solid P_4S_{10} and P_4S_9 and show that the major vapor components are molecular P_4S_{10} and the terminal sulfur decomposition product P_4S_9. Another sharp 750.6-cm^{-1} band, with an associated 508.5-cm^{-1} absorption, is dominant in superheated vapor; these bands are probably due to molecular P_2S_5, which likely has the same structure as molecular P_2O_5. Additional weaker bands are identified as PS and PS_2.

The present infrared matrix experiments with P_4S_{10} suggest that at 175 °C P_4S_{10} evaporates into three comparable fractions—molecular P_4S_{10}, the terminal sulfur dissociation product P_4S_9, and smaller phosphorus and diphosphorus sulfides—on the basis of the reasonable assumption of similar infrared extinction coefficients for these species. The spectra further suggest that the cage dissociation reactions (2a) and (2b) together are as important as the terminal sulfur dissociation reaction (1).

The thermal decomposition of P_4S_{10} follows the pyrolysis of P_4O_{10} in several ways: the major decomposition products (P_4S_9 and P_4O_9) involve the loss of a simple terminal atom, and the loss of *two* terminal atoms plays only a minor role.[10] Although P_2S_5 is a major thermolysis product of P_4S_{10}, little P_2O_5 was observed from P_4O_{10} whereas PO_2 was a major product from P_4O_{10}, but PS_2 was only a minor product from P_4S_{10}.

$$P_4S_{10} \longrightarrow P_4S_9 + S \quad (1)$$

$$P_4S_{10} \longrightarrow 2P_2S_5 \longrightarrow 2P_2S_4 + 2S \quad (2a)$$

$$P_4S_9 \longrightarrow P_2S_5 + P_2S_4 \quad (2b)$$

$$P_2S_5 \longrightarrow PS + PS_2 + S_2 \quad (2c)$$

$$P_2S_4 \longrightarrow 2PS_2 \quad (2d)$$

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Stability and Stereochemistry of Tetrahedral Nickel Nitrosyl Complexes: Crystal and Molecular Structures of (*R**,*S**)-*anti*-[NiNCS(NO){1,2-C_6H_4(PMePh)$_2$}] and (*R**,*S**)-*anti*-[NiNO{P(OMe)$_3$}{1,2-C_6H_4(PMePh)$_2$}]PF_6

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The tetrahedral complexes (*R**,*R**)-(±)- and (*R**,*S**)-*anti*-[NiX(NO){1,2-C_6H_4(PMePh)$_2$}] rearrange in nitrobenzene-d_5 at 25 °C with inversion at the metal stereocenter [$t_{1/2}$ ca. 5 s (X = Cl), 9 s (X = NCS), and 3.5 h (X = CN)] and intermolecular exchange of X [$t_{1/2}$ ca. 8 h (X = CN)]. The salts (R*,*R**)-(±)- and (*R**,*S**)-*anti*-[NiL(NO){1,2-C_6H_4(PMePh)$_2$}]PF_6 rearrange with $t_{1/2}$(inversion) of ca. 6 min and $t_{1/2}$(redistribution) of ca. 12 h (L = PMe_2Ph). The crystal structures of (*R**,*S**)-*anti*-[NiNCS(NO){1,2-C_6H_4(PMePh)$_2$}] [(*R**,*S**)-*anti*-**1** (X = NCS)] and (*R**,*S**)-*anti*-[NiNO{P(OMe)$_3$}{1,2-C_6H_4(PMePh)$_2$}]PF_6 [(*R**,*S**)-*anti*-**2** [L = P(OMe)$_3$]] at 21 ± 1 °C have been determined. Crystal data: for (*R**,*S**)-*anti*-**1** (X = NCS), monoclinic, a = 10.336 (3) Å, b = 17.663 (5) Å, c = 11.743 (3) Å, β = 91.51 (2)°, Z = 4, $R(F_o)$ = 0.041, $R_w(F_o)$ = 0.043; for (*R**,*S**)-*anti*-**2** [L = P(OMe)$_3$], monoclinic, a = 15.547 (4) Å, b = 11.191 (3) Å, c = 19.137 (6) Å, β = 107.04 (2)°, Z = 4, $R(F_o)$ = 0.051, $R_w(F_o)$ = 0.054. The stereochemistry around the nickel atom in each complex is distorted tetrahedral with the bond angle Ni–N–O being equal to 159.5 (3)° in the isothiocyanato complex and equal to 178.0 (5)° in the phosphite complex. The ligand redistribution studies were conducted with use of isotopically labeled substances and NMR spectroscopy.

Introduction

Although many pseudotetrahedral[1] (pseudooctahedral)[2] complexes of the type [(η^5-C_5H_5)MABC] are known to be configurationally stable at the stereogenic metal center (indeed, the enantiomers of (±)-[(η^5-C_5H_5)FeCO(COMe)(PPh_3)] are available commercially for use in asymmetric synthesis[3]), little is known about the configurational stability or the stereochemistry of substitution of purely tetrahedral transition-metal complexes containing one or more unidentate ligands.[4,5] Of relevance to the present work, however, are the observations that the complexes [Co($AsPh_3$)CO(NO)(PPh_3)] and [Ni(phen)$_3$][CoCN(CO)NO(PPh_3)]$_2$ have been isolated (as racemates),[6] [CoCO(NO)(PMe_2Ph)$_2$] is configurationally stable in solution up to 100 °C,[7] and diastereomers of complexes of the type (±)-[Fe(CO)(NNAr)(NO){PPh_2(NRR*)}] have been separated.[5] In an attempt to identify tetrahedral complexes with metal–halogen bonds for use in asymmetric synthesis, we have characterized (*R**,*R**)-(±)- and (*R**,*S**)-*anti*-[NiX(NO){1,2-C_6H_4(PMePh)$_2$}] (where X = Cl, Br, I, CN, or NCS) [(*R**,*R**)- and (*R**,*S**)-*anti*-**1**] and (*R**,*R**)-(±)- and (*R**,*S**)-*anti*[NiL(NO){1,2-C_6H_4(PMePh)$_2$}]PF_6 [where L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, or P(OMe)$_3$] [(*R**,*R**)- and (*R**,*S**)-*anti*-**2**].[8,9]

Results

The compounds described in this work are listed in Tables I and II. The crystal and molecular structures of two of the complexes, neutral (*R**,*S**)-*anti*-**1** (X = NCS) and ionic (*R**,*S**)-*anti*-**2** [L = P(OMe)$_3$], have been determined; the results are presented in Tables III–VI. The solution behavior of the complexes has been investigated with use of NMR spectroscopy. The various aspects of the work will be introduced in the sections that follow.

(a) The Neutral Complexes [NiX(NO){1,2-C_6H_4(PMePh)$_2$}]. The complexes (*R**,*R**)- and (*R**,*S**)-**1** (X = Cl) were prepared

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Table I. Selected NMR and Related Data for $[NiX(NO)\{1,2\text{-}C_6H_4(PMePh_2)_2\}]$ (**1**)

compd	$^{31}P\{^1H\}$ NMR,[a] δ (P)	^1H NMR,[b] δ (PMe)	T_c,[c] K	ΔG_c^*,[d] kJ mol^{-1}	$t_{1/2}$(25 °C),[e] s
(*R*,R**)-**1** (X = Cl)	32.9, 40.7 (AB q)	2.43 d, 2.53 d	353	76.1	5
(*R*,R**)-**1** (X = Br)	30.2, 36.6 (AB q)	2.43 d, 2.60 d	368	77.6	9
(*R*,R**)-**1** (X = I)	27.0, 31.7 (AB q)	2.36 d, 2.60 d	398	83.0	80
(*R*,R**)-**1** (X = CN)	37.0, 41.8 (AB q)	2.44 d, 2.62 d	403	85.4	211
(*R*,R**)-**1** (X = NCS)	35.8, 42.7 (AB q)	2.33 d, 2.44 d	363	77.6	9
(*R*,S**)-*anti*-**1** (X = Cl)	42.6 s	2.07 t			
(*R*,S**)-*anti*-**1** (X = Br)		2.20 t			
(*R*,S**)-*anti*-**1** (X = I)	33.1 s	2.32 t			
(*R*,S**)-*anti*-**1** (X = CN)	43.4 s	2.21 t			
(*R*,S**)-*anti*-**1** (X = NCS)	44.1 s	2.09 t			

[a] Chemical shifts quoted relative to external 85% H_3PO_4 for dichloromethane-d_2 solutions. [b] Chemical shifts quoted relative to internal Me_4Si for nitrobenzene-d_5 solutions. [c] Determined from ln k plots. [d] Calculated by substitution of $k_c = \pi\Delta\nu/\sqrt{2}$ into Eyring equation. [e] Determined with use of k(298 K).

Table II. Selected NMR Data for $[NiL(NO)\{1,2\text{-}C_6H_4(PMePh_2)_2\}]PF_6$ (**2**)

compd	$^{31}P\{^1H\}$ NMR,[a] δ (P)	^1H NMR,[b] δ (PMe–diph[c])	^1H NMR,[b] δ (PMe–L)
(*R*,R**)-**2** (L = PMe_3)	−8.5, 37.7, 38.9 (ABX)	1.46 d, 2.41 d	0.53 d
(*R*,R**)-**2** (L = $PMePh_2$)	19.8, 37.6, 38.3 (ABX)	1.74 d, 2.44 d	1.34 d
(*R*,R**)-**2** (L = PMe_2Ph)	3.6, 37.8, 38.7 (ABX)	1.80 d, 2.42 d	1.22 d, 1.37 d
(*R*,R**)-**2** (L = PPh_3)	34.6, 35.4, 38.3 (ABX)	1.43 d, 2.30 d	
(*R*,S**)-*anti*-**2** (L = PMe_3)	−7.0 t, 34.3 d	2.19 d	1.53 d
(*R*,S**)-*syn*-**2** (L = PMe_3)	−9.3 t, 40.3 d	2.44 d	0.67 d
(*R*,S**)-*anti*-**2** (L = $PMePh_2$)	20.2 t, 34.1 d	1.83 d	1.85 d
(*R*,S**)-*syn*-**2** (L = $PMePh_2$)	19.1 t, 39.5 d	2.45 d	0.47 d
(*R*,S**)-*anti*-**2** (L = PMe_2Ph)	4.8 t, 34.3 d	1.94 d	1.73 d
(*R*,S**)-*syn*-**2** (L = PMe_2Ph)	3.2 t, 40.0 d	2.42 d	0.75 d
(*R*,S**)-*anti*-**2** (L = PPh_3)	35.0 d, 40.5 t	1.66 d	
(*R*,S**)-*anti*-**2** [L = $P(OMe)_3$]	39.0 d, 161.2 t	2.19 d	3.82 d
(*R*,S**)-*syn*-**2** [L = $P(OMe)_3$)]	39.5 d, 159.5 t	2.44 d	3.16 d

[a] Chemical shifts quoted relative to external 85% H_3PO_4 for dichloromethane-d_2 solutions. [b] Chemical shifts quoted relative to Me_4Si for nitrobenzene-d_5 solutions. [c] Abbreviation diph = $1,2\text{-}C_6H_4(PMePh_2)_2$.

Table III. Crystallographic Data for (*R*,S**)-*anti*-**1** (X = NCS) and (*R*,S**)-*anti*-**2** [L = $P(OMe)_3$]

chem formula	$C_{21}H_{20}N_2NiOP_2S$	$C_{23}H_{29}F_6NNiO_4P_4$
fw	469.1	680.1
space group	$P2_1/n$ (nonstd No. 14)	$P2_1/n$ (nonstd No. 14)
a, Å	10.336 (3)	14.547 (4)
b, Å	17.663 (5)	11.191 (3)
c, Å	11.743 (3)	19.137 (6)
β, deg	91.51 (2)	107.04 (2)
V, Å^3	2143.1	2978.7
Z	4	4
T, °C	−150	−150
λ, Å	0.710 69	0.710 69
d_{calcd}, g cm^{-3}	1.45	1.52
μ, cm^{-1}	11.6	9.6
$R(F_o)$, %	4.1	5.1
$R_w(F_o)$, %	4.3	5.4

Table IV. Selected Bond Distances and Angles

(*R*,S**)-*anti*-**1** (X = NCS)		(*R*,S**)-*anti*-**2** [L = $P(OMe)_3$]	
Bond Lengths (Å)			
Ni–N(1)	1.651 (3)	Ni–N	1.638 (5)
Ni–N	1.945 (3)	Ni–P(1)	2.213 (1)
Ni–P(1)	2.213 (1)	Ni–P(2)	2.220 (1)
Ni–P(2)	2.234 (1)	Ni–P(3)	2.190 (1)
N(1)–O(1)	1.167 (3)	N–O	1.153 (5)
N–C	1.162 (4)		
C–S	1.629 (3)		
Bond Angles (deg)			
Ni–N(1)–O(1)	159.5 (3)	Ni–N–O	178.0 (5)
Ni–N–C	163.5 (2)	N–Ni–P(1)	120.6 (2)
N–C–S	179.2 (3)	N–Ni–(2)	121.1 (2)
N(1)–Ni–N	126.0 (1)	N–Ni–P(3)	119.8 (2)
N(1)–Ni–P(1)	109.0 (1)	P(1)–Ni–P(2)	86.8 (1)
N(1)–Ni–P(2)	120.5 (1)		
N–Ni–P(1)	103.0 (1)	P(1)–Ni–P(3)	101.4 (1)
N(1)–Ni–P(2)	120.5 (1)	P(2)–Ni–P(3)	100.7 (1)
N–Ni–P(2)	101.1 (1)		
P(1)–Ni–P(2)	90.4 (3)		

Table V. Final Positional Parameters for (*R*,S**)-*anti*-**1** (X = NCS)

atom	x	y	z
Ni	1718.9 (4)	918.8 (2)	−383.6 (3)
P(1)	3452.0 (7)	1521.0 (4)	293.7 (6)
P(2)	438.3 (7)	1790.8 (4)	379.9 (6)
N	1648 (3)	1216 (2)	−1979 (2)
N(1)	1735 (3)	42 (2)	105 (2)
O(1)	1946 (3)	−468 (2)	714 (3)
S	1912.7 (9)	1250.8 (5)	−4338.3 (7)
C	1768 (3)	1231 (2)	−2960 (3)
C(1)	2873 (3)	2405 (2)	891 (2)
C(2)	1535 (3)	2532 (2)	918 (2)
C(3)	1079 (3)	3207 (2)	1382 (3)
C(4)	1942 (3)	3742 (2)	1809 (3)
C(5)	3268 (3)	3615 (2)	1779 (3)
C(6)	3731 (3)	2948 (2)	1324 (3)
C(m1)	4749 (4)	1797 (2)	−643 (3)
C(11)	4256 (3)	1050 (2)	1493 (2)
C(12)	3770 (3)	1116 (2)	2589 (3)
C(13)	4326 (3)	716 (2)	3488 (3)
C(14)	5361 (3)	241 (2)	3312 (3)
C(15)	5842 (3)	165 (2)	2230 (3)
C(16)	5292 (3)	564 (2)	1325 (3)
C(m2)	−687 (3)	2293 (2)	−558 (3)
C(21)	−471 (3)	1534 (2)	1628 (2)
C(22)	−1627 (3)	1888 (2)	1894 (3)
C(23)	−2249 (4)	1685 (2)	2894 (3)
C(24)	−1727 (4)	1149 (2)	3612 (3)
C(25)	−594 (4)	788 (2)	3348 (3)
C(26)	33 (4)	981 (2)	2352 (3)

in good yields by either of two methods: one involved the treatment of (*R*,R**)-(±)- or (*R*,S**)-$[NiCl_2\{1,2\text{-}C_6H_4(PMePh_2)_2\}]$ (generated from the corresponding zerovalent nickel carbonyl compounds by reaction with sulfuryl chloride[10]) with sodium nitrite and carbon monoxide;[11] the other method involved the treatment

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Table VI. Final Positional Parameters for (*R**,*S**)-*anti*-**2** [L = $P(OMe)_3$]

atom	*x*	*y*	*z*
Ni	2619.8 (5)	2604.2 (6)	635.5 (3)
P(1)	1608.9 (10)	3693.1 (12)	−223.7 (7)
P(2)	3037.2 (9)	1716.5 (12)	−263.4 (7)
P(3)	3821.6 (11)	3848.2 (13)	1037.5 (8)
N	2233 (3)	1827 (4)	1218 (2)
O	1937 (4)	1270 (5)	1611 (3)
C(1)	2151 (4)	3738 (5)	−971 (3)
C(2)	2775 (3)	2814 (4)	−1001 (3)
C(3)	3198 (4)	2757 (6)	−1564 (3)
C(4)	3007 (5)	3626 (7)	−2087 (3)
C(5)	2409 (5)	4566 (7)	−2054 (4)
C(6)	1968 (4)	4617 (5)	−1504 (3)
C(11)	444 (4)	2989 (4)	−615 (3)
C(12)	142 (4)	2092 (5)	−231 (3)
C(13)	−728 (4)	1518 (6)	−529 (4)
C(14)	−1314 (4)	1841 (6)	−1199 (4)
C(15)	−1031 (4)	2734 (6)	−1584 (3)
C(16)	−154 (4)	3314 (5)	−1297 (3)
C(m1)	1323 (4)	5238 (5)	−79 (3)
C(21)	2367 (4)	375 (5)	−658 (3)
C(22)	1484 (4)	457 (5)	−1185 (3)
C(23)	954 (4)	−573 (6)	−1451 (3)
C(24)	1322 (5)	−1677 (6)	−1189 (4)
C(25)	2201 (6)	−1757 (6)	−667 (4)
C(26)	2726 (5)	−742 (5)	−391 (3)
C(m2)	4289 (4)	1298 (5)	−120 (3)
O(31)	3807 (3)	4866 (3)	461 (2)
O(32)	4895 (3)	3369 (3)	1195 (2)
O(33)	3914 (3)	4488 (4)	1791 (2)
C(31)	4510 (5)	5842 (5)	618 (4)
C(32)	5270 (6)	2490 (7)	1760 (4)
C(33)	2080 (6)	5007 (7)	1922 (4)

of $[Ni(1,5\text{-}C_8H_{12})_2]$ with 1 equiv each of the appropriate diastereomer of the bis(tertiary phosphine) and nitrosyl chloride.[11] The complexes are deep blue crystalline solids that are sensitive to the air and to light, especially in solution.

In (*R**,*R**)-**1** (X = Cl), the P*Me* groups (and the P nuclei) are diastereotopic (Figure 1). Accordingly, the ^1H NMR spectrum of the complex in nitrobenzene-d_5 at 25 °C exhibits two P*Me* resonances, and the $^{31}P\{^1H\}$ NMR spectrum of the compound in the same solvent consists of an AB quartet (Table I). At elevated temperatures, however, the ^1H NMR resonances for the P*Me* groups broaden and coalesce with T_c = 353 K. From the variable-temperature NMR data, it can be calculated[12] that $\Delta G^{\ddagger}$(353 K) = 76.1 kJ mol^{-1}, which corresponds to $t_{1/2}$(rearrangement) of ca. 5 s at 25 °C.[13] The complexes (*R**,*R**)-**1** (X = Br, I, CN, NCS) behave similarly when heated in nitrobenzene-d_5 with the following values for $t_{1/2}$(rearrangement) being calculated from the ^1H NMR data: 9 s (X = Br or NCS), 80 s (X = I), and 211 s (X = CN). The experimental data are summarized in Table I. In each case $t_{1/2}$ is independent of the concentration of the complex. For X = CN it was possible to determine the relative rates of internal and external (intermolecular) rearrangement. Thus, it was shown by $^{13}C\{^1H\}$ NMR spectroscopy that intermolecular exchange of cyanide between (*R**,*R**)-**1** (X = ^{13}CN) and (*R**,*S**)-**1** (X = CN) in nitrobenzene-d_5 occurs with $t_{1/2}$(equilibrium) ca. 8 h at 25 °C:

(*R**,*R**)-**1** (X = ^{13}CN) + (*R**,*S**)-**1** (X = CN) ⇄
(*R**,*R**)-**1** (X = CN) + (*R**,*S**)-**1** (X = ^{13}CN)

For (*R**,*S**)-**1** (X = Cl), syn and anti diastereomers may exist (Figure 1). The P*Me* groups in each of the diastereomers are enantiotopic and are therefore ^1H NMR equivalent. For (*R**,*S**)-**1** (X = Cl), a single sharp P*Me* resonance is observed over the temperature range −90 to +130 °C in the $^1H\{^{31}P\}$ NMR spectrum (spectrum from −90 to +20 °C recorded in dichloromethane-d_2; spectrum from 20 to 100 °C recorded in nitrobenzene-d_5), and in the $^{31}P\{^1H\}$ NMR spectrum of the compound under similar conditions, a singlet resonance is observed. These observations are consistent with a single diastereomer of tetrahedral coordination. (The square-planar allogon of this complex is chiral with diastereotopic phosphorus nuclei.) Substitution of chloride in (*R**,*S**)-**1** (X = Cl) by bromide, iodide, cyanide, or thiocyanate also gives discrete derivatives, viz. (*R**,*S**)-**1** (X = Br, I, CN, NCS) (Table I). In the solid state, the isothiocyanato ligand occupies the less hindered diastereotopic coordination site on the nickel adjacent to the methyl groups (Figure 2); crystal data for the complex, henceforth designated (*R**,*S**)-*anti*-**1** (X = NCS), are given in Table III, and Table IV lists positional parameters employing the atom-numbering scheme of Figure 1 of the supplementary material. Table V lists the most important bond distances and angles in the complex. With an Ni–N–C angle of 163.5 (2)°, a freely rotating linear isothiocyanato group (N–C–S = 179.2°) in solution would occupy a larger volume than the nitrosyl group, which has a similar angle of coordination; viz., Ni–N–O = 159.5 (3)°. The compound $[Ni(NCS)(NO)(PPh_3)_2]$ has a similar structure with an N–C–S angle of 179.1 (6)° and

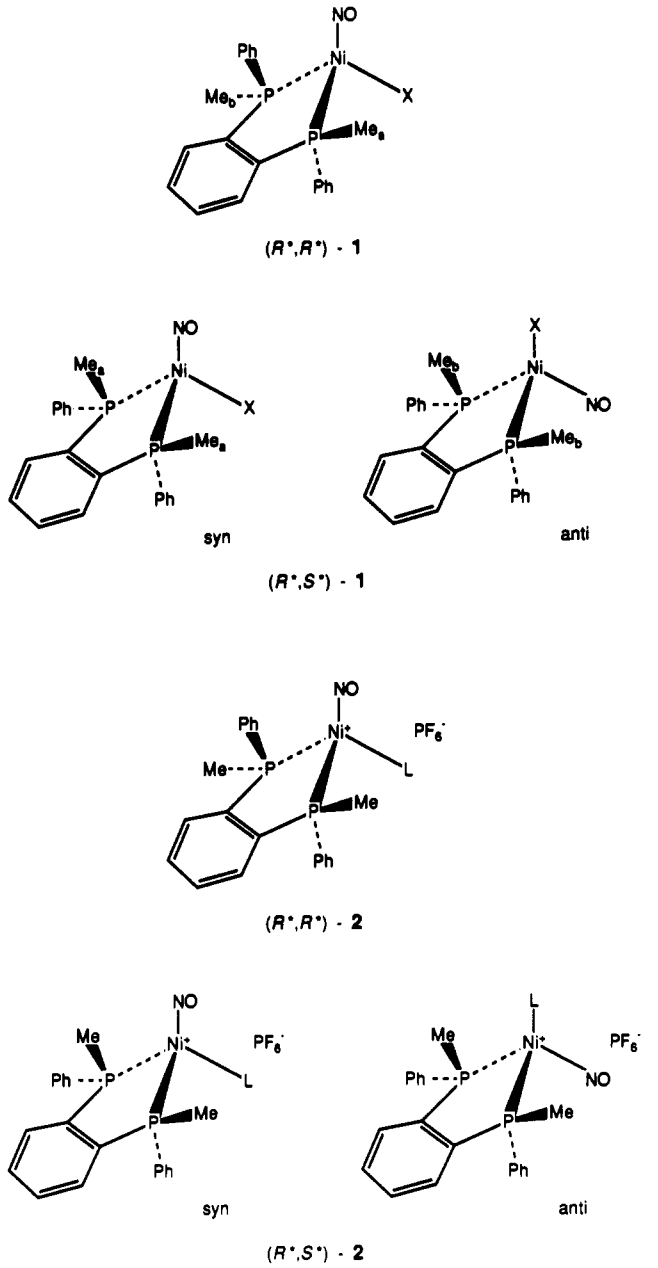

Figure 1. Diastereomers of (*R**,*R**)- and (*R**,*S**)-**1** and of cations of (*R**,*R**)- and (*R**,*S**)-**2**. The *R* enantiomer of the (*R**,*R**) diastereomer is depicted in each case.

(12) Binsch, G.; Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 411–428.
(13) The $t_{1/2}$ value at 25 °C was calculated from the calculated rate constant *k* at 25 °C by substitution of $\Delta G^{\ddagger}$ at T_c into the Eyring equation, assuming $\Delta S^{\ddagger}$ ca. 0.

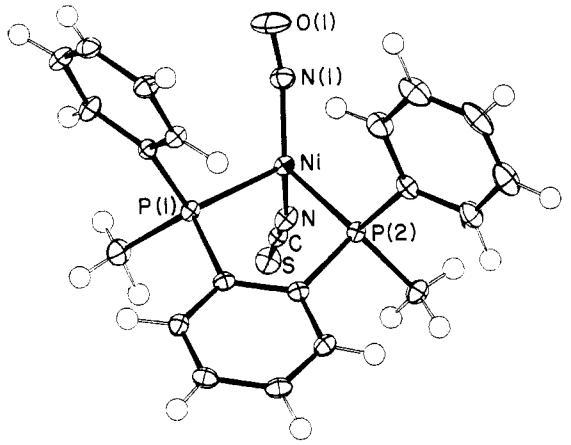

Figure 2. ORTEP view of (*R**,*S**)-*anti*-**1** (X = NCS) showing the atom-labeling scheme for non-hydrogen atoms. Thermal ellipsoids enclose 35% probability levels.

an Ni–N–O angle of 161.5 (5)°.[14] The stereochemistry around the nickel in (*R**,*S**)-**1** (X = NCS) in the solid state is distorted tetrahedral. Tetrahedral coordination in the complex is retained in solution according to the $^{31}P\{^{1}H\}$ NMR data (Table I). Because of the similarity of the chemical shifts for the P*Me* groups in each of the complexes, the anti stereochemistry appears to have been retained in the substitution reactions. Thus, anation of these purely tetrahedral nickel complexes occurs with retention of configuration at the metal center.[15] The behavior of the pseudotetrahedral complexes $[(\eta^5\text{-}C_5H_5)FeX(CO)(PR_3)]$ during substitution of X also occurs with retention of configuration at iron.[1]

(b) The Salts [NiL(NO){1,2-C_6H_4(PMePh)$_2$}]PF_6. The neutral complex (*R**,*R**)-(±)-**1** (X = Cl) reacts with unidentate tertiary phosphines (L) in the presence of ammonium hexafluorophosphate to give high yields of the deep red salts (*R**,*R**)-(±)-**2** (L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3). Spectroscopic data and related information for the complexes are presented in Table II. For each of the complexes, an ABX spectrum for the phosphorus nuclei in the $^{31}P\{^{1}H\}$ NMR spectrum is observed, and for the P*Me* groups, a doublet ($^{2}J_{PH}$ = ca. 10 Hz) in the ^{1}H NMR spectrum is observed. The spectrum of (*R**,*R**)-**2** (L = PMe_2Ph, PPh_3) in nitrobenzene-d_5 is invariant over the temperature range 20–130 °C. With use of the upper limit for temperature, it can be calculated from the NMR data for the dimethylphenylphosphine derivative that, for internal rearrangement, $\Delta G^{\ddagger}$(403 K) > 79.6 kJ mol^{-1} ($t_{1/2}$ > 21 s at 25 °C) and, for the triphenylphosphine derivative, $\Delta G^{\ddagger}$(403 K) > 81.2 kJ mol^{-1} ($t_{1/2}$ > 39 s at 25 °C).[16]

Reactions of (*R**,*S**)-*anti*-**1** (X = Cl) with the same unidentate tertiary phosphines (except triphenylphosphine), or trimethyl phosphite, produce mixtures of the expected products, *viz.* (*R**,*S**)-*syn*/*anti*-**2** [L = PMe_3, PMe_2Ph, $PMePh_2$, or $P(OMe)_3$]. With triphenyphosphine, a single diastereomer of the product is isolated from the reaction mixture. For trimethyl phosphite, the reaction yields a 1:9 mixture of the syn and anti diastereomers as a red solid, but the slow crystallization of this material from dichloromethane–methanol affords a stereochemically homogeneous sample of the major diastereomer in a second-order asymmetric transformation.[17] An X-ray crystal structure determination on this complex confirmed the anti stereochemistry that had been predicted from the ^{1}H NMR data after consideration of shielding patterns in the two isomers.

The structure of (*R**,*S**)-*anti*-**2** [L = $P(OMe)_3$] is shown in Figure 3; crystal data for the complex are given in Table III, and Table IV lists positional parameters employing the atom-numbering scheme in Figure 2 of the supplementary material. Table V lists the most important bond distances and angles in the complex. The stereochemistry around the nickel is distorted tetrahedral with the bulky phosphite ligand occupying the coordination site adjacent to the less sterically demanding methyl groups of the bis(tertiary phosphine) (Figure 3). Unlike the related neutral complex, however, the Ni–N–O bond angle in this complex is almost linear (178.0°). Almost linear Ni–N–O bond angles have been found in $[Ni(NO)\{P(OCH_2)_3CMe\}_3]PF_6$ (176.8°)[18] and $[Ni(NO)(PMe_3)_3]PF_6$(175.4°),[19] and in $[Ni(NO)\{(Et_2PCH_2)_3CMe\}]PF_6$, the Ni–N–O bond angle is 180.0°.[20]

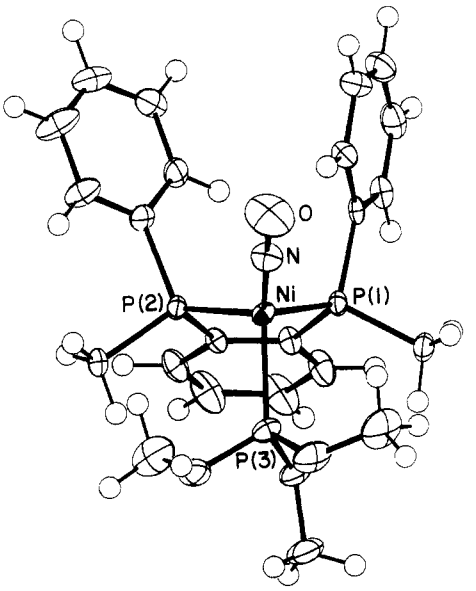

Figure 3. ORTEP view of (*R**,*S**)-*anti*-**2** [L = $P(OMe)_3$] showing atom-labeling scheme for non-hydrogen atoms. Thermal ellipsoids enclose 35% probability levels.

With knowledge of the molecular structure of the major diastereomer of the trimethyl phosphite complex, we were able to assign stereochemistries to the other unidentate tertiary phosphine complexes (Table I). In each case, the upfield bis(tertiary phosphine) P*Me* resonance and the upfield unidentate tertiary phosphine P*Me* resonance (for methylated phosphines) have been assigned to the diastereomer of anti stereochemistry. For the initial products, that is, the products isolated from relatively rapid crystallizations, syn:anti = 3:2 (L = PMe_3), 1:1 (L = PMe_2Ph), and 2:3 (L = $PMePh_2$). Slower recrystallizations of these mixtures from dichloromethane–methanol yielded in each case >70% yields of the anti diastereomers in typical second-order asymmetric transformations. When redissolved in dichloromethane-d_2, the pure anti compounds rearranged into equilibrium mixtures of diastereomers ($t_{1/2}$ ca. 6 min at 25 °C for L = PMe_2Ph) of composition equal to that found for the initial material. We believe the rearrangements are intramolecular processes predominantly since exchange of unidentate tertiary phosphine between (*R**,*R**)-**2** [L = $P(Me\text{-}d_3)_2Ph$] and (*R**,*S**)-*anti*-**2** (L = PMe_2Ph), an intermolecular process, in dichloromethane-d_2 occurs with $t_{1/2}$(equilibrium) of ca. 12 h at 25 °C. Triphenylphosphine reacts with (*R**,*S**)-*anti*-**1** (X = Cl) to give a single diastereomer of (*R**,*S**)-**2** (L = PPh_3). We have assigned the anti stereochemistry to this product in view of the bulk of the triphenylphosphine ligand, which would presumably cause it to favor the less hindered methyl side of the NiP_2 plane.

Experimental Section

Complexes were prepared and stored under an argon atomsphere in the dark.[21] ^{1}H NMR spectra at 20 °C were recorded in dichloro-

(14) Haller, K. J.; Enemark, J. H. *Inorg. Chem.* **1978**, *17*, 3552–3558.
(15) The experimental data presented here do not exclude inversion of configuration during anation followed by rapid rearrangement at the metal into the thermodynamically favored diastereomer.
(16) The $t_{1/2}$ value at 25 °C was calculated from the calculated rate constant at 25 °C by substitution of $\Delta G^{\ddagger}$ at 130 °C into the Eyring equation.
(17) Jacques, J.; Collet, A.; Wilen, S. H. *Enantiomers, Racemates, and Resolutions*; Wiley: New York, 1981.
(18) Meiners, J. H.; Rix, C. J.; Clardy, J. C.; Verkade, J. G. *Inorg. Chem.* **1975**, *14*, 705–710. Albright, J. O.; Tanzella, F. L.; Verkade, J. G. *J. Coord. Chem.* **1976**, *5*, 225–229.
(19) Elbaze, G.; Dahan, F.; Dartiguenave, M.; Dartiguenave, Y. *Inorg. Chim. Acta* **1984**, *87*, 91–97.
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methane-d_2 on a Bruker CXP-200 spectrometer. Variable-temperature ^1H NMR spectra above 20 °C were recorded in nitrobenzene-d_5 and $^{13}C\{^1H\}$ (50 MHz) and $^{31}P\{^1H\}$ (80.98 MHz) NMR spectra were recorded in dichloromethane-d_2 at 20 °C on the same instrument. IR spectra were recorded on KBr disks with use of a Perkin-Elmer 683 spectrophotometer. Elemental analyses were performed by staff within the Research School of Chemistry.

(*R*,*R*)-(±)- and (*R*,*S*)-1,2-phenylenebis(methylphenylphosphine) were obtained by the literature method[23] and the derivatives [*T*-4-(*R**,*R**)]-(±)-[Ni(CO)$_2${1,2-C_6H_4(PMePh)$_2$}] and [*T*-4-(*R**,*S**)]-[Ni(CO)$_2${1,2-C_6H_4(PMePh)$_2$}] were prepared as described in ref 10.

[*T*-4-(*R,*S**)]-*anti*-Chloronitrosyl[1,2-phenylenebis(methylphenylphosphine)]nickel(0) [(*R**,*S**)-1 (X = Cl)]. Method A.** Solid (*R**,*S**)-1,2-C_6H_4(PMePh)$_2$ (0.18 g, 0.56 mmol) was added to a stirred suspension of [Ni(1,5-COD)$_2$][23] (0.15 g, 0.56 mmol) in diethyl ether (20 mL) at −15 °C. After ca. 2 h, a solution of nitrosyl chloride (0.037 g, 0.56 mmol) in toluene (20 mL) was added to the reaction mixture, which was then warmed to room temperature over 2 h. The resulting precipitate was collected, washed with diethyl ether, and dried in vacuo. Recrystallization of the crude product from dichloromethane–ethanol (1:1) by slow evaporation of the dichloromethane gave the pure product as deep blue needles: mp 156–158 °C, yield 0.14 g (55%). Anal. Calcd for $C_{20}H_{20}ClNNiOP_2$: C, 53.8; H, 4.5; N, 3.1. Found: C, 53.8; H, 4.6; N, 3.0. ^1H NMR: δ 2.07 (t, 6 H, $|^2J_{PH} + {}^4J_{P'H}|$ = 10.5 Hz, P*Me*), 7.39–7.72 (m, 14 H, aromatics). $^{31}P\{^1H\}$ NMR: δ 42.6 (s, 2 P). IR: ν(NO) 1760 cm^{-1}.

Method B. A solution of sulfuryl chloride (0.40 g, 3 mmol) in CH_2Cl_2 (5 mL) was added dropwise into a stirred solution of [*T*-4-(*R**,*R**)]-(±)-[Ni(CO)$_2${1,2-C_6H_4(PMePh)$_2$}] (1.4 g, 3 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The resulting green solution was evaporated to dryness and the dichloro derivative [*T*-4-(*R**,*R**)]-(±)-[NiCl$_2${1,2-C_6H_4(PMePh)$_2$}][10] was washed with diethyl ether and dried *in vacuo* (1.3 g, 96%). [The dichloro compound can also be prepared in high yield by treating [*T*-4-(*R**,*R**)]-(±)-[Ni(CO)$_2${1,2-C_6H_4(PMePh)$_2$}] (1.4 g, 3 mmol) in benzene (30 mL) at 15 °C with a solution of chlorine (0.21 g, 3 mmol) in carbon tetrachloride (20 mL).] The dichloro compound (0.54 g, 1.2 mmol) was redissolved in dimethylformamide–acetone (1:2, 30 mL), and a solution of sodium nitrite (0.105 g, 1.5 mmol) in water (3 mL) was added. A stream of carbon monoxide was then passed through the solution at its boiling point for 3–4 h. The final blue solution was concentrated to ca. 20 mL, and water was added to give a deep blue precipitate of the crude product, which was collected, washed with water and diethyl ether, and then dried in vacuo. The crude material was dissolved in CH_2Cl_2 (30 mL), and the solution was washed with water; the organic layer was dried ($MgSO_4$), filtered, and diluted with an equal volume of ethanol. Slow evaporation of the solution gave the pure product as deep blue needles (0.3 g, 46%).

Method C. [*T*-4-(*R**,*S**)]-[Ni(CO)$_2${1,2-C_6H_4(PMePh)$_2$}] (1.0 g, 2.25 mmol) and tetra-*n*-butylammonium chloride (0.97 g, 3.5 mmol) were dissolved in dichloromethane (30 mL), and the solution was diluted with benzene (5 mL) and ethanol (10 mL). The solution was cooled to 0 °C, solid nitrosyl hexafluorophosphate (0.4 g, 2.25 mmol) was added, and the reaction mixture was stirred for 30 min at 0 °C and for a further 2 h at room temperature. The solvent was then removed, and the residue was extracted with dichloromethane and the extract washed with water. Dilution of the dried ($MgSO_4$) organic fraction, after concentration, with methanol gave the product in 60% yield.

[*T*-4-(*R,*R**)]-(±)-Chloronitrosyl[1,2-phenylenebis(methylphenylphosphine)]nickel(0) [(*R**,*R**)-1 (X = Cl)]** was prepared by Method A: deep blue prisms from CH_2Cl_2–EtOH in 55% yield; mp 151–153 °C. Anal. Calcd for $C_{20}H_{20}ClNNiOP_2$: C, 53.8; H, 4.5; N, 3.1. Found: C, 53.9; H, 4.5; N, 3.0. ^1H NMR: δ 2.13 (d, 3 H, $^2J_{PH}$ = 9.3 Hz, P*Me*), 2.15 (d, 3 H, $^2J_{PH}$ = 7.3 Hz, P*Me*), 7.32–7.81 (m, 14 H, aromatics). $^{31}P\{^1H\}$ NMR: δ 32.9, 40.7 (AB q, 2 P, $^2J_{PP}$ = 39.1 Hz). IR: ν(NO) 1745 cm^{-1}.

[*T*-4-(*R,*S**)]-*anti*-Bromonitrosyl[1,2-phenylenebis(methylphenylphosphine)]nickel(0) [(*R**,*S**)-1 (X = Br)].** The complex (*R**,*S**)-1 (X = Cl) (0.45 g, 1 mmol) was dissolved in dichloromethane (10 mL), and a solution of potassium bromide (0.48 g, 4 mmol) in water (5 mL) was added. The mixture was stirred for 18 h at room temperature. The organic layer was separated, washed with water, dried and filtered; removal of the solvent left a blue solid, which, when recrystallized from dichloromethane–methanol afforded deep blue crystals of the product: mp 155–157 °C; 95% yield. Anal. Calcd for $C_{20}H_{20}BrNNiOP_2$: C, 48.9; H, 4.1; N, 2.8. Found: C, 48.8; H, 4.1; N, 2.6. ^1H NMR: δ 2.20 (t, 6 H, $|^2J_{PH} + {}^4J_{P'H}|$ = 10.3 Hz, P*Me*), 7.32–7.69 (m, 14 H, aromatics).

The following compounds were prepared similarly.

[*T*-4-(*R,*R**)]-(±)-Bromonitrosyl[1,2-phenylenebis(methylphenylphosphine)]nickel(0) [(*R**,*R**)-1 (X = Br)]**: blue needles: mp 109–111 °C; 95% yield. Anal. Calcd for $C_{20}H_{20}BrNNiOP_2$: C, 48.9; H, 4.1; N, 2.8. Found: C, 48.6; H, 4.1; N, 2.9. ^1H NMR: δ 2.15 (d, 3 H, $^2J_{PH}$ = 7.7 Hz, P*Me*), 2.20 (d, 3 H, $^2J_{PH}$ = 9.7 Hz, P*Me*), 7.33–7.72 (m, 14 H, aromatics). $^{31}P\{^1H\}$ NMR: δ 30.2, 36.6 (AB q, 2 P, $^2J_{PP}$ = 36.6 Hz).

[*T*-4-(*R,*S**)]-*anti*-Iodonitrosyl[1,2-phenylenebis(methylphenylphosphine)]nickel(0) [(*R**,*S**)-1 (X = I)]**: deep blue crystals; mp 181–183 °C; 96% yield. Anal. Calcd for $C_{20}H_{20}INNiOP_2$: C, 44.7; H, 3.8; N, 2.6. Found: C, 44.4; H, 3.7; N, 2.6. ^1H NMR: δ 2.32 (t, 6 H, $|^2J_{PH} + {}^4J_{P'H}|$ = 10.1 Hz, P*Me*), 7.29–7.78 (m, 14 H, aromatics). $^{31}P\{^1H\}$ NMR: δ 33.10 (s, 2 P). IR: ν(NO) 1770 cm^{-1}.

[*T*-4-(*R,*R**)]-(±)-Iodonitrosyl[1,2-phenylenebis(methylphenylphosphine)]nickel(0) [(*R**,*R**)-1 (X = I)]**: deep blue crystals; mp 125–127 °C; 97% yield. Anal. Calcd for $C_{20}H_{20}INNiOP_2$: C, 44.7; H, 3.8; N, 2.6; I, 23.6. Found: C, 44.9; H, 3.8; N, 2.7; I, 23.5. ^1H NMR: δ 2.17 (d, 3 H, $^2J_{PH}$ = 8.6 Hz, P*Me*), 2.31 (d, 3 H, $^2J_{PH}$ = 9.5 Hz, P*Me*), 7.33–7.72 (m, 14 H, aromatics). $^{31}P\{^1H\}$ NMR: δ 27.0, 31.7 (AB q, 2 P, $^2J_{PP}$ = 31.7 Hz). IR: ν(NO) 1752 cm^{-1}.

[*T*-4-(*R,*S**)]-*anti*-Cyanonitrosyl[1,2-phenylenebis(methylphenylphosphine)]nickel(0) [(*R**,*S**)-1 (X = CN)]**: blue crystals; mp 159–161 °C; 97% yield. Anal. Calcd for $C_{21}H_{20}N_2NiOP_2$: C, 57.7; H, 4.6; N, 6.4. Found: C, 57.2; H, 4.5; N, 6.4. ^1H NMR: δ 2.21 (t, 6 H, $|^2J_{PH} + {}^4J_{P'H}|$ = 10.0 Hz, P*Me*), 7.36–7.81 (m, 14 H, aromatics). $^{31}P\{^1H\}$ NMR: δ 43.4 (s, 2 P). IR: ν(NO) 1765 cm^{-1}; ν(CN) 2055 cm^{-1}.

[*T*-4-(*R,*R**)]-(±)-Cyanonitrosyl[1,2-phenylenebis(methylphenylphosphine)]nickel(0) [(*R**,*R**)-1 (X = CN)]**: blue crystals; mp 188–190 °C; 95% yield. ^1H NMR: δ 2.17 (d, 3 H, $^2J_{PH}$ = 7.6 Hz, P*Me*), 2.24 (d, 3 H, $^2J_{PH}$ = 9.5 Hz, P*Me*), 7.28–7.70 (m, 14 H, aromatics). $^{31}P\{^1H\}$ NMR: δ 37.0, 41.8 (AB q, 2 P, $^2J_{PP}$ = 12.2 Hz). IR: ν(NO) 1770 cm^{-1}; ν(CN) 2110 cm^{-1}.

[*T*-4-(*R,*S**)]-*anti*-(Isothiocyanato)nitrosyl[1,2-phenylenebis(methylphenylphosphine)]nickel(0) [(*R**,*S**)-1 (X = NCS)]**: blue crystals mp 179–181 °C; 96% yield. Anal. Calcd for $C_{21}H_{20}N_2NiOP_2S$: C, 53.8; H, 4.3; N, 6.0. Found: C, 53.9; H, 4.3; N, 5.9. ^1H NMR: δ 2.09 (t, 6 H, $|^2J_{PH} + {}^4J_{P'H}|$ = 9.9 Hz, P*Me*), 7.39–7.70 (m, 14 H, aromatics). $^{31}P\{^1H\}$ NMR: δ 44.1 (s, 2 P). IR: ν(NO) 1755 cm^{-1}; ν(CN) 2045 cm^{-1}.

[*T*-4-(*R,*R**)]-(±)-(Isothiocyanato)nitrosyl[1,2-phenylenebis(methylphenylphosphine)]nickel(0) [(*R**,*R**)-1 (X = NCS)]**: blue crystals; mp 123–125 °C; 97% yield. Anal. Calcd for $C_{21}H_{20}N_2NiOP_2S$: C, 53.8; H, 4.3; N, 6.0. Found: C, 53.8; H, 4.3; N, 5.9. ^1H NMR: δ 2.10 (d, 3 H, $^2J_{PH}$ = 9.5 Hz, P*Me*), 2.21 (d, 3 H, $^2J_{PH}$ = 8.0 Hz, P*Me*), 7.43–7.74 (m, 14 H, aromatics). $^{31}P\{^1H\}$ NMR: δ 35.8, 42.7 (AB q, 2 P, $^2J_{PP}$ = 31.8 Hz).

[*T*-4-(*R,*R**)]-(±)-(Cyano-^{13}C)nitrosyl[1,2-phenylenebis(methylphenylphosphine)]nickel(0) [(*R**,*R**)-1 (X = ^{13}CN)]**: blue crystals; mp 188–190 °C; 92% yield. ^1H NMR: identical with that of (*R**,*R**)-1 (X = CN). $^{13}C\{^1H\}$ NMR: δ 14.43 (d of d, 1 C, $^1J_{PC}$ = 18 Hz, $^3J_{CC}$ = 6 Hz, P*Me*), 15.10 (d, 1 C, $^1J_{PC}$ = 18 Hz, P*Me*), 128.89–132.16 (m, 18 C, aromatics), 143.81 (X of ABX, 1 C, $|^2J_{PC}|$ = 7.3 Hz, $|^2J_{PC}|$ = 9.8 Hz, ^{13}CN). $^{31}P\{^1H\}$ NMR: δ 37.2, 42.0 (AB of ABX, 2 P, $|^2J_{PP}|$ = 12.2 Hz, $|^2J_{PC}|$ = 7.3 Hz, $|^2J_{PC}|$ = 9.8 Hz). IR: ν(NO) 1770 cm^{-1}; ν(CN) 2065 cm^{-1}.

[*T*-4-(*R,*S**)]-*anti*-Nitrosyl[1,2-phenylenebis(methylphenylphosphine)](trimethylphosphine)nickel(0) Hexafluorophosphate [(*R**,*S**)-2 (L = PMe$_3$)]**: (*R**,*S**)-1 (X = Cl) (0.446 g, 1 mmol) and excess ammonium hexafluorophosphate (1.0 g) were dissolved in methanol (20 mL), and the solution was diluted with acetone (40 mL). The reaction mixture was stirred for 30 min at room temperature, and then it was cooled to 0 °C and treated with a solution of trimethylphosphine (0.091 g, 1.2 mmol) in methanol (10 mL). The reaction mixture was then stirred for ca. 1 h at 0 °C, and then it was warmed to room temperature. After removal of solvent, the residue was extracted into dichloromethane, and the extract was washed with water, dried, and filtered. The volume of the solution was then reduced to ca. 15 mL, and ethanol was added. Cooling of the concentrate to 0 °C produced fine red needles of the anti diastereomer: mp 208–210 °C; 0.60 g, 95%. Anal. Calcd for $C_{23}H_{29}F_6NNiOP_4$: C, 43.7; H, 4.6; N, 2.2. Found: C, 44.0; H, 4.7; N, 2.0. ^1H NMR: δ 1.53 (d, 9 H, $^2J_{PH}$ = 9.2 Hz, P*Me*$_3$), 2.19 (d, 6 H, $^2J_{PH}$ = 9.0 Hz, P*Me*), 7.15–7.92 (m, 14 H, aromatics). $^{31}P\{^1H\}$ NMR: δ −7.0 (t, 1 P, $^2J_{PP}$ = 6.3 Hz, *P*Me$_3$), 34.3 (d, 2 P, $^2J_{PP}$ = 6.3 Hz, *P*Me). IR: ν(NO) 1775 cm^{-1}. ^1H NMR (at equilibrium): δ 0.65 (d, 5.4 H, $^2J_{PH}$ = 9.2 Hz, P*Me*$_3$-*syn*), 1.53 (d, 3.6 H, $^2J_{PH}$ = 9.2 Hz, P*Me*$_3$-*anti*), 2.19 (d, 2.4 H, $^2J_{PH}$ = 9.0 Hz, P*Me*-*anti*), 2.44 (d, 3.6 H, $^2J_{PH}$ = 9.2 Hz, P*Me*-*syn*), 7.15–7.92 (m, 14 H, aromatics). $^{31}P\{^1H\}$ NMR (at equilibrium): δ −9.3 (t, 0.6 P, $^2J_{PP}$ = 3.9 Hz, *P*Me$_3$-*syn*), −7.0 (t, 0.4 P, $^2J_{PP}$ = 6.3 Hz, *P*Me$_3$-*anti*), 34.3 (d, 1.2 P, $^2J_{PP}$ = 6.3 Hz, *P*Me-*anti*), 40.3 (d, 0.8 P, $^2J_{PP}$ = 3.9 Hz, *P*Me-*syn*).

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The following compounds were prepared similarly.

[*T*-4-(*R,*R**)]-(±)-Nitrosyl[1,2-phenylenebis(methylphenylphosphine)](trimethylphosphine)nickel(0) Hexafluorophosphate [(*R**,*R**)-2 (L = PMe_3)]**: red crystals; mp 194–196 °C; 96% yield. Anal. Calcd for $C_{23}H_{29}F_6NNiOP_4$: C, 43.7; H, 4.6; N, 2.2. Found: C, 43.8; H, 4.6; N, 2.2. ^1H NMR: δ 0.53 (d, 9 H, $^2J_{PH}$ = 9.4 Hz, P*Me*$_3$), 1.46 (d, 3 H, $^2J_{PH}$ = 9.1 Hz, P*Me*), 2.41 (d, 3 H, $^2J_{PH}$ = 8.6 Hz, P*Me*), 7.16–7.74 (m, 14 H, aromatics). $^{31}P\{^1H\}$ NMR: δ −8.5, 37.7, 38.9 (ABX, 3 P, $|^2J_{PP}|$ = 7.9 Hz, $|^2J_{PP}|$ = 3.7 Hz, $|^2J_{PP}|$ = 4.9 Hz).

[*T*-4-(*R,*S**)]-*anti*-(Dimethylphenylphosphine)nitrosyl[1,2-phenylenebis(methylphenylphosphine)]nickel(0) Hexafluorophosphate [(*R**,*S**)-2 (L = PMe_2Ph)]**: red needles; mp 139–141 °C; 95% yield. Anal. Calcd for $C_{28}H_{31}F_6NNiOP_4$: C, 48.4; H, 4.5; N, 2.0. Found: C, 47.9; H, 4.6; N, 1.9. ^1H NMR: δ 1.73 (d, 6 H, $^2J_{PH}$ = 8.5 Hz, P*Me*$_2$Ph), 1.94 (d, 6 H, $^2J_{PH}$ = 9.2 Hz, P*Me*), 7.21–7.74 (m, 19 H, aromatics). $^{31}P\{^1H\}$ NMR: δ 4.8 (t, 1 P, $^2J_{PP}$ = 6.3 Hz, *P*Me$_2$Ph), 34.3 (d, 2 P, $^2J_{PP}$ = 6.3 Hz, *P*Me). IR: ν(NO) 1800 cm^{-1}. ^1H NMR (at equilibrium): δ 0.75 (d, 3.6 H, $^2J_{PH}$ = 8.7 Hz, P*Me*$_2$Ph-*syn*), 1.73 (d, 2.4 H, $^2J_{PH}$ = 8.5 Hz, P*Me*$_2$Ph-*anti*), 1.94 (d, 2.4 H, $^2J_{PH}$ = 9.2 Hz, P*Me*-*anti*), 2.42 (d, 3.6 H, $^2J_{PH}$ = 9.0 Hz, P*Me*-*syn*), 7.21–7.74 (m, 19 H, aromatics). $^{31}P\{^1H\}$ NMR (at equilibrium): δ 3.2 (t, 0.6 P, $^2J_{PP}$ = 3.4 Hz, *P*Me$_2$Ph-*syn*), 4.8 (t, 0.4 P, $^2J_{PP}$ = 6.3 Hz, *P*Me$_2$Ph-*anti*), 34.3 (d, 0.8 P, $^2J_{PP}$ = 6.3 Hz, *P*Me-*anti*), 40.0 (d, 1.2 P, $^2J_{PP}$ = 3.4 Hz, *P*Me-*syn*).

[*T*-4-(*R,*R**)]-(±)-(Dimethylphenylphosphine)nitrosyl[1,2-phenylenebis(methylphenylphosphine)]nickel(0) Hexafluorophosphate [(*R**,*R**)-2 (L = PMe_2Ph)]**: red needles; mp 135–137 °C; 94% yield. ^1H NMR: δ 1.22 (d, 3 H, $^2J_{PH}$ = 8.8 Hz, P*Me*$_a$Me$_b$Ph), 1.37 (d, 3 H, $^2J_{PH}$ = 9.8 Hz, PMe$_a$*Me*$_b$Ph), 1.80 (d, 3 H, $^2J_{PH}$ = 8.5 Hz, P*Me*), 2.42 (d, 3 H, $^2J_{PH}$ = 8.5 Hz, P*Me*), 7.10–7.73 (m, 19 H, aromatics). $^{31}P\{^1H\}$ NMR: δ 3.6, 37.8, 38.7 (ABX, 3 P, $|^2J_{PP}|$ = 7.3 Hz, $|^2J_{PP}|$ = 4.0 Hz, $|^2J_{PP}|$ = 1.8 Hz).

[*T*-4-(*R,*S**)]-*anti*-(Methyldiphenylphosphine)nitrosyl[1,2-phenylenebis(methylphenylphosphine)]nickel(0) Hexafluorophosphate [(*R**,*S**)-2 (L = $PMePh_2$)]**: red needles; mp 197–200 °C; 96% yield. Anal. Calcd for $C_{33}H_{33}F_6NNiOP_4$: C, 52.4; H, 4.4; N, 1.8. Found: C, 52.1; H, 4.3; N, 1.8. ^1H NMR: δ 1.83 (d, 6 H, $^2J_{PH}$ = 9.5 Hz, P*Me*), 1.85 (d, 3 H, $^2J_{PH}$ = 7.8 Hz, P*Me*Ph$_2$), 6.97–7.84 (m, 24 H, aromatics). $^{31}P\{^1H\}$ NMR: δ 20.2 (t, 1 P, $^2J_{PP}$ = 5.9 Hz, *P*MePh$_2$), 34.1 (d, 2 P, $^2J_{PP}$ = 5.9 Hz, *P*Me). ^1H NMR (at equilibrium): δ 0.47 (d, 1.5 H, $^2J_{PH}$ = 8.3 Hz, P*Me*Ph$_2$-*syn*), 1.83 (d, 3 H, $^2J_{PH}$ = 9.5 Hz, P*Me*-*anti*), 1.85 (d, 1.5 H, $^2J_{PH}$ = 7.8 Hz, P*Me*Ph$_2$-*anti*), 2.45 (d, 3 H, $^2J_{PH}$ = 9.3 Hz, P*Me*-*syn*), 6.97–7.84 (m, 24 H, aromatics). $^{31}P\{^1H\}$ NMR (at equilibrium): δ 19.1 (t, 0.5 P, $^2J_{PP}$ = 2.4 Hz, *P*MePh$_2$-*syn*), 20.2 (t, 0.5 P, $^2J_{PP}$ = 5.9 Hz, *P*MePh$_2$-*anti*), 34.1 (d, 1 P, $^2J_{PP}$ = 5.9 Hz, *P*Me-*anti*), 39.5 (d, 1 P, $^2J_{PP}$ = 2.4 Hz, *P*Me-*syn*).

[*T*-4-(*R,*R**)]-(±)-(Methyldiphenylphosphine)nitrosyl[1,2-phenylenebis(methylphenylphosphine)]nickel(0) Hexafluorophosphate [(*R**,*R**)-2 (L = $PMePh_2$)]**: red crystals; mp 92–97 °C; 94% yield. Anal. Calcd for $C_{33}H_{33}F_6NiOP_4$: C, 52.4; H, 4.4; N, 1.8. Found: C, 52.3; H, 4.4; N, 1.7. ^1H NMR: δ 1.34 (d, 3 H, $^2J_{PH}$ = 7.8 Hz, P*Me*Ph$_2$), 1.74 (d, 3 H, $^2J_{PH}$ = 8.6 Hz, P*Me*), 2.44 (d, 3 H, $^2J_{PH}$ = 8.3 Hz, P*Me*), 6.71–7.58 (m, 24 H, aromatics). $^{31}P\{^1H\}$ NMR: δ 19.8, 37.6, 38.3 (ABX, 3 P, $|^2J_{PP}|$ = 6.9 Hz, $|^2J_{PP}|$ = 4.0 Hz, $|^2J_{PP}|$ = 1.3 Hz).

[*T*-4-(*R,*S**)]-*anti*-Nitrosyl[1,2-phenylenebis(methylphenylphosphine)](triphenylphosphine)nickel(0) Hexafluorophosphate [(*R**,*S**)-2 (L = PPh_3)]**: red needles; mp 135–140 °C; 85% yield. ^1H NMR: δ 1.66 (d, 6 H, $^2J_{PH}$ = 9.5 Hz, P*Me*), 7.22–7.79 (m, 29 H, aromatics). $^{31}P\{^1H\}$ NMR: δ 35.0 (d, 2 P, $^2J_{PP}$ = 6.3 Hz, *P*Me), 40.5 (t, 1 P, $^2J_{PP}$ = 6.3 Hz, *P*Ph$_3$). IR: ν(NO) 1790 cm^{-1}.

[*T*-4-(*R,*R**)]-(±)-Nitrosyl[1,2-phenylenebis(methylphenylphosphine)](triphenylphosphine)nickel(0) Hexafluorophosphate [(*R**,*R**)-2 (L = PPh_3)]**: red crystals; mp 214–216 °C; 86% yield. Anal. Calcd for $C_{38}H_{35}F_6NNiOP_4$: C, 55.8; H, 4.3; N, 1.7. Found: C, 55.6; H, 4.2; N, 1.7. ^1H NMR: δ 1.43 (d, 3 H, $^2J_{PH}$ = 8.8 Hz, P*Me*), 2.30 (d, 3 H, $^2J_{PH}$ = 8.0 Hz, P*Me*), 6.74–7.75 (m, 29 H, aromatics). $^{31}P\{^1H\}$ NMR: δ 34.6, 35.4, 38.3 (ABX, 3 P, $|^2J_{PP}|$ = 8.0 Hz, $|^2J_{PP}|$ = 3.7 Hz, $|^2J_{PP}|$ = 8.5 Hz).

[*T*-4-(*R,*S**)]-*anti*-Nitrosyl[1,2-phenylenebis(methylphenylphosphine)](trimethyl phosphite)nickel(0) Hexafluorophosphate [(*R**,*S**)-2 [L = $P(OMe)_3$]]**: red needles; mp 186–188 °C; 97% yield. Anal. Calcd for $C_{23}H_{29}F_6NNiO_4P_4$: C, 40.6; H, 4.3; N, 2.1. Found: C, 40.4; H, 4.3; N, 1.5. ^1H NMR: δ 2.19 (d, 6 H, $^2J_{PH}$ = 10.3 Hz, P*Me*), 3.82 (d, 9 H, $^2J_{PH}$ = 12.1 Hz, P(O*Me*)$_3$), 7.35–7.73 (m, 14 H, aromatics). $^{31}P\{^1H\}$ NMR: δ 39.0 (d, 2 P, $^2J_{PP}$ = 26.2 Hz, *P*Me), 161.2 (t, 1 P, $^2J_{PP}$ = 25.8 Hz, *P*(OMe)$_3$). IR: ν(NO) 1825 cm^{-1}. ^1H NMR (equilibrium): δ 2.19 (d, 5.4 H, $^2J_{PH}$ = 10.3 Hz, P*Me*-*anti*), 2.44 (d, 0.6 H, $^2J_{PH}$ = 10.3 Hz, P*Me*-*syn*), 3.16 (d, 0.9 H, $^2J_{PH}$ = 12.1 Hz, P(O*Me*)$_3$-*syn*), 3.82 (d, 8.1 H, $^2J_{PH}$ = 12.1 Hz, P(O*Me*)$_3$-*anti*), 7.35-7.73 (m, 14 H, aromatics). $^{31}P\{^1H\}$ NMR (equilibrium): δ 39.0 (d, 1.8 P, $^2J_{PP}$ = 26.2 Hz, *P*Me-*anti*), 39.5 (d, 0.2 P, $^2J_{PP}$ = 26.2 Hz, *P*Me-*syn*), 159.5 (t, 0.1 P, $^2J_{PP}$ = 25.8 Hz, *P*(OMe)$_3$-*syn*), 161.2 (t, 0.9 P, $^2J_{PP}$ = 25.8 Hz, *P*(OMe)$_3$-*anti*).

[*T*-4-(*R,*R**)]-(±)-(Dimethyl-d_6-phenylphosphine)nitrosyl[1,2-phenylenebis(methylphenylphosphine)]nickel(0) Hexafluorophosphate [(*R**,*R**)-2 [L = P(Me-d_3)$_2$Ph]]**: red crystals; mp 81–82 °C; 85% yield. Anal. Calcd for $C_{28}H_{25}D_6F_6NNiOP_4$: C, 48.0; (H + D), 5.3; N, 2.0. Found: C, 47.9; (H + D), 4.7; N, 1.8. ^1H NMR: δ 1.80 (d, 3 H, $^2J_{PH}$ = 8.5 Hz, P*Me*), 2.42 (d, 3 H, $^2J_{PH}$ = 8.5 Hz, P*Me*), 7.10–7.73 (m, 19 H, aromatics).

Structural Analyses. Single crystals of (*R**,*S**)-*anti*-**1** (X = NCS) were obtained from a dichloromethane–methanol solution of the complex by slow evaporation of the dichloromethane. The crystals of (*R**,*S**)-*anti*-**2** [L = $P(OMe)_3$] were obtained from the slow crystallization from dichloromethane–ethanol of the initial syn:anti = 1:9 mixture of diastereomers.

Computer Programs. The programs used in this work were written by F.S.S.

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Supplementary Material Available: For (*R**,*S**)-*anti*-**1** (X = NCS) and (*R**,*S**)-*anti*-**2** [L = $P(OMe)_3$], description of the crystal structure determinations, figures showing the atom-labeling schemes, and tables of final positional parameters, bond distances and angles, anisotropic thermal parameters of non-hydrogen atoms, and calculated hydrogen atom parameters (23 pages); tables of observed and calculated structure factors for both structures (36 pages). Ordering information is given on any current masthead page.