of the ethoxycarbonyl moiety to either the nitrogen of the added isothiocyanate molecule or to one of the sulfur atoms if CS_2 is the added heteroallene. With the nonactivated PhNCS and MeNCS molecules a third reactivity mode, yielding the corresponding isocyanide ligands, is observed.

This study is significant in several aspects. It is believed to be the first in which all three types of reaction products have been isolated and characterized for the same metal system; in particular isolation of the 1:1 ethoxycarbonyl isothiocyanate adduct is an important development since it allows the preparation of a variety of heteroallene condensation products, which prove useful for delineating the reaction mechanism. This study is also the first in which the coupling of *two* isothiocyanate molecules by C–N, rather than by C–S, bond formation is clearly established. A scheme is presented for these two-metal-center induced coupling reactions that can be applied, with slight modifications, to related mononuclear chemistry and is therefore attractive in that it outlines a unified approach to heteroallene coupling reactions.

The presence of the second metal center in these reactions has a very significant effect on the chemistry as compared with that displayed by the mononuclear analogues. Coordination of the heteroallene sulfur atom by the second metal lowers its nucleophilicity with the result that subsequent condensation reactions occur at nitrogen rather than at sulfur. This modification of reactivity by the second metal center has obvious relevance to organic synthesis. So, for example, in this study we observe the syntheses of a variety of new isothiocyanate molecules by the coupling of the ethoxycarbonyl isothiocyanate molecule with other heteroallenes followed by the 1,3 shift of the ethoxycarbonyl group.

Acknowledgment. We thank NSERC (Canada) and the University of Alberta for support of this research, the University of Alberta for a scholarship to J.A.E.G., and Dr. R. G. Ball for X-ray data collection.

Registry No. 1, 73680-37-2; 2, 79272-83-6; 3, 89618-34-8; 4, 89618-35-9; 5, 89618-36-0; 6, 89618-37-1; 7, 89636-96-4; 8, 89618-38-2; 9, 89618-39-3; 10, 89618-40-6; 11, 89618-41-7; 12, 89618-42-8; 13, 89618-43-9; 14, 89618-44-0; 15, 89618-45-1; 16, 89618-46-2; EtOC(O)NCS, 16182-04-0; PhC(O)NCS, 532-55-8; PhNCS, 103-72-0; MeNCS, 556-61-6; CS_2, 75-15-0; allene, 463-49-0.

Supplementary Material Available: A figure of the $^{31}P\{^1H\}$ NMR spectrum of compound **15** and tables of anisotropic thermal parameters, the derived hydrogen parameters, least-squares planes, and the observed and calculated structure factor amplitudes for $[Rh_2Cl_2(CO)(\mu\text{-}SCNC(S)N(Ph)C(O)OEt)(DPM)_2]\cdot 0.5C_7H_8$ (11 pages). Ordering information is given on any current masthead page.

Synthesis and Reactivity of (Chlorovinyl)nickel Complexes: An Unusual Symmetrization Reaction. X-ray Crystal Structure of $[Ni(CCl{=}CCl_2)_2(PMe_2Ph)_2]$

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Received March 8, 1983

The oxidative addition of $CCl_2{=}CCl_2$, $CCl_2{=}CHCl$, *trans*-$CHCl{=}CHCl$, and $CH_2{=}CCl_2$ to $[Ni(PPh_3)_n]$, prepared in situ from $NiCl_2$, PPh_3, and $NaBH_4$, gives square-planar *trans*-$[NiCl(\text{chlorovinyl})(PPh_3)_2]$. The addition takes place at the less hindered C–Cl bond, with retention of geometry. The PPh_3 ligand is replaced by dppe in $[NiCl(C_2Cl_3)(PPh_3)_2]$ giving $[NiCl(C_2Cl_3)dppe]$ whereas the action of N-donor bidentate ligands gives a symmetrization reaction, forming $[NiCl_2(LL)]$ and $[Ni(C_2Cl_3)_2(LL)]$ (LL = 2,2′-bpy and *o*-phen). The ligand bpy may be replaced by phosphines like PMe_2Ph and PEt_3 in the trichlorovinyl complex. The crystal structure of *trans*-$[Ni(C_2Cl_3)_2(PMe_2Ph)_2]$ (monoclinic, space group $P2_1/c$, $a = 9.203$ (2) Å, $b = 16.005$ (3) Å, $c = 9.604$ (2) Å, $\beta = 114.79$ (3)°, $Z = 2$) shows the presence of the anti and syn isomers in the solid. The Ni–P bond distance and the mean Ni–C bond distance are 2.201 (1) and 1.91 (1) Å, respectively. ^{31}P and ^{13}C NMR spectra indicate that similar amounts of syn and anti isomers are present in solution.

Introduction

The reaction of polyhaloethylenes with low-valent transition-metal complexes of Ni, Pd, and Pt gives different types of compounds. The reaction between fluorinated olefins and M(0) complexes leads initially to the compounds $[M(\text{olefin})L_2]$ which contain a rigid σ-bonded three-membered ring and which can become the σ-alkenyl complexes $[MX(\text{fluorovinyl})L_2]$.

Table I. Analytical, Decomposition, and Spectral Data of $[NiClR(PPh_3)_2]$ and $[Ni(C_2Cl_3)_2L_2]$[a]

R or L	decomp pt, °C	% C		% H		% Cl		% N		¹H NMR
		found	calcd	found	calcd	found	calcd	found	calcd	
$CCl{=}CCl_2$ (1)	188-190	61.0	60.92	4.0	4.04	19.1	18.35			*b*
$CH{=}CCl_2$ (2)	149-152	62.6	63.86	4.2	4.38	14.8	14.88			4.65 ppm[b]
$CCl{=}CH_2$ (3)	103-107	67.1	67.09	4.7	4.75	10.5	10.42			*c*
trans-$CH{=}CHCl$ (4)	110-112	67.2	67.09	4.7	4.75	10.6	10.42			*c*
bpy (5)	202-205	36.6	35.35	1.7	1.70	44.9	44.74	5.9	5.89	
o-phen (6)	248-250	38.4	38.46	1.76	1.62	41.7	42.57	5.55	5.61	
PEt_3 (8)	170-172	34.8	34.57	5.4	5.44	37.8	38.27			*d*
PMe_2Ph (7)	169-173	40.5	40.32	3.7	3.73	35.4	35.70			*d*

[a] All the analytical data of the compounds not shown in this table are in the supplementary material. [b] Two broad signals at 7.75 and 7.40 ppm due to the ortho and meta-para protons of PPh_3. [c] Unstable in solution. [d] See Table VII.

The olefin compounds are easily isolated when M = Pt,[1,2] but when M = Ni,[3,4] they are more unstable. The mechanism of vinyl rearrangement of $[Pt(C_2F_3Br)L_2]$ (L = PPh_3, $PMePh_2$) has been studied.[5]

The σ-alkenyl derivatives can be obtained from [M(fluoroolefin)L_2] or directly by the action of halopolyfluoroethylenes on $[ML_4]$ complexes. This reaction has been observed with a variety of phosphine ligands and leads to a large number of compounds of Pt,[1,2] Pd,[6,7] and Ni.[8] The vinyl and divinyl derivatives $[MXRL_2]$ and $[MR_2L_2]$ have also been obtained by the action of $BrMgCF{=}CF_2$ or $LiCF{=}CF_2$ on the compounds $[MX_2(PEt_3)_2]$ (M = Pt, Pd, Ni).[9] An excess of polyfluoroethylene can give five-membered-ring compounds like $[M(CF_2)_4L_2]$. This reaction is observed on treating $[NiL_4]$ with an excess of C_2F_4.[3,4,10] When M = Pt, the olefin compounds initially formed cannot add another C_2F_4 molecule. $[Pt(CF_2)_4(1,5\text{-}C_8H_{15})]$ has been obtained by irradiating a mixture of [Pt-*i*-Pr_2(COD)] and C_2F_4.[2]

The compounds containing polychlorolefins have been less extensively studied. Some complexes of the type [Pt(olefin)L_2] have obtained from $[Pt(PPh_3)_4]$ or $[Pt(PPh_3)_2$(*trans*-stilbene)]. These complexes contain weak Pt–olefin bonds, and the olefins are easily replaced by an excess of PPh_3. The corresponding vinyl derivatives *cis*- and *trans*-$[PtXRL_2]$ (R = C_2Cl_3, $CH{=}CCl_2$, *trans*-C_2H_2Cl, $CCl{=}CH_2$) can be obtained from [Pt(olefin)L_2].[11,12] Five-membered-ring compounds such as those obtained with C_2F_4 have not been described.

The reaction of C_2Cl_4, C_2HCl_3, and *cis*- and *trans*-1,2-$C_2H_2Cl_2$ with $[Pd(PPh_3)_4]$ gives directly the *trans*-vinyl derivatives with retention of configuration of the olefin.[13]

The preparation and study of the chlorovinyl derivatives of nickel have not been carried out systematically; only compounds with the trichlorovinyl group have been described: *trans*-$[NiCl(CCl{=}CCl_2)L_2]$, L = PEt_3,[14] $PMePh_2$,[15b] PMe_2Ph,[15a] PMe_3,[15b] PPh_3,[16] and $[Ni(CCl{=}CCl_2)L'L_2]ClO_4$.[15b] However, these compounds must be intermediates in the cross-coupling reactions of magnesium reagents with vinyl halides. Thus, yields higher than 80% have been obtained in the coupling reactions of PhMgBr with 1,2-dichloroethylene in the presence of catalytic amounts of $[NiX_2L_2]$ complexes.[17-19]

The stability and reactivity of the vinyl compounds obtained by the reaction of $[Ni(PPh_3)_n]$ and the polychloroethylenes C_2Cl_4, C_2HCl_3, 1,1-$C_2H_2Cl_2$, and *trans*-$C_2H_2Cl_2$ are described. Only the σ-chlorovinyl derivatives [NiCl(chlorovinyl)$(PPh_3)_2$] are obtained. When PPh_3 is substituted by bidentate nitrogenous ligands (N-N) such as bpy or *o*-phen, an unusual symmetrization process is observed, with the formation of $[Ni(C_2Cl_3)_2$(N-N)]. Although a symmetrization process has been postulated in the decomposition mechanism of some [NiX(aryl)L_2][21,22] complexes, to our knowledge the formation of $[NiEt_2$(bpy)] from [NiClEt(bpy)] and $[Ni(C{\equiv}CR)_2(PBu_3)_2]$ from $[NiBr(C{\equiv}CR)(PBu_3)_2]$ are the only cases described.[23]

Results and Discussion

The compounds $[NiClR(PPh_3)_2]$, R = $CCl{=}CCl_2$ (1), $CH{=}CCl_2$ (2), $CCl{=}CH_2$ (3), and *trans*-$CH{=}CHCl$ (4) have been obtained by oxidative addition of the corresponding polychloroethylenes to $[Ni(PPh_3)_n]$ prepared "in situ". The reaction is carried out with a mixture of $NiCl_2{\cdot}6H_2O$, PPh_3, and an excess of RCl to which an ethanol solution of $NaBH_4$ is added dropwise. To obtain **1**, the reaction should be carried out at 50 °C since Ni(I) compounds precipitate at room temperature. To obtain **3** and **4**, the reaction should be carried out at −10 °C to precipitate the organometallic compounds. **2** is prepared at room temperature.

The reaction to obtain the organometallic compound

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with *cis*-CHCl=CHCl under the same conditions does not allow us to isolate the expected compound. The addition of *cis*-CHCl=CHCl on $[Pt(PPh_3)_4]$ leads to $[PtCl_2(PPh_3)_2]$.[12] We have not been able to prepare compounds of the type $[Ni(olefin)(PPh_3)_2]$ analogous to those described with C_2F_4.[3] Neither has it been possible to add more than one polychloroethylene molecule to obtain a species of the type $[Ni(CF_2)_4L_2]$.[4,10]

The new compounds are yellow solids. **1** and **2** are air stable, but the two monochloro derivatives **3** and **4** decompose in a few weeks even under nitrogen. **1** is stable in refluxing benzene; conversely, benzene solutions of **3** retain their color for a few minutes, but those of **4** instantly decolorize. A nitrogen atmosphere or the addition of free PPh_3 markedly retards the decomposition of these organometallic compounds.

The stability of these compounds is determined by the electronegativity of R and by the possible blocking of the coordination sites of Ni perpendicular to the plane of the complex. **1** and **2** possess three and two chlorine atoms in the vinyl group, and both compounds contain one chlorine cis to the nickel atom (ortho effect). The monochloro derivatives **3** and **4** do not contain chlorine atoms cis on the β-carbon; compound **3** with the chlorine atom bonded to the α-carbon is more stable than **4**, as a result of the predictably larger electronegativity of the $CCl{=}CH_2$ group.

All of the compounds are diamagnetic and have a square-planar geometry. A trans arrangement of the phosphine ligands is indicated by the absence in the IR spectrum of the PPh_3 band at 550 cm^{-1} typical of cis complexes.[20] The ^{31}P NMR spectrum of compound **1** shows only a signal at δ 22.0 (referenced to H_3PO_4).

The analytical results and decomposition temperatures are given in Table I. The decomposition temperatures markedly decrease on decreasing the number of chlorine atoms in the ligand. NMR spectra have been obtained for **1** and **2** which are the only stable compounds in solution.

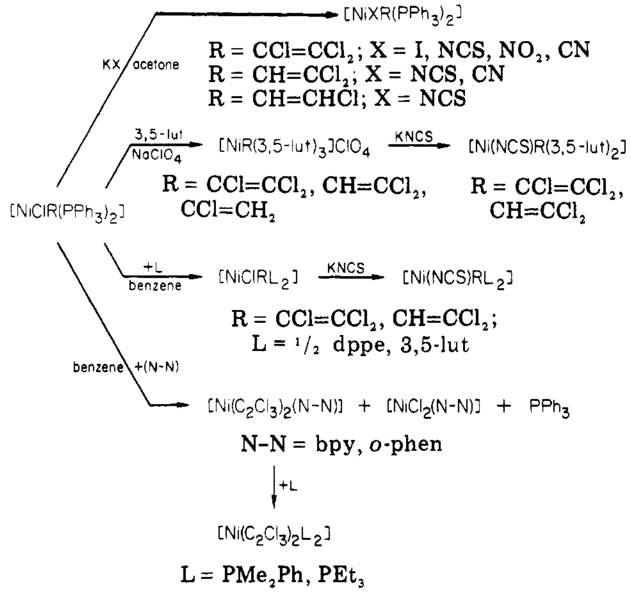
The retention of configuration in the oxidative addition reaction of the polychlorovinyl group is confirmed by the decomposition in solution of the organometallic compounds with HCl or Cl_2. The benzene solutions of **1** and **2** treated at room temperature with a stream of HCl are decomposed in 30 min. The compounds recovered are $CHCl{=}CCl_2$ and $CH_2{=}CCl_2$, in agreement with the proposed formulation. This confirms that the oxidative addition of $CHCl{=}CCl_2$ on the Ni(0) species takes place also at the less hindered C–Cl bond.[21] The reaction of **3** and **4** with chloroform solutions saturated with Cl_2 gives $CCl_2{=}CH_2$ and *trans*-CHCl=CHCl, respectively, also in agreement with the expected formulation.

Reactivity. The results obtained both for the Cl or PPh_3 exchange and for the formation of the ionic species are given in Scheme I. The reactions are always carried out under nitrogen and in the presence of an excess of neutral ligand. The study of the monochlorovinyl derivatives is restricted by their low stability in solution.

The substitution reactions of PPh_3 are worth mentioning. If the entering ligand is a phosphine or monodentate amine, the substitution product is obtained, but for a bidentate nitrogenous ligand the substitution reaction is accompanied by a symmetrization process.

Substitution of the Chloride Ligand. The substitution of the chloride ligand in **1** is carried out in refluxing acetone when the entering ligand is I^- or NCS^- but should be carried out at room temperature and in the presence of free phosphine for the entering ligands NO_2^- or CN^-; otherwise the complexes are decomposed.

Scheme I



The substitution in complex **2** for X = NCS^- or CN^- should be carried out at room temperature and in the presence of PPh_3 to avoid decomposition. KNO_2 causes decomposition of the starting organometallic compound.

The substitutions in **3** and **4** are carried out under nitrogen and with free PPh_3. Unidentified polymeric materials appear when CN^- and NCS^- are used. Only [NiNCS(*trans*-CH=CHCl)$(PPh_3)_2$] gives correct analyses. This result suggests that the ligands NCS^-, CN^-, and NO_2^- besides replacing the ligand Cl^- are able to replace also the phosphine.

Ionic Compounds. Silver salts cannot be used systematically with (triphenylphosphine)nickel complexes, since the phosphine and the Ag^+ ion form stable and scarcely soluble compounds, which precludes formation of the ionic derivatives $[NiRL(PPh_3)_2]ClO_4$.[24]

The action of a neutral ligand such as 3,5-lutidine (lut) on the benzene solutions of $[NiClR(PPh_3)_2]$ containing a large anion ($NaClO_4$) causes the replacement of PPh_3 and gives the ionic species $[NiR(3,5\text{-lut})_3]ClO_4$. The reaction is carried out in benzene, in which the ionic compound is scarcely soluble.

The ionic compound with R = $CCl{=}CCl_2$ precipitates directly but those with R = $CH{=}CCl_2$ and $CCl{=}CH_2$ are obtained after the solutions are concentrated to dryness under reduced pressure. The organometallic compound decomposes when R = CH=CHCl. The greater stability of the monochlorovinyl derivative containing a chlorine atom bonded to the α-carbon of the polychlorovinyl group may be related to the predictably larger electronegativity of this group. The ionic compounds are not obtained, and the starting products are recovered when the reaction is attempted with α-picoline. This may be related to the difficulty of introducing four ligands with ortho substituents around the metallic atom.

If acetone solutions of $[NiR(3,5\text{-lut})_3]ClO_4$ are treated with KNCS at room temperature, *trans*-$[Ni(NCS)R(3,5\text{-lut})_2]$ is obtained only for R = $CCl{=}CCl_2$ or $CH{=}CCl_2$. The action of KCl, instead of KNCS, does not lead to the analogous compound, the starting product being recovered. The compounds have a *trans* geometry as indicated by the ^1H NMR spectrum of $[Ni(NCS)(C_2Cl_3)(3,5\text{-lut})_2]$. The spectrum at room temperature shows only three signals

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(δ 2.20, 7.20, and 8.40) which correspond to the methyl and aromatic protons in the ortho and para positions of 3,5-lutidine, respectively. The presence of one signal for each type of proton indicates the equivalence of the two lutidine ligands of the complex in solution.

Exchange of Neutral Ligands: Symmetrization Process. The exchange reactions of PPh_3 by dppe carried out in benzene give new organometallic compounds only from **1** and **2**; decomposition occurs in the other cases. The reaction of **1** and 3,5-lutidine at room temperature for 6 h does not yield pure $[NiCl(CCl{=}CCl_2)(3,5\text{-lut})_2]$.

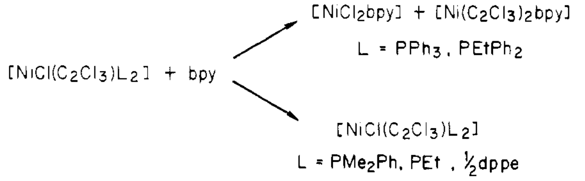
A green precipitate of $[NiCl_2(N\text{-}N)]$ is observed if the exchange reaction of PPh_3 by the bidentate nitrogenous ligands bpy or *o*-phen is carried out in refluxing benzene solutions of **1**; from the resulting solution $[Ni(C_2Cl_3)_2(N\text{-}N)]$ complexes [N-N = bpy (**5**) and *o*-phen (**6**)] are obtained.

For the preparation of more soluble bis(trichlorovinyl) complexes, bpy can be replaced by PMe_2Ph or PEt_3 in refluxing benzene for 24 h. Compounds $[Ni(C_2Cl_3)_2L_2]$ [L = PMe_2Ph (**7**) and PEt_3 (**8**)] obtained can be studied by NMR.

Analytical and decomposition data for these compounds are given in Table I. The crystal structure of $[Ni(C_2Cl_3)_2(PMe_2Ph)_2]$ has also been determined. The action of bpy on the benzene solutions of the other organometallic **2**, **3**, and **4** leads to decomposition.

The solutions of **5**, **6**, **7**, and **8** are stable toward a stream of HCl at room temperature for 2 h. Passing chlorine into $CHCl_3$ solutions decomposes the organometallic compounds rapidly, and perchlorobutadiene is obtained. This oxidatively induced reductive elimination is common when the compounds $[MR_2L_2]$ are treated with oxidants.[25,26]

No symmetrization products are detected after benzene solutions of $[NiCl(C_2Cl_3)L_2]$ (L = PPh_3, PMe_2Ph) are refluxed under nitrogen for 24 h; starting material is recovered unaltered. The symmetrization process is induced when the phosphine (PPh_3 or $PEtPh_2$) is substituted by a bidentate nitrogenous ligand such as bpy or *o*-phen.



If the substitution occurs with a bidentate phosphine such as dppe, then the exchange takes place without symmetrization.

The process of symmetrization occurs regardless of the ligand X since the same reaction is observed for X = Cl or NCS (L = PPh_3). The same reaction is observed in benzene, acetone, or C_2Cl_4.

It has not been possible to prepare $[NiCl(C_2Cl_3)bpy]$ by reacting $[NiCl_2(bpy)]$ with C_2Cl_4 and $NaBH_4$ nor by treating $[NiCl(C_2Cl_3)(PPh_3)_2]$ with bpy under mild conditions.

Description of the Crystal Structure of $[Ni(C_2Cl_3)_2(PMe_2Ph)_2]$. The crystal structure of *trans*-$[Ni(C_2Cl_3)_2(PMe_2Ph)_2]$ consists of two discrete molecules in each unit cell separated by normal van der Waals interactions. The syn and anti isomers are present in the lattice.

Figure 1 shows a view of the molecule with the atom numbering. The carbon atoms of the trichlorovinyl group can be located in two different sites, so then four different molecular distributions are possible in the network, two for each isomer. The chlorine atoms are in the same position in both isomers. The numbers (9), (10) and (9)′, (10)′ denote the two different sites of the carbon atoms according to Figure 1. The underline denotes analogous atoms of the opposite ligand.

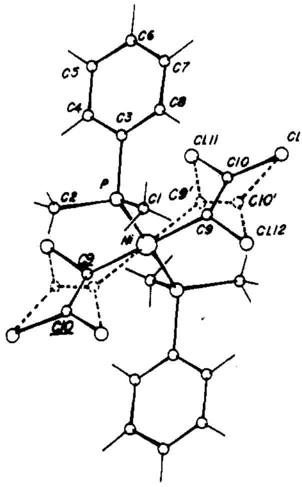


Figure 1. Molecular structure $[Ni(C_2Cl_3)_2(PMe_2Ph)_2]$, with the numbering scheme.

Table II. Crystallographic Data

Crystal Data
monoclinic
space group: $P2_1/c$
$a = 9.203\ (2)$ Å[a]
$b = 16.005\ (3)$
$c = 9.604\ (2)$
$\beta = 114.79\ (3)$
$V = 1284.3\ (8)$ Å^3
$Z = 2$
d(calcd) = 1.54 Mg m^{-3}

Measurement of Intensity Data
diffractometer: Nonius CAD-4
radiation: Mo Kα
monochromator: graphite crystal
scan type: ω scan
data collected: 1900$|F_{hkl}|$
obsd reflctns: 1535 ($I > 2.5\sigma(I)$)
$2\theta_{max}$: 47°

[a] Accurate centering of 25 reflections resulted in unit cell dimensions.

Crystal data, bond distances and angles, and the positional and thermal parameters are given in Tables II–V.

The Ni–P bond distance 2.201 (1) Å and the mean Ni–C bond distance 1.91 (1) Å are similar to those found in $[Ni(C_6F_5)_2(PMePh_2)_2]$[27] (Ni–P = 2.206 (1) Å and Ni–C = 1.939 (3) Å) or in $[Ni(C_6Cl_5)(C_6F_5)(PMePh_2)_2]$[28] (Ni–P = 2.230 (2) Å, Ni–C_6Cl_5 = 1.905 (10) Å, and Ni–C_6F_5 = 1.978 (10) Å). For $[Ni(C_6Cl_5)(C_6F_5)(PMePh_2)_2]$, the C_6Cl_5 ligands forms an angle of 85.02° with the $[NiC_2P_2]$ plane and an angle of 5.62° with the C_6F_5 ligand (the C_6F_5 group defines an angle of 79.42° with the $[NiC_2P_2]$ plane). Furthermore, each of the C_6F_5 ligands forms an angle of 86.13° with the $[NiC_2P_2]$ plane in centrosymmetric $[Ni(C_6F_5)_2(PMePh_2)_2]$.

The inner coordination sphere of the molecule $[NiC_2P_2]$ is square planar in the anti isomer but is distorted square planar in the syn isomer.

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Table III. Bond Lengths (Å) and Angles (deg) for [Ni(C_2Cl_3)$_2$(PMe_2Ph)$_2$] with Estimated Standard Deviations in Parentheses

Bond Lengths

Ni-P	2.201 (1)	C(3)-C(8)	1.363 (9)	C(9)-Cl(12)	1.846 (8)
Ni-C(9)	1.91 (1)	C(4)-C(5)	1.41 (1)	C(9)'-Cl(11)	1.855 (8)
Ni-C(9)'	1.93 (3)	C(5)-C(6)	1.38 (1)	C(10)-Cl(11)	1.698 (9)
P-C(1)	1.808 (8)	C(6)-C(7)	1.37 (1)	C(10)-Cl(13)	1.690 (9)
P-C(2)	1.821 (7)	C(7)-C(8)	1.42 (1)	C(10)'-Cl(12)	1.62 (1)
P-C(3)	1.843 (6)	C(9)-C(10)	1.37 (2)	C(10)'-Cl(13)	1.85 (1)
C(3)-C(4)	1.356 (9)	C(9)'-C(10)'	1.28 (3)		

Bond Angles

P-Ni-*p*	180.0 (1)	C(1)-P-C(3)	107.5 (3)	Ni-C(9)-C(10)	128 (1)
C(9)-Ni-C($\underline{9}$)	180.0 (1)	C(2)-P-C(3)	104.9 (3)	Ni-C(9)'-C(10)'	126 (2)
C(9)'-Ni-C($\underline{9}$)'	180.0 (1)	P-C(3)-C(4)	117.6 (5)	Ni-C(9)-Cl(12)	119 (1)
C(9)-Ni-C(9)'	21.3 (2)	P-C(3)-C(8)	119.0 (5)	Ni-C(9)'-Cl(11)	115 (1)
P-Ni-C(9)	88.5 (3)	C(4)-C(3)-C(8)	123.4 (6)	C(9)-C(10)-Cl(11)	112 (1)
P-Ni-C(9)'	92.9 (5)	C(3)-C(4)-C(5)	119.3 (8)	C(9)-C(10)-Cl(13)	125 (1)
C($\underline{9}$)'-Ni-C(9)	158.7 (2)	C(4)-C(5)-C(6)	118.0 (9)	Cl(11)-C(10)-C(13)	123 (1)
Ni-P-C(1)	113.1 (3)	C(5)-C(6)-C(7)	122.1 (8)	C(9)'-C(10)'-Cl(12)	120 (2)
Ni-P-C(2)	117.5 (2)	C(6)-C(7)-C(8)	119.2 (8)	C(9)'-C(10)'-Cl(13)	116 (2)
Ni-P-C(3)	112.0 (2)	C(7)-C(8)-C(3)	117.9 (8)	Cl(12)-C(10)'-Cl(13)	124 (2)
C(1)-P-C(2)	100.8 (4)				

Table IV. Positional Parameters (×10^4) for the Atoms of [Ni(C_2Cl_3)$_2$(PMe_2Ph)$_2$]

	x/a	*y/b*	*z/c*
Ni	0 (0)	0 (0)	0 (0)
P	1965 (2)	204 (1)	2277 (2)
C(1)	1453 (14)	930 (6)	3443 (11)
C(2)	3796 (10)	676 (6)	2349 (10)
C(3)	2615 (8)	−776 (4)	3371 (7)
C(4)	3683 (10)	−1258 (5)	3102 (9)
C(5)	4139 (14)	−2039 (7)	3850 (11)
C(6)	3457 (15)	−2280 (7)	4821 (13)
C(7)	2388 (14)	−1782 (8)	5095 (12)
C(8)	1968 (9)	−995 (5)	4362 (9)
C(9)	−1280 (16)	−400 (9)	996 (16)
C(9)'	−1062 (33)	−788 (19)	781 (28)
C(10)	−1557 (18)	−1208 (16)	1281 (16)
C(10)'	−2033 (22)	−610 (7)	1384 (21)
Cl(11)	535 (3)	1900 (1)	−691 (3)
Cl(12)	2544 (3)	−350 (2)	−1451 (3)
Cl(13)	2729 (4)	1506 (3)	−2157 (4)
H(C1)	2000 (14)	763 (6)	4643 (11)
H(C1)'	172 (14)	975 (6)	3060 (11)
H(C1)''	1883 (85)	1512 (46)	3097 (79)
H(C2)	4320 (10)	314 (6)	1728 (10)
H(C2)'	4679 (10)	779 (6)	3507 (10)
H(C2)''	3667 (84)	1210 (46)	1821 (84)
H(C4)	4190 (10)	−1052 (5)	2330 (9)
H(C5)	4985 (14)	−2436 (7)	3656 (11)
H(C6)	3782 (15)	−2882 (7)	5372 (13)
H(C7)	1910 (14)	−1993 (8)	5887 (12)
H(C8)	1130 (9)	−593 (5)	4558 (9)

The mean plane of these atoms in the syn isomer NiC(9)C($\underline{9}$)'P$\underline{P}$ is $-4.757x + 13.628y + 2.853z = 0.139$. The deviations of each atom are as follows: Ni, −0.139; P, −0.146; C(9), 0.209; $\underline{P}$, −0.132; C($\underline{9}$)', 0.208 Å.

The trichlorovinyl ligands are in the same plane in the anti isomer, but in the syn isomer there are some deviations from the mean plane defined for [NiC_4]. The mean planes and deviations (Å) of the atoms are given in Table VI.

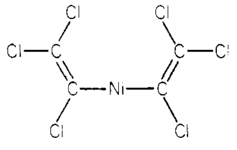
The angles between the planes anti (no prime)–anti (prime) is 2.76°. The mean planes of the inner coordination sphere of the molecule [NiC_2P_2] and the mean planes defined by the trichlorovinyl ligands are at angles of 82.3° for the anti isomer and 95.6° for the syn isomer.

The chlorine atoms are in the same position in both isomers within the limits of error for the structural determination. This fact is most likely caused by steric interactions among the different chlorine atoms and the nickel atom since the distances Cl(11)–Ni = 3.194 (2) Å, Cl(11)–Cl(13) = 2.973 (3) Å, Cl(12)–Cl(13) = 3.067 (4) Å, and Cl(12)–Ni = 3.236 (2) Å are similar or shorter than the sum of the Van der Waals radii (Cl–Cl = 3.5 Å and Cl–Ni = 3.2 Å).

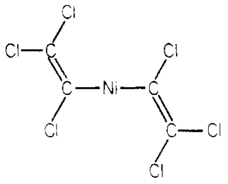
The C_2Cl_3 ligand is slightly distorted with an increase of the Ni–C(9)–C(10) and C(9)–C(10)–Cl(13) angles with mean values of 127 (1) and 122 (1)°, respectively, and a shortening of the C(10)–C(9)–Cl(12) angle of 114 (1)°. However, the vibration of the double bond in the ligand occurs at 1540 cm^{-1}, typical of the vinyl groups. Therefore, the distortion seems to be of steric origin.

The steric protection of the coordination positions perpendicular to the plane of the complex is caused not only by Cl(11) (ortho effect) but also by Cl(12).

Compounds 7 and 8 in Solution. The ^1H, ^{31}P, and ^{13}C NMR spectra of the compounds 7 and 8 show the presence of the two isomers syn and anti in solution.



syn



anti

The ^{31}P NMR spectra of 7 and 8 (Table VII) show two signals of similar intensity, and since the phosphorous atoms are equivalent in each isomer, each signal must correspond to one isomer. The slightly more intense signal can be assigned to the anti isomer taking into account that it is the less hindered isomer.

The ^1H NMR spectrum of 8 (Table VII) shows the typical pseudoquintuplet corresponding to the methyl protons of the phosphine which appear usually when the two phosphine ligands are trans to each other. The ^1H NMR spectrum of 7 shows a pseudoquintuplet due to the PMe_2Ph methyl groups. This multiplet must be considered as three superimposed triplets with a central triplet of intensity similar to the sum of the other two. The syn isomer must give only a triplet since all the methyl protons are equivalent; conversely, the anti isomer, lacking a symmetry plane through the P–Ni–P axis, gives two triplet signals.[29,30]

The ^{13}C NMR spectrum of 7 shows the signal for each carbon atom of the molecule. The signals for the methyl carbon atoms of either the phosphines or the vinyl groups

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Table V. Thermal Parameters for the Atoms of [Ni(C_2Cl_3)$_2$(PMe_2Ph)$_2$][a]

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni	364 (9)	589 (9)	305 (9)	69 (5)	79 (6)	−121 (5)
P	394 (11)	578 (11)	317 (11)	−2 (7)	59 (8)	−104 (7)
C(1)	951 (73)	773 (63)	667 (49)	−23 (47)	357 (52)	44 (55)
C(2)	569 (46)	715 (49)	637 (50)	106 (43)	95 (38)	−275 (41)
C(3)	413 (38)	657 (39)	244 (31)	10 (28)	24 (28)	−117 (31)
C(4)	789 (50)	650 (42)	482 (43)	22 (34)	186 (37)	106 (39)
C(5)	1044 (83)	902 (58)	642 (61)	−73 (49)	53 (59)	236 (58)
C(6)	1086 (75)	715 (62)	789 (64)	249 (52)	0 (57)	−103 (57)
C(7)	883 (81)	1158 (88)	650 (61)	417 (61)	132 (55)	−258 (73)
C(8)	538 (41)	713 (45)	546 (40)	100 (36)	171 (32)	−140 (35)
C(9)	339 (64)	313 (85)	214 (65)	53 (59)	76 (47)	−90 (60)
C(9)′	860 (187)	352 (158)	691 (138)	−178 (136)	147 (123)	99 (145)
C(10)	501 (82)	760 (198)	247 (80)	34 (96)	185 (61)	−399 (106)
C(10)′	1045 (107)	206 (50)	997 (119)	130 (59)	661 (102)	73 (65)
Cl(11)	815 (15)	519 (12)	847 (16)	22 (10)	236 (12)	−28 (10)
Cl(12)	746 (15)	1060 (19)	996 (20)	−266 (15)	488 (14)	77 (13)
Cl(13)	1161 (23)	1781 (31)	943 (20)	180 (20)	611 (18)	−655 (21)

[a] All the quantities given in the table are ×10⁴. The temperature factor is in the form $\exp(-2\pi^2\Sigma U_{ij}h_ih_ja^*_ia^*_j)$.

Table VI

Anti Isomer

Plane: C(10), C(9), Ni, C($\underline{9}$), C($\underline{10}$)
$4.334x + 0.552y + 5.789z = 0$
C(10), C(9), Ni, C($\underline{9}$), C($\underline{10}$), 0.000
Cl(11), 0.063; Cl(12), −0.243; Cl(13), −0.017

Plane: C(10)′, C(9)′, Ni, C($\underline{9}$)′, C($\underline{10}$)′
$3.950x + 0.756y + 6.136z = 0$
C(10)′, C(9)′, Ni, C($\underline{9}$)′, C($\underline{10}$)′, 0.000
Cl(11), 0.069; Cl(12), −0.088; Cl(13), 0.132

Syn Isomer

Plane: C(10), C(9), Ni, C($\underline{9}$)′, C($\underline{10}$)′
$4.040x + 0.950y + 6.049z = 0.031$
Ni, −0.030; C(9), 0.017; C(10), 0.001
C($\underline{9}$)′, 0.001; C($\underline{10}$)′, 0.011
Cl(11), −0.009; Cl(12), −0.147; Cl(13), 0.029
Cl($\underline{11}$), −0.052; Cl($\underline{12}$), 0.086; Cl($\underline{13}$), −0.090

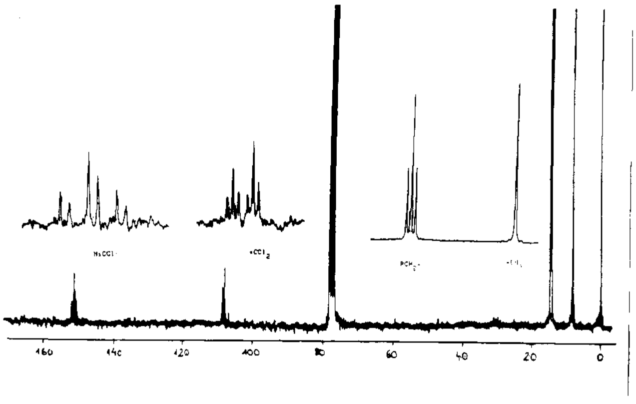

Figure 2. $^{13}C\{^1H\}$ spectra of [Ni(C_2Cl_3)$_2$(PEt_3)$_2$].

Table VII. NMR Spectra of [Ni(C_2Cl_3)$_2L_2$]
[L = PMe_2Ph (7) and L = PEt_3 (8)]

	^{1}H NMR,[a] δ				
	CH_2	CH_3			others
anti-**7**		1.66 t 1.62 (t, J_{PH} = 4 Hz)[b]			H(2,6) 7.5 H(3,4,5) 7.4
syn-**7**		1.64 (t, J_{PH} = 4 Hz)[b]			
8	1.64[c]	1.20 (q, J_{PH} = 7.5 Hz)[b]			
	^{13}C NMR,[a] δ				
	CH_2	CH_3	NiCCl=	=CCl_2	others
7		13.0[c]	150.3[c]	108.2[c]	C(1) 134.3[c] C(2,6) [c] 130.3[c] C(3,5) 128.1 C(4) 129.5
anti-**8**	14.37 (t, J_{CP} = 12.8 Hz)[b]	8.1	150.6 (t, $^2J_{CP}$ = 33 Hz)	107.4 (t, $^3J_{CP}$ = 6.6 Hz)	
syn-**8**			150.4 (t, $^2J_{CP}$ = 33.1 Hz)	107.9 (t, $^3J_{CP}$ = 6.8 Hz)	
		7		**8**	
		anti	syn	anti	syn
^{31}P NMR,[d] δ		0.35	−0.25	13.16	12.80

[a] Me_4Si reference. [b] "Virtual coupling". [c] Broad unresolved signal. [d] 85% H_3PO_4 reference; +, lower fields.

are not sufficiently simplified. The signals for carbons 1, 2, and 6 of the aromatic ring seem to be formed by pairs of triplets which would correspond to the couplings of the two isomers with the two trans phosphorous atoms (virtual coupling).

The ^{13}C NMR spectrum of compound 8 (Figure 2) shows the triplet of the methylene carbons of the phosphine in accord with the trans structure of the molcule, due to the virtual coupling with the two phosphorous atoms observed in this type of compound. The signals for the vinyl carbons correspond to the superimposing of two triplets. The coupling with two equal cis phosphorous atoms gives two triplets that appear duplicated due to the difference between the carbons of both isomers syn and anti of the molecule in solution. The more intense signal is tentatively assigned to the less hindered anti isomer.

Increasing the temperature of a chlorobenzene solution of 7 does not cause coalescence of the peaks in the ^{31}P spectra. This suggests that rotation of the trichlorovinyl ligands about the Ni–C bonds is restricted.

Experimental Section

General Remarks. The oxidative addition reactions and those with the organometallic compounds containing monochlorovinyl ligands were carried out under carefully deoxygenated nitrogen. NMR spectra were obtained on a Perkin-Elmer R12-A spectrometer or on a Varian XL 200 spectrometer. Gas chromatographic analyses were carried out on a Hewlett-Packard 5710 A gas chromatograph with a 5% SE-30 on a Gas Chrom Q column connected to a Hewlett-Packard 3390 A integrator. IR spectra were recorded on a Beckman IR-20 A spectrophotomer. Elemental analyses were carried out at the Institut de Qui̊mica Bio-Orgànica de Barcelona (C.S.I.C.).

Preparative Methods. Preparation of $[NiClR(PPh_3)_2]$ (1–4). $NaBH_4$ (0.38 g, 10 mmol) in ethanol was added dropwise to a mixture of $NiCl_2{\cdot}6H_2O$ (1.2 g, 5 mmol), PPh_3 (4 g, 15 mmol), and $C_2H_nCl_{4-n}$ (25 mmol) in ethanol (25 mL) at 50, 20, an −10° C, respectively, for C_2Cl_4, $CHCl_3$, and 1,1- and *trans*-1,2-$C_2H_2Cl_2$. After the addition, the mixture was left to stir. The solids $[NiClR(PPh_3)_2]$ were filtered and washed with several portions of 1% HCl, water, and ethanol. When possible (R = $CCl{=}CCl_2$ and $CH{=}CCl_2$) the products were recrystallized from dichloromethane/ethanol. The yields were about 50–70%.

Preparation of $[NiX(C_2Cl_3)(PPh_3)_2]$ (X = I, NCS). $[NiCl(CCl{=}CCl_2)(PPh_3)_2]$ (0.5 g) was dissolved in acetone (25 mL), an excess of KX was added, and the resulting solution was refluxed for 1.5 h. After being filtered, the solution was concentrated under reduced pressure to dryness. The resulting solid was washed with water and recrystallized from dichloromethane/ethanol. The yield was about 75% for X = I and 95% for X = NCS.

Preparation of $[NiXR(PPh_3)_2]$ (X = CN, NO_2, R = $CCl{=}CCl_2$; X = CN, NCS, R = $CH{=}CCl_2$; X = NCS, R = *trans*-$CH{=}CHCl$). $[NiClR(PPh_3)_2]$ (0.6 mmol) was dissolved in acetone (50 mL), KX (0.7 mmol) and PPh_3 (0.2 mmol) were added, and the solution was stirred at room temperature for 10 min for X = NCS and R = *trans*-$CH{=}CHCl$ and up to 4 h for X = CN and R = $CH{=}CCl_2$. After being filtered, the solution was concentrated under reduced pressure to dryness. The solid was rinsed with water, filtered, and recrystallized from chloroform/ethanol for R = $CCl{=}CCl_2$. The yields were about 60–90% except for [NiNCS(*trans*-$CH{=}CHCl$)$(PPh_3)_2$] (10%).

Preparation of [NiClR(dppe)] (R = $CCl{=}CCl_2$, $CH{=}CCl_2$). 1,2-Bis(diphenylphosphino)ethane (dppe; 1.2 g, 3 mmol) was added to a solution of $[NiClR(PPh_3)_2]$ (1.5 mmol) in benzene (50 mL) under nitrogen, and the resulting mixture was stirred at refluxing temperature for R = $CCl{=}CCl_2$ and at room temperature for R = $CH{=}CCl_2$. After being filtered, the solution was concentrated to dryness and the solid washed several times with ether. The yields were about 80%.

Preparation of $[NiR(3{,}5\text{-lut})_3]ClO_4$ (R = $CCl{=}CCl_2$, $CH{=}CCl_2$, $CCl{=}CH_2$). $[NiClR(PPh_3)_2]$ (0.15 mmol) was dissolved in benzene (50 mL), and finely powdered $NaClO_4$ (0.30 mmol) and 3,5-lutidine (5 mmol) were added. The mixture was stirred at room temperature for 1.5 h. (R = $CCl{=}CCl_2$), 30 min (R = $CH{=}CH_2$), or 15 min (R = $CCl{=}CH_2$). The precipitate was filtered when R = $CCl{=}CH_2$, but in the other cases concentration under reduced pressure to dryness was necessary. The solid was washed several times with 1% HCl and water. $[Ni(C_2Cl_3)(3{,}5\text{-lut})_3]ClO_4$ was recrystallized from chloroform/ethanol. The yields were about 40–60%.

Preparation of $[Ni(NCS)R(3{,}5\text{-lut})_2]$ (R = $CCl{=}CCl_2$, $CH{=}CCl_2$). $[NiR(3{,}5\text{-lut})_3]ClO_4$ (0.2 mmol) was dissolved in acetone (40 mL), and KNCS (0.08 g) was added. The solution was stirred at room temperature for 1 h (R = $CCl{=}CCl_2$) or 0.5 h (R = $CH{=}CCl_2$). Then it was concentrated under reduced pressure to dryness. The solids were washed with water. Yields were 90% (R = $CCl{=}CCl_2$) and 40% (R = $CH{=}CCl_2$).

Preparation of $[Ni(C_2Cl_3)_2(N\text{-}N)]$ [N-N = bpy (5), *o*-phen (6)]. $[NiCl(C_2Cl_3)(PPh_3)_2]$ (1.21 g, 1.6 mmol) and bpy or *o*-phen (3.2 mmol) were dissolved in benzene (100 mL). The solution was refluxed for 2 h and then filtered and concentrated under reduced pressure to dryness. The solid obtained was washed with 1% HCl, water, and ether. The product was recrystallized from chloroform/ethanol. The yields were about 60%.

Preparation of $[Ni(C_2Cl_3)L_2]$ [L = PEt_3 (8), PMe_2Ph (7)]. PMe_2Ph or PEt_3 (4 mmol) was added under nitrogen to $[Ni(C_2Cl_3)_2(bpy)]$ (0.5 g, 1 mmol) dissolved in benzene (50 mL), and the mixture was refluxed for 24 h. After being filtered the solution was concentrated under reduced pressure to dryness. The solid was washed with 5% HCl, water, and ethanol, and recrystallized from chloroform/ethanol. The yields were about 70%.

Structure Solution and Refinement. A 0.1 × 0.1 × 0.2 mm prismatic crystal was chosen and mounted on a Nonius CAD-4 four-circle diffractometer. The intensities were corrected for Lorentz–polarization factors.

Initial atomic coordinates for Ni and P atoms were obtained by using the MULTAN-81 procedure, and the structure was solved subsequently by standard Fourier and difference Fourier syntheses. Isotropic and anisotropic refinements was made by the full-matrix least-squares method using the SHELX computer program. All hydrogen atoms were located by a new difference synthesis at $R = 0.104$. The final R value was 0.072 ($R_w = 0.079$) for all observed reflections.

Acknowledgment. We thank the Comisión Asesora Cientifica y Tecnica for financial support.

Registry No. **1**, 89576-68-1; **2**, 89486-76-0; **3**, 89486-77-1; **4**, 89486-78-2; **5**, 89486-79-3; **6**, 89486-80-6; **7**, 89486-81-7; „ 89486-82-8; $NiI(CCl{=}CCl_2)(PPh_3)_2$, 89486-83-9; $Ni(NCS)(CCl{=}CCl_2)(PPh_3)_2$, 89486-84-0; $Ni(NO_2)(CCl{=}CCl_2)(PPh_3)_2$, 89486-85-1; $Ni(CN)(CCl{=}CCl_2)(PPh_3)_2$, 89486-86-2; $Ni(NCS)(CH{=}CCl_2)(PPh_3)_2$, 89486-87-3; $Ni(CN)(CH{=}CCl_2)(PPh_3)_2$, 89486-88-4; $Ni(NCS)(CH{=}CHCl)(PPh_3)_2$, 89509-62-6; $NiCl(CCl{=}CCl_2)$(dppe), 89509-63-7; $NiCl(CH{=}CCl_2)$(dppe), 89486-89-5; $[Ni(CCl{=}CCl_2)(3{,}5\text{-lut})_3]ClO_4$, 89509-65-9; $[Ni(CH{=}CCl_2)(3{,}5\text{-lut})_3]ClO_4$, 89486-91-9; $[Ni(CCl{=}CH_2)(3{,}5\text{-lut})_3]ClO_4$, 89486-93-1; $Ni(NCS)(CCl{=}CCl_2)(3{,}5\text{-lut})_2$, 89486-94-2; $Ni(NCS)(CH{=}CCl_2)(3{,}5\text{-lut})_2$, 89509-66-0; $NiCl_2$, 7718-54-9; $NiCl_2$(bpy), 22775-90-2; $NiCl_2$(*o*-phen), 22980-76-3; $CCl_2{=}CCl_2$, 127-18-4; $CCl_2{=}CHCl$, 79-01-6; *trans*-$CHCl{=}CHCl$, 156-60-5; $CH_2{=}CCl_2$, 75-35-4; KI, 7681-11-0; KNCS, 333-20-0; KNO_2, 7758-09-0; KCN, 151-50-8.

Supplementary Material Available: Tables of analytical data and decomposition temperatures and observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.