The ligand capacities span the range from bulky carbanionic substituents (comparable to silylmethanides) to chelating phosphine donors and may be controlled primarily by adjusting their steric demand. Thus, not only is a new fruitful field of Sn(II) chemistry opened, but also a general application to other main group element coordination compounds clearly lies at hand.

Reactions of Ethyl Cyanoformate with (np3)Ni, (np3)CoH [np3 = N(CH2CH2PPh2)3], and (triphos)Ni [triphos = MeC(CH2PPh2)3]. Crystal Structures of the Ethoxycarbonyl Complexes [(np3)Ni(CO2Et)]BPh4 and (triphos)Ni(CN)(CO2Et)

Claudio Bianchini,* Dante Masi, Andrea Meli, and Michal Sabat

Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione CNR, 50132 Firenze, Italy

Ethyl cyanoformate, NCCO2Et, is used as starting material to introduce ethoxycarbonyl and/or cyanide groups into complex frameworks. Thus, NCOO2Et reacts with the Ni(0) complex (np3)Ni (1) [np3 = N(CH2CH2PPh2)3] or with the Ni(0) fragment (triphos)Ni [triphos = MeC(CH2PPh2)3] to give [(np3)-Ni(CO2Et)]+ (3) and (triphos)Ni(CN)(CO2Et) (4), respectively. The crystal structures of 3·BPh4 and 4 have been determined by standard X-ray methods. Compound 3·BPh4 crystallizes in the monoclinic space group $C2/c$ with $a = 33.429$ (10) Å, $b = 8.929$ (2) Å, $c = 38.773$ (11) Å, $\beta = 100.25$ (2)°, and $Z = 8$. The structure was refined to an R factor of 0.068 ($R_w = 0.068$) by using 2908 reflections with $I > 3\sigma(I)$. The coordination polyhedron of the nickel(II) atom can be described as a trigonal bipyramid whose equatorial plane is defined by the three phosphorus atoms of np3. Compound 4 crystallizes in the orthorhombic space group $Pn2_1a$ with $a = 26.957$ (8) Å, $b = 13.480$ (4) Å, $c = 10.690$ (3) Å, and $Z = 4$. The structure was refined to an R factor of 0.055 ($R_w = 0.056$) by using 1897 reflections with $I > 3\sigma(I)$. The compound exhibits quite regular square-pyramidal environment of the nickel(II) atom. Reaction of NCCO2Et with the Co(I) hydride (np3)CoH (5) yields (np3)Co(CN) and HCO2Et.

Introduction

Alkoxycarbonyl metal complexes constitute a ubiquitous class of compounds whose chemistry is presently the object of intense speculation. In fact, these organometallic compounds can participate as starting,[1] final,[1a,2] or intermediate[1a,e,3] products in several important reactions involving carbon oxides and other carbonyl-derived functional groups.

At least six different synthetic routes to alkoxycarbonyl complexes are available. These include alkoxide ion attack on carbonylmetal cations,[1a,d,e] nucleophilic attack on chloroformates by anionic metal complexes,[1a] oxidative addition of chloroformates to coordinatively unsaturated metal fragments,[1a] alkylation of η^1-CO2 complexes,[2] carbonylation of alkoxo complexes,[3b] and, finally, reaction of alkoxide ions with neutral metal carbonyls or halometal carbonyls.[3c]

In this paper we report on the potential applications of ethyl cyanoformate, NCCO2Et, to synthesize ethoxycarbonyl derivatives. Ethyl cyanoformate reacts with the Ni(0) complex (np3)Ni[4] (1) [np3 = N(CH2CH2PPh2)3] or with the Ni(0) metal fragment (triphos)Ni (2) [triphos = MeC(CH2PPh2)3] to give the stable Ni(II) ethoxycarbonyls [(np3)Ni(CO2Et)]+ (3) and (triphos)Ni(CN)(CO2Et) (4), respectively. The structures of 3·BPh4 and 4 have been established by X-ray methods. The reaction between the Co(I) hydride (np3)CoH[4] (5) and NCCO2Et is also presented.

Results and Discussion

Reaction of 1 with NCCO2Et. Reaction of the Ni(0) complex 1 in THF with a slight excess of NCCO2Et, fol-

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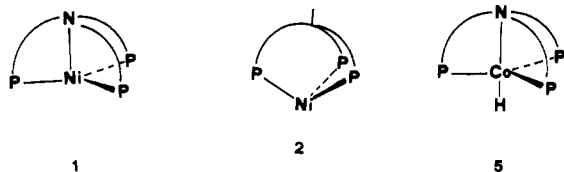
lowed by addition of $NaBPh_4$ in n-butyl alcohol gives red crystals of 3·BPh_4 in 95% yield (eq 1).

$$(np_3)Ni + NCCO_2Et + NaBPh_4 \rightarrow$$
$$[(np_3)Ni(CO_2Et)]BPh_4 + NaCN \quad (1)$$
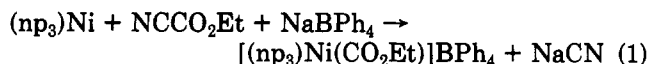
Compound 3·BPh_4 is diamagnetic and air-stable in the solid state. It is soluble in common organic solvents in which it behaves as a 1:1 electrolyte (molar conductance value in 10^{-3} M nitroethane solution = 42 cm^2 Ω^{-1} mol^{-1}).[5,6] The infrared spectrum exhibits strong bands at 1640 and 1035 cm^{-1}, characteristic of ν(CO) and ν(C-O-C) of alkoxycarbonyl groups.[1a] The ^{1}H NMR spectrum in CD_2Cl_2 at 293 K contains a quartet at δ 3.82 and a triplet at δ 0.58 which are typical of the ethoxy protons of COOEt groups.[3a] The $^{31}P\{^1H\}$NMR spectrum in CD_2Cl_2 consists of a singlet at 14.19 ppm. This pattern is consistent with rapid intramolecular exchange of the three phosphorus atoms of np_3 around the metal atom.[5] The large deshielding (coordination chemical shift of δ 33.75) found for this complex suggests that a ring contribution is present, indicating that no coordination change occurs on going from solid state to solution. The reflectance spectrum, with one absorption at 21 200 cm^{-1} is comparable with those of trigonal-bipyramidal nickel(II) complexes such as [(np_3)NiR]BPh$_4$ (R = Me, Et, COMe).[6] On the basis of all of these data a structure may be assigned to 3·BPh_4 in which nickel is five-coordinate by the np_3 ligand and the carbon atom of an ethoxycarbonyl group. The X-ray structural analysis confirms such an arrangement of the donor atoms. Alternative syntheses of 3·BPh_4 involving ethoxide ion attack on (np_3)Ni(CO) or [(np_3)Ni(CO)]BPh$_4$ have been previously reported by us.[1e] At variance with the present route, the yields are very low (15–20%).

Interestingly, 3 is not stable in its reaction mixture. The displacement reaction (2) occurs, in fact, when 3 is not immediately precipitated as BPh$_4^-$ salt. Thus, it is rea-

$$[(np_3)Ni(CO_2Et)]^+ + CN^- \rightarrow$$
$$[(np_3)Ni(CN)]^+ + [CO_2Et]^- \quad (2)$$

sonable to assume that the magenta cyano complex [(np_3)Ni(CN)]BPh$_4$ (6), obtained by adding NaBPh$_4$ to the reaction mixture, is thermodynamically more stable than the ethoxycarbonyl derivative. On the basis of analytical, spectroscopic [IR 2120 cm^{-1} [ν(CN)]; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 293 K) 19.51 ppm (s); reflectance spectrum 20 500 cm^{-1}], and conductivity data [molar conductance value in 10^{-3} M nitroethane solution = 40 cm^2 Ω^{-1} mol^{-1}], 6 is assigned a structure in which the nickel atom is coordinated by the nitrogen atom and the three phosphorus atoms of np_3 and by a cyanide ion.
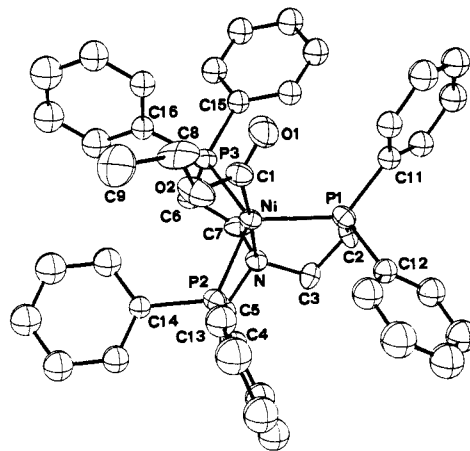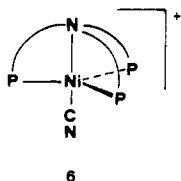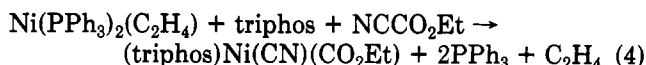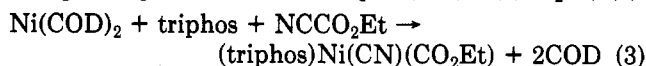

Figure 1. ORTEP drawing of the [(np_3)Ni(CO$_2$Et)]$^+$ complex cation (3). Hydrogen atoms are omitted for clarity.

Reaction of 2 with NCCO$_2$Et. The ability of the 18-electron species 1 to oxidatively add the CO$_2$Et group from NCCO$_2$Et prompted us to investigate the reaction of the 16-electron fragment (triphos)Ni with the latter reagent. The (triphos)Ni unit is formed in THF solution by treatment of suitable Ni(0) species such as Ni(COD)$_2$ or Ni(PPh$_3$)$_2$(C$_2$H$_4$) with triphos. Ethyl cyanoformate oxidatively adds to 2 according to eq 3 and 4 to give a red-orange complex of formula (triphos)Ni(CN)(CO$_2$Et) (4).

$$Ni(COD)_2 + triphos + NCCO_2Et \rightarrow$$
$$(triphos)Ni(CN)(CO_2Et) + 2COD \quad (3)$$

$$Ni(PPh_3)_2(C_2H_4) + triphos + NCCO_2Et \rightarrow$$
$$(triphos)Ni(CN)(CO_2Et) + 2PPh_3 + C_2H_4 \quad (4)$$

Compound 4 is diamagnetic and air-stable in the solid state and in solution as well. It is soluble in common organic solvents in which it behaves as a nonelectrolyte. The IR spectrum shows absorptions at 1650 and 1025 cm^{-1} which are assigned to ν(C=O) and ν(C-O-C) of the ethoxycarbonyl group, respectively. A further band at 2105 cm^{-1} indicates the presence of a cyanide ligand. The ^{1}H NMR spectrum in CD_2Cl_2 contains a quartet at δ 3.45 and a triplet at δ 0.77 (intensity ratio 2:3), which are typical of the ethoxy protons. The $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 consists of a resonance at ~5.50 ppm. This pattern, unchanged even at ~60 °C, is consistent with rapid intramolecular exchange of the three phosphorus atoms of triphos around the nickel atom.[7] The reflectance spectrum shows a band at 21 300 cm^{-1}. All the information gathered from the spectroscopic measurements is suggestive of a structure in which the nickel atom is five-coordinate by the three phosphorus atoms of triphos, by a cyanide ion, and by an ethoxycarbonyl group. The X-ray structural analysis, presented below, confirms such an arrangement of the ligands in 4.

Reaction of 5 with NCCO$_2$Et. The hydride 5 in THF reacts with neat NCCO$_2$Et to give the known trigonal-bipyramidal Co(I) cyano complex (np_3)Co(CN) (7) and ethyl formate (eq 5). The formation of HCO$_2$Et in the course of the reaction was detected by GLC.

$$(np_3)CoH + NCCO_2Et \rightarrow (np_3)Co(CN) + HCO_2Et \quad (5)$$
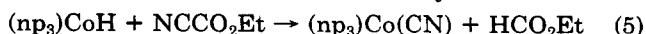
Description of the Structure of 3·BPh$_4$. As shown by an earlier MO analysis[8] the (np_3)Ni fragment has an

6

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Table I. Summary of Crystal Structure Data

	3·BPh$_4$	4
formula	C$_{69}$H$_{67}$BNO$_2$P$_3$Ni	C$_{45}$H$_{44}$NO$_2$P$_3$Ni
M_r	1104.75	782.49
cryst form	red needle	red-orange prism
cryst size, mm	0.1 × 0.17 × 0.6	0.2 × 0.2 × 0.15
cryst system	monoclinic	orthorhombic
space group	C2/c	Pn2$_1$a
a, Å	33.429 (10)	26.967 (8)
b, Å	8.929 (2)	13.480 (4)
c, Å	38.773 (11)	10.690 (3)
β, deg	100.25 (2)	
V, Å^3	11389	3885
Z	8	4
d(calcd), g cm^{-3}	1.29	1.34
d(measd), g cm^{-3}	1.28	1.34
μ(Mo Kα), cm^{-1}	4.7	6.6
radiatn	graphite-monochromated Mo Kα, λ = 0.710 69 Å	
scan type	θ/2θ	θ/2θ
2θ range, deg	5–45	5–50
scan width, deg	0.9	0.8
scan speed, deg s^{-1}	0.06	0.04
total data	8041	3857
unique data I > 3σ(I)	2908	1897
no. of parameters	279	226
R	0.068	0.055
R$_w$	0.068	0.056
w 1.0[σ^2(F) + pF^2]$^{-1}$	p = 0.0005	p = 0.001

axial σ-hybrid that can be utilized in the formation of several stable five-coordinate complexes with various organic fragments. The compound 3·BPh$_4$ is an example of the stabilization gained by means of the σ-hybrid. The structure of the [(np$_3$)Ni(CO$_2$Et)]$^+$ cation is presented in Figure 1. The coordination polyhedron of the nickel(II) atom can be described as a trigonal bipyramid whose equatorial plane is defined by the three phosphorus atoms of the np$_3$ ligand. The nitrogen atom of the tripodal ligand and the carbon atom of the ethoxycarbonyl group occupy the axial positions. Generally, the geometrical features of the np$_3$–Ni moiety are close to those found previously in other Ni(II) complexes with np$_3$,[6] although the Ni–N distance of 2.129 (8) Å is significantly shorter than that observed n the acyl derivative [(np$_3$)Ni(COMe)]$^+$ [2.31 (3) Å].[9] The Ni–C bond length has a value of 1.90 (1) Å that is characteristic for typical Ni–C σ-bonds.[9,10] The geometry of the ethoxycarbonyl fragment is essentially similar to that found in the square-planar complex Pt(PPh$_3$)$_2$-(CO$_2$Et)$_2$.[11] Thus, the C=O bond length in 3·BPh$_4$ [1.18 (1) Å] can be compared to that of 1.228 (7) Å in the Pt compound, while the remaining C–O distances, 1.33 (1) and 1.47 (1) Å, correspond to the analogous separations of the Pt complex [1.351 (7) and 1.46 (1) Å, respectively]. The O–C–O angles of the ethoxycarbonyl group are the same within the estimated standard deviations in both compounds having values of 120.5 (13)° for 3·BPh$_4$ and of 119.5 (6)° for the Pt derivative.

Description of the Structure of 4. Previous studies[12] have indicated that the cyanide anion has a particular influence in stabilizing pentacoordination of the nickel complexes. These complexes usually have a trigonal-bipyramidal geometry. On the other hand, the present compound exhibits quite regular square-pyramidal environment of the Ni(II) atom (Figure 2). The apical Ni–P(3) distance, 2.405 (4) Å, is of the same order as that observed
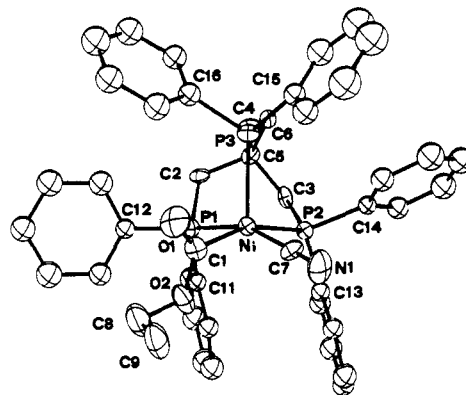
(9) Stoppioni, P.; Dapporto, P.; Sacconi, L. *Inorg. Chem.* **1978**, *17*, 718.

(10) (a) Sacconi, L; Dapporto, P.; Stoppioni, P. *Inorg. Chem.* **1976**, *15*, 325. (b) Sacconi, L.; Dapporto, P.; Stoppioni, P.; Innocenti, P.; Benelli, C. *Inorg. Chem.* **1977**, *16*, 1669.

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(12) Hope, H.; Olmstead, M. M.; Power, P. P.; Viggiano, M. *Inorg. Chem.* **1984**, *23*, 326 and references therein.

Figure 2. ORTEP drawing of the (triphos)Ni(CN)(CO$_2$Et) complex molecule (4). Hydrogen atoms have been omitted for clarity.

in the square-pyramidal complex Ni(CN)$_2$[P(CH$_2$OH)-Ph$_2$]$_3$[12] (8), 2.400 (3) Å, and is believed to be the longest Ni–P bond length for a nickel(II) phosphine complex. Note that in the latter structure the three phosphines act as monodentate ligands, while in the former one the phosphorus atoms come from the tripod-like ligand. Thus, even though the apical Ni–P distance might have been a subject of the constraints imposed by the geometry of the tridentate ligand, it reaches the same value as that found in 8 with an unrestricted phosphine moiety. Notice that 8 is considered the five-coordinate Ni(II) complex which represents the closest approach to dissociation [to the square-planar bis(phosphine) derivative] while overall structural integrity is maintained. With regard to the structure of 8, Power et al. emphasize the role of steric factors in influencing the Ni–P(apical) bond length. We agree that the long Ni–P(apical) distance in low-spin square-pyramidal phosphine cyano complexes of nickel(II) may depend also on steric factors. On the other hand, as it has been pointed out by Rossi and Hoffmann,[13] the predominant role is played by the electronic factors. In a sense, the following considerations confirm the importance of the frontier orbitals and their population in determining the geometrical features of five-coordinate nickel(II) complexes. Five-coordinate Ni(II) compounds with triphos are extremely rare.[7,14] Generally, in fact, when two further ligands are added to the (triphos)Ni(II) moiety, one arm of triphos spontaneously leaves the metal which becomes square planarly coordinated.[7,14b] This, however, does not happen in the case of 4 which maintains the solid-state configuration also in solution (see the ^{31}P NMR data). The only authenticated examples of five-coordinate Ni(II) complexes with triphos are the diamagnetic complex 4 and the high-spin paramagnetic square-pyramidal derivative (triphos)Ni(SeO$_4$) (9).[14a] In the latter complex, the Ni–P(apical) bond length is 2.299 (6) vs. 2.405 (4) Å in 4. Such a difference is easily rationalized in terms of the different electronic population of the frontier orbitals.[13] In particular, the energetic gap between the LUMO ($x^2 - y^2$) and the HOMO (z^2) is apparently smaller in 9, which contains basal oxygen donor atoms, than in 4 which has cyanide and ethoxycarbonyl basal ligands. This explains the difference in the Ni–P-(apical) distances and the magnetic properties of both compounds as well. The Ni–CN distance of 1.87 (1) Å in 4 approaches the values observed in several Ni(II) cyano complexes.[12,15] In fact, the length of the Ni–CN bond

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Table II. Positional Parameters ($\times 10^4$) for [(np$_3$)Ni(CO$_2$Et)]BPh$_4$

atom	x	y	z	atom	x	y	z
Ni	1425.4 (4)	1756 (2)	3701.0 (4)	C64	2613 (2)	660 (8)	4270 (2)
P1	1570 (1)	1962 (4)	3134 (1)	C15	600 (2)	4258 (9)	3539 (2)
P2	1807 (1)	-13 (4)	4038 (1)	C25	758 (2)	4678 (9)	3244 (2)
P3	875 (1)	2876 (3)	3840 (1)	C35	541 (2)	5661 (9)	3000 (2)
O1	1741 (3)	4625 (11)	3768 (2)	C45	167 (2)	6255 (9)	3051 (2)
O2	1913 (3)	3203 (10)	4225 (2)	C55	9 (2)	5804 (9)	3347 (2)
N	1031 (3)	-35 (10)	3500 (2)	C65	226 (2)	4821 (9)	3591 (2)
C1	1730 (3)	3437 (16)	3898 (4)	C16	845 (2)	3778 (9)	4257 (2)
C2	1138 (3)	874 (13)	2913 (3)	C26	1025 (2)	5186 (9)	4319 (2)
C3	1090 (3)	-472 (13)	3141 (3)	C36	1008 (2)	5938 (9)	4631 (2)
C4	1569 (3)	-1704 (13)	3828 (3)	C46	811 (2)	5283 (9)	4882 (2)
C5	1115 (3)	-1393 (13)	3736 (3)	C56	631 (2)	3876 (9)	4820 (2)
C6	530 (3)	1261 (12)	3808 (3)	C66	648 (2)	3124 (9)	4507 (2)
C7	595 (3)	425 (12)	3487 (3)	B	860 (4)	922 (15)	1282 (3)
C8	2133 (4)	4459 (15)	4418 (5)	C17	1341 (3)	306 (9)	1329 (2)
C9	2165 (7)	4224 (24)	4786 (6)	C27	1617 (3)	740 (9)	1625 (2)
C11	1554 (2)	3653 (8)	2857 (2)	C37	2021 (3)	280 (9)	1667 (2)
C21	1296 (2)	3758 (8)	2533 (2)	C47	2150 (3)	-616 (9)	1413 (2)
C31	1285 (2)	5071 (8)	2337 (2)	C57	1874 (3)	-1050 (9)	1116 (2)
C41	1532 (2)	6280 (8)	2465 (2)	C67	1469 (3)	-589 (9)	1074 (2)
C51	1790 (2)	6175 (8)	2789 (2)	C18	551 (2)	-44 (8)	967 (1)
C61	1801 (2)	4861 (8)	2985 (2)	C28	236 (2)	-922 (8)	1049 (1)
C12	2006 (3)	979 (9)	3016 (2)	C38	-25 (2)	-1671 (8)	783 (1)
C22	2355 (3)	853 (9)	3272 (2)	C48	29 (2)	-1542 (8)	436 (1)
C32	2695 (3)	114 (9)	3202 (2)	C58	345 (2)	-664 (8)	354 (1)
C42	2685 (3)	-560 (9)	2876 (2)	C68	606 (2)	85 (8)	619 (1)
C52	2336 (3)	-464 (9)	2620 (2)	C19	844 (2)	2762 (10)	1180 (2)
C62	1996 (3)	305 (9)	2690 (2)	C29	1117 (2)	3749 (10)	1377 (2)
C13	1736 (2)	-263 (7)	4494 (2)	C39	1103 (2)	5273 (10)	1297 (2)
C23	1475 (2)	675 (7)	4638 (2)	C49	816 (2)	5810 (10)	1018 (2)
C33	1415 (2)	448 (7)	4981 (2)	C59	543 (2)	4823 (10)	821 (2)
C43	1616 (2)	-717 (7)	5180 (2)	C69	557 (2)	3299 (10)	901 (2)
C53	1877 (2)	-1655 (7)	5036 (2)	C110	708 (2)	652 (8)	1664 (2)
C63	1937 (2)	-1428 (7)	4693 (2)	C210	788 (2)	-732 (8)	1829 (2)
C14	2351 (2)	-401 (8)	4086 (2)	C310	642 (2)	-1045 (8)	2136 (2)
C24	2509 (2)	-1706 (8)	3964 (2)	C410	414 (2)	25 (8)	2279 (2)
C34	2928 (2)	-1949 (8)	4025 (2)	C510	334 (2)	1409 (8)	2114 (2)
C44	3189 (2)	-889 (8)	4209 (2)	C610	481 (2)	1723 (8)	1807 (2)
C54	3032 (2)	416 (8)	4331 (2)				

seems to be an invariable parameter along the nickel compounds containing CN$^-$ ligands, regardless their coordination geometries. The metrical features of the ethoxycarbonyl ligand closely resemble those found in 3·BPh$_4$, described above. The ligand is disposed approximately in a perpendicular manner with respect to the basal plane of the complex to avoid a steric crowding in the presence of the bulky triphos ligand.

Conclusions

Most likely, eq 1–3 are oxidative-addition reactions. Indeed, 1 can transfer electrons into appropriate empty orbitals of incoming reagents by using either one σ-hybrid (VI) or two π-hybrids (VII).[8] The latter pair of frontier orbitals are attained when the geometry of the d^{10} (np$_3$)Ni fragment changes from trigonal pyramidal (VIII) to hemioctahedral (IX).[8]

VII

VIII   IX
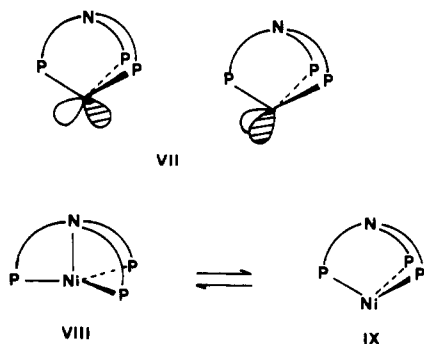
The hemioctahedral fragment is the best candidate for interacting with ethyl cyanoformate to give a five-coor-

dinate intermediate of type X (notice that a strongly antibonding MO orbital is centered at the C$_1$–C$_2$ bond of ethyl cyanoformate).

X
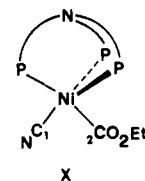
Resumption to shape VIII by the (np$_3$)Ni fragment and, consequently, formation of the final ethoxycarbonyl complex may be then achieved through displacement of the cyanide ligand by the previously uncoordinated apical nitrogen atom, followed by shifting of the CO$_2$Et group over the threefold axis. Decisive support to this reaction path is provided by reaction III yielding the stable cyano ethoxycarbonyl complex 4. The latter compound closely resembles intermediate X. However, at variance with X, 4 is not destabilized by a ligand which competes for coordination with the CN and CO$_2$Et groups as the apical N atom does in X. Also, remember that a d^{10} ML$_3$ system such as (triphos)Ni possesses a high-lying occupied xz, yz pair propitious for a low activation energy for oxidative additions.[16]

Perhaps the most straightforward interpretation of eq 5 is to think of an oxidative-addition reaction producing (np$_3$)CoH(CN)(CO$_2$Et), followed by the reductive elimination of ethyl formate. Alternatively, a concerted

(16) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* 1984, *106*, 2006.

Table III. Positional Parameters (×10⁴) for (triphos)Ni(CN)(CO₂Et)

atom	x	y	z
Ni	3752 (1)	5000	6508 (1)
P1	3950 (1)	3849 (3)	7862 (3)
P2	3038 (1)	5249 (3)	7546 (3)
P3	4177 (1)	6255 (3)	7695 (3)
C1	4222 (6)	4443 (11)	5342 (11)
C2	3993 (4)	4384 (9)	9432 (11)
C3	3123 (4)	5084 (11)	9244 (9)
C4	3858 (4)	6296 (9)	9232 (11)
C5	3657 (4)	5282 (9)	9732 (10)
C6	3619 (5)	5369 (11)	11142 (11)
C7	3520 (4)	5579 (10)	5028 (12)
C8	4426 (7)	3091 (14)	4052 (16)
C9	4393 (8)	3490 (14)	2739 (15)
O1	4607 (4)	4801 (9)	5036 (9)
O2	4064 (4)	3588 (8)	4875 (9)
N1	3379 (5)	5906 (11)	4112 (12)
C11	3493 (3)	2834 (7)	7978 (6)
C21	3270 (3)	2525 (7)	6867 (6)
C31	2921 (3)	1760 (7)	6885 (6)
C41	2796 (3)	1303 (7)	8013 (6)
C51	3020 (3)	1612 (7)	9124 (6)
C61	3368 (3)	2377 (7)	9106 (6)
C12	4532 (3)	3135 (6)	7697 (8)
C22	4532 (3)	2222 (6)	7083 (8)
C32	4977 (3)	1723 (6)	6873 (8)
C42	5423 (3)	2137 (6)	7278 (8)
C52	5424 (3)	3050 (6)	7893 (8)
C62	4978 (3)	3549 (6)	8102 (8)
C13	2526 (3)	4434 (6)	7131 (7)
C23	2419 (3)	4354 (6)	5857 (7)
C33	2034 (3)	3743 (6)	5454 (7)
C43	1754 (3)	3211 (6)	6324 (7)
C53	1861 (3)	3291 (6)	7597 (7)
C63	2246 (3)	3902 (6)	8001 (7)
C14	2715 (3)	6455 (6)	7476 (7)
C24	2280 (3)	6583 (6)	8162 (7)
C34	2049 (3)	7510 (6)	8200 (7)
C44	2255 (3)	8308 (6)	7550 (7)
C54	2690 (3)	8180 (6)	6864 (7)
C64	2920 (3)	7254 (6)	6827 (7)
C15	4155 (4)	7554 (7)	7223 (8)
C25	4183 (4)	7736 (7)	5940 (8)
C35	4147 (4)	8704 (7)	5489 (8)
C45	4081 (4)	9491 (7)	6321 (8)
C55	4053 (4)	9309 (7)	7604 (8)
C65	4090 (4)	8341 (7)	8054 (8)
C16	4845 (3)	6123 (7)	8111 (7)
C26	5030 (3)	6258 (7)	9318 (7)
C36	5534 (3)	6123 (7)	9554 (7)
C46	5853 (3)	5853 (7)	8585 (7)
C56	5668 (3)	5718 (7)	7378 (7)
C66	5164 (3)	5853 (7)	7142 (7)

Table IV. Bond Distances and Angles for 3·BPh₄

(a) Bond Distances (Å)

Ni-P1	2.340 (3)	O1-C1	1.18 (1)
Ni-P2	2.289 (3)	O2-C1	1.33 (1)
Ni-P3	2.242 (3)	O2-C8	1.47 (1)
Ni-N	2.129 (8)	N-C3	1.49 (1)
Ni-C1	1.90 (1)	N-C5	1.51 (1)
P1-C2	1.82 (1)	N-C7	1.51 (1)
P1-C11	1.848 (8)	C2-C3	1.52 (1)
P1-C12	1.826 (9)	C4-C5	1.52 (1)
P2-C4	1.83 (1)	C6-C7	1.50 (1)
P2-C13	1.837 (9)	C8-C9	1.43 (2)
P2-C14	1.829 (8)	B-C17	1.68 (2)
P3-C6	1.84 (1)	B-C18	1.69 (2)
P3-C15	1.83 (8)	B-C19	1.69 (2)
P3-C16	1.823 (8)	B-C110	1.67 (2)

(b) Bond Angles (deg)

P1-Ni-P2	113.8 (1)	Ni-N-C3	111.2 (6)
P1-Ni-P3	120.5 (1)	Ni-N-C5	110.2 (6)
P2-Ni-P3	124.6 (1)	Ni-N-C7	109.9 (7)
P1-Ni-N	86.2 (3)	C3-N-C5	108.2 (9)
P2-Ni-N	86.4 (3)	C3-N-C7	108.9 (8)
P3-Ni-N	86.7 (3)	C5-N-C7	108.2 (8)
P1-Ni-C1	97.4 (4)	O1-C1-O2	120.5 (13)
P2-Ni-C1	96.4 (4)	C1-O2-C8	118.1 (11)
P3-Ni-C1	87.4 (4)	P1-C2-C3	107.8 (7)
Ni-P1-C2	96.9 (4)	C2-C3-N	112.4 (9)
C2-P1-C11	102.8 (4)	P2-C4-C5	106.9 (8)
C2-P1-C12	103.1 (5)	C4-C5-N	111.0 (9)
C11-P1-C12	100.9 (4)	P3-C6-C7	105.4 (7)
Ni-P2-C4	99.3 (4)	C6-C7-N	112.9 (9)
C4-P2-C13	101 (4)	O2-C8-C9	109.8 (14)
C4-P2-C14	103.5 (5)	C17-B-C18	111.1 (8)
C13-P2-C14	100.1 (4)	C17-B-C19	109.4 (8)
Ni-P3-C6	99.6 (4)	C17-B-C110	107.1 (8)
C6-P3-C15	104.3 (5)	C18-B-C19	109.7 (8)
C6-P3-C16	105.9 (5)	C18-B-C110	109.1 (8)
C15-P3-C16	99.6 (3)	C19-B-C110	110.4 (8)

mechanism as that shown in XI may be operative. In this respect, notice that both the hydride 5[8,17,18] and ethyl cyanoformate[19] possess suitable electronic and steric requirements to support intermediate 9 and its overall rearrangement to give 8 and HCO₂Et as well.
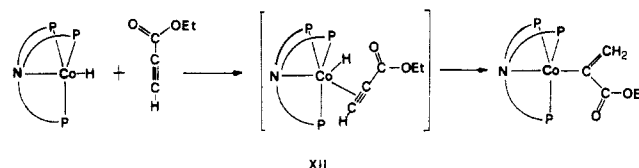

XI
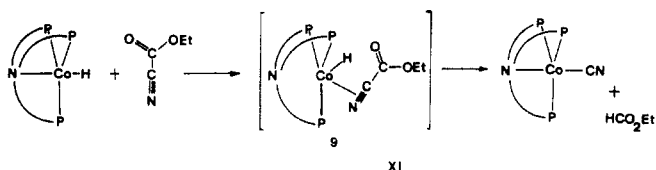
Some support to pathway XI is provided by the reaction of 5 with ethyl propiolate, HC≡CCO₂Et, to give the σ-

alkenyl complex [(np₃)CoC(CO₂et)≡CH₂]⁺.[17] The concerted addition of the Co–H moiety across the C–C triple bond (XII) was suggested as important mechanistic step for the formation of the final product.

XII

Indeed, the isoelectronic HC≡CCO₂Et and N≡CCO₂Et molecules exhibit close structural and electronic features. In particular, the CH group can be formally replaced by the isoelectronic N atom. Therefore, at least in principle, a direct comparison between the reactions of ethyl propiolate and ethyl cyanoformate with 5 is pertinent and useful to understand the chemistry under way.

Finally, we wish to remark the usefulness of ethyl cyanoformate as starting material to introduce ethoxycarbonyl and/or cyanide ligands in a complex framework. This might be extremely interesting for nickel since cyanonickel(II) complexes are known to play important roles in many catalytic and stoichiometric processes such as the carbonylation of organic halides.[20]

Experimental Section

General Remarks. All reactions and manipulations were routinely performed under a nitrogen atmosphere except where

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(19) Storhoff, B.; Lewis, H. C., Jr. *Coord. Chem. Rev.* **1977**, *23*, 1.

(20) (a) Parshall, G. W. *The Application and Chemistry of Soluble Metal Complexes*; Wiley: New York, 1980; pp 70–71. (b) Favero, G. *J. Organomet. Chem.* **1980**, *202*, 225. (c) Joo, F.; Alper, H. *Organometallics* **1985**, *4*, 1775.

Table V. Bond Distances (Å) and Angles (deg) for 4

(a) Bond Distances

Ni–P1	2.187 (4)	P3–C15	1.82 (1)
Ni–P2	2.245 (3)	P3–C16	1.86 (1)
Ni–P3	2.405 (4)	O1–C1	1.19 (2)
Ni–C1	1.93 (1)	O2–C1	1.33 (2)
Ni–C7	1.87 (1)	O2–C8	1.48 (2)
P1–C2	1.83 (1)	N1–C7	1.14 (2)
P1–C11	1.846 (9)	C2–C5	1.55 (2)
P1–C12	1.849 (9)	C3–C5	1.55 (1)
P2–C3	1.84 (1)	C4–C5	1.56 (2)
P2–C13	1.820 (9)	C5–C6	1.52 (2)
P2–C14	1.847 (9)	C8–C9	1.51 (2)
P3–C4	1.86 (1)		

(b) Bond Angles

P1–Ni–P2	89.3 (1)	C3–P2–C14	101.8 (5)
P1–Ni–P3	91.9 (1)	C13–P2–C14	99.4 (4)
P1–Ni–C1	89.5 (4)	Ni–P3–C4	105.4 (4)
P1–Ni–C7	159.5 (4)	Ni–P3–C15	120.9 (3)
P2–Ni–P3	92.4 (1)	Ni–P3–C16	121.3 (3)
P2–Ni–C1	160.0 (5)	C4–P3–C15	101.7 (5)
P2–Ni–C7	94.0 (4)	C4–P3–C16	103.8 (4)
P3–Ni–C1	107.6 (5)	C15–P3–C16	100.9 (5)
P3–Ni–C7	108.2 (4)	Ni–C1–O1	126.3 (12)
C1–Ni–C7	80.5 (5)	Ni–C1–O2	111.8 (11)
Ni–P1–C2	110.1 (4)	O1–C1–O2	121.8 (13)
Ni–P1–C11	114.0 (3)	C1–O2–C8	114.1 (13)
Ni–P1–C12	120.9 (3)	P1–C2–C5	117.5 (9)
C2–P1–C11	105.8 (5)	P2–C3–C5	115.2 (7)
C2–P1–C12	103.8 (5)	P3–C4–C5	115.9 (8)
C11–P1–C12	100.8 (4)	C2–C5–C6	107.8 (10)
Ni–P2–C3	111.2 (3)	C3–C5–C6	106.6 (9)
Ni–P2–C13	116.1 (3)	C4–C5–C6	107.2 (10)
Ni–P2–C14	121.0 (3)	Ni–C7–N1	178.1 (13)
C3–P2–C13	105.2 (5)	O2–C8–C9	110.7 (13)

stated otherwise. The complexes were collected on a sintered-glass frit and washed successively with ethanol and petroleum ether (bp 40–70 °C) before being dried in a stream of nitrogen. Triphos and the complexes 1,[4] 5,[4] and Ni(PPh₃)₂(C₂H₄)[21] were prepared according to the literature methods. Ethyl cyanoformate was obtained from Aldrich and was used as supplied. Ni(COD)₂ was purchased from Strem. THF was dried over sodium benzophenone ketyl and distilled. All other solvents and materials were of reagent grade quality and were used without further purification. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer as Nujol mulls between KBr plates. ¹H and ³¹P NMR spectra were obtained by using a Varian CFT 20 spectrometer. Peak positions are relative to tetramethylsilane and phosphoric acid with downfield values reported as positive. Conductivity measurements were made on a WTW Model LBR/B conductance bridge. Ultraviolet–visible spectra were recorded on a Beckman DK-2A spectrophotometer.

Reaction of NCCO₂Et with 1. Neat NCCO₂Et (0.065 mL, 0.9 mmol) was added by a syringe to a solution of 1 (0.53 g, 0.75 mmol) in THF (40 mL). There was an immediate color change from deep-red to orange-brown. After 10 min, the reaction mixture was evaporated under vacuum to about 10 mL, and NaBPh₄ (0.34 g, 1 mmol) in acetone (10 mL) was then added. Addition of a 1:3 mixture of n-butyl alcohol/n-butyl ether (40 mL) precipitated in a short time red-orange crystals of 3·BPh₄ which were promptly separated from the mother liquor. The yield was 65%. Well-shaped crystals suited for X-ray analysis were obtained by recrystallization from CH₂Cl₂/ethanol. Anal. Calcd for C₆₉H₆₇BNNiO₂P₃: C, 75.01; H, 6.11; N, 1.26; Ni, 5.31. Found: C, 74.83; H, 6.19; N, 1.11; Ni, 5.27. When 3·BPh₄ is left standing in its reaction mixture, it slowly transforms into the cyano complex 6. A complete transformation of 3·BPh₄ into 6 occurs in 24 h. Anal. Calcd for C₆₇H₆₂BN₂NiP₃: C, 76.08; H, 5.90; N, 2.64; Ni, 5.55. Found: C, 75.91; H, 5.97; N, 2.61; Ni, 5.50.

Reaction of NCCO₂Et with Ni(COD)₂ and triphos. Neat NCCO₂Et (0.087 mL, 1.2 mmol) was pipetted into a mixture of

Ni(COD)₂ (0.27 g, 1 mmol) and triphos (0.62 g, 1 mmol) in THF (30 mL) at –10 °C. The resulting solution was allowed to warm to room temperature, and then n-butyl ether (40 mL) was added. Red-orange crystals of 4 precipitated in a few minutes; yield 70%.

Reaction of NCCO₂Et with Ni(PPh₃)₂(C₂H₄) and triphos. A solution of Ni(PPh₃)₂(C₂H₄) (0.61 g, 1 mmol) in THF (30 mL) was treated at –10 °C with neat NCCO₂Et (0.087 mL, 1.2 mmol). After 30 min solid triphos (0.62 g, 1 mmol) was added and the resulting mixture allowed to warm up to room temperature. On addition of n-butyl ether (20 mL), 4 was obtained in 60% yield. Anal. Calcd for C₄₅H₄₄NNiO₂P₃: C, 69.07; H, 5.66; N, 1.79; Ni, 7.50. Found: C, 69.14; H, 5.63; N, 1.81; Ni, 7.46.

Reaction of NCCO₂Et with 5. Neat NCCO₂Et (0.087 mL, 1.2 mmol) was added by a syringe to a solution of 5 (0.71 g, 1 mmol) in THF (40 mL). There was an immediate color change from red-orange to red-brown. Slow evaporation of the solvent gave red crystals of 7, which were identified as the known low-spin Co(I) cyano complex (np₃)CoCN[4] by comparison with an authentic specimen. Ethyl formate, 0.9 mmol, was found by GLC.

X-ray Data Collection and Structure Determination. A summary of crystal data is shown in Table I. All X-ray measurements were performed on a Philips PW 1100 diffractometer using Mo Kα radiation. The unit cells were determined from the setting angles of 20 (3·BPh₄) and 24 (4) randomly oriented reflections. Systematic absences observed for 3·BPh₄, namely, hkl, h + k = 2n + 1 and h0l, l = 2n + 1 indicated space groups Cc or C2/c. The latter one has been chosen on the basis of the successful structure solution and refinement. In the case of compound 4, the systematic absences 0kl with k + l = 2n + 1 and hk0 with h = 2n + 1 were indicative of the space groups Pn2₁a or Pnma. The former one which is equivalent to the acb setting of the standard space group Pna2₁ (No. 33)[22] was selected on the basis of the density measurements and the completed structural analysis. Intensities of three standard reflections were remeasured every 120 min for both compounds showing that no significant decay occurred during the data collection. Intensity data were corrected for Lp and absorption effects, the latter ones by numerical methods with the transmission factors ranging from 0.92 to 0.96 for 3·BPh₄ and 0.89 to 0.94 for 4. The structures were solved and refined by using the SHELX76 program package.[23] The positions of the Ni atoms were located from Patterson maps. The remaining non-hydrogen atoms were easily found from the subsequent Fourier maps. Full-matrix least squares refinement with anisotropic thermal parameters for all non-hydrogen atoms of the complex cations but the phenyl carbon atoms converged at final R of 0.068 (R_w = 0.068) for 3·BPh₄ and 0.055 (R_w = 0.056) for 4. The function minimized was $\sum w(|F_o| - |F_c|)^2$. The phenyl rings were treated as rigid groups of D_{6h} symmetry with C–C distances fixed at 1.395 Å and calculated hydrogen atom positions (C–H = 1.0 Å). Contribution from the remaining hydrogen atoms in positions fixed by geometry have also been included during final cycles of the refinement. Atomic scattering factors were those tablulated by Cromer and Waber[24] with anomalous dispersion corrections taken from ref 25. Final difference maps for 3·BPh₄ and 4 showed few peaks each ca. 0.5 e/Å³ high located near phenyl rings. Final atomic coordinates for 3·BPh₄ and 4 are presented in Tables II and III, respectively.

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(25) Reference 24, p 149.