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.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Mr. J. Riede for the data collection and Dr. F. R. Kreissl for the mass spectroscopic measurements of 4.

Registry No. 1, 70377-69-4; 4, 102505-21-5; 6, 102493-28-7; 7, 102505-22-6; 8, 28926-61-6; 9, 102505-23-7; 12, 102493-27-6; 13, 102505-20-4; 14, 102505-24-8; $SnCl_2$, 7772-99-8.

Supplementary Material Available: Tables of additional crystal structure data, thermal parameters, H atom coordinates, and observed and calculated structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

Reactions of Ethyl Cyanoformate with $(np_3)Ni$, $(np_3)CoH$ [np_3 = $N(CH_2CH_2PPh_2)_3$], and (triphos)Ni [triphos = $MeC(CH_2PPh_2)_3$]. Crystal Structures of the Ethoxycarbonyl Complexes $[(np_3)Ni(CO_2Et)]BPh_4$ and (triphos)Ni(CN)(CO_2Et)

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Received January 6, 1986

Ethyl cyanoformate, $NCCO_2Et$, is used as starting material to introduce ethoxycarbonyl and/or cyanide groups into complex frameworks. Thus, $NCOO_2Et$ reacts with the Ni(0) complex $(np_3)Ni$ (1) [np_3 = $N(CH_2CH_2PPh_2)_3$] or with the Ni(0) fragment (triphos)Ni [triphos = $MeC(CH_2PPh_2)_3$] to give $[(np_3)Ni(CO_2Et)]^+$ (3) and (triphos)Ni(CN)(CO_2Et) (4), respectively. The crystal structures of $3{\cdot}BPh_4$ and 4 have been determined by standard X-ray methods. Compound $3{\cdot}BPh_4$ crystallizes in the monoclinic space group $C2/c$ with a = 33.429 (10) Å, b = 8.929 (2) Å, c = 38.773 (11) Å, β = 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 np_3. 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 $NCCO_2Et$ with the Co(I) hydride $(np_3)CoH$ (5) yields $(np_3)Co(CN)$ and HCO_2Et.

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-CO_2 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, $NCCO_2Et$, to synthesize ethoxycarbonyl derivatives. Ethyl cyanoformate reacts with the Ni(0) complex $(np_3)Ni$[4] (1) [np_3 = $N(CH_2CH_2PPh_2)_3$] or with the Ni(0) metal fragment (triphos)Ni (2) [triphos = $MeC(CH_2PPh_2)_3$] to give the stable Ni(II) ethoxycarbonyls $[(np_3)Ni(CO_2Et)]^+$ (3) and (triphos)Ni(CN)(CO_2Et) (4), respectively. The structures of $3{\cdot}BPh_4$ and 4 have been established by X-ray methods. The reaction between the Co(I) hydride $(np_3)CoH$[4] (5) and $NCCO_2Et$ is also presented.

Results and Discussion

Reaction of 1 with $NCCO_2Et$. Reaction of the Ni(0) complex 1 in THF with a slight excess of $NCCO_2Et$, fol-

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(1) (a) Angelici, R. J. *Acc. Chem. Res.* **1972**, *5*, 335. (b) King, R. B.; Bisnette, M. B.; Fronzaglia, A. *J. Organomet. Chem.* **1966**, *5*, 341. (c) Frazer, P. J.; Roper, W. R.; Stone, F. G. A. *J. Organomet. Chem.* **1974**, *66*, 155. (d) Buhro, W. E.; Wong, A.; Merrifield, J. H.; Lin, G.-Y.; Constable, A. C.; Gladysz, J. A. *Organometallics* **1983**, *2*, 1852. (e) Bianchini, C.; Meli, A. *J. Organomet. Chem.* **1984**, *276*, 413.

(2) (a) Harlow, R. L.; Kinney, J. B.; Herskovitz, T. *J. Chem. Soc., Chem. Commun.* **1980**, 813. (b) Forschner, T.; Menard, K.; Cutler, A. *J. Chem. Soc., Chem. Commun.* **1984**, 121.

(3) (a) Thorn, D. L. *Organometallics* **1982**, *1*, 197. (b) Ungvary, F.; Marko, L. *Organometallics* **1983**, *2*, 1608. (c) Tasy, M.; Palyi, G. *Organometallics* **1985**, *4*, 1523.

(4) Sacconi, L.; Ghilardi, C. A.; Mealli, C.; Zanobini, F. *Inorg. Chem.* **1975**, *14*, 1380.

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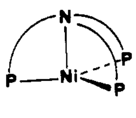

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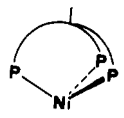

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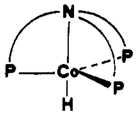

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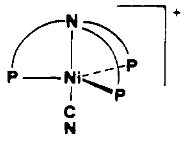
lowed by addition of $NaBPh_4$ in *n*-butyl alcohol gives red crystals of $3\cdot BPh_4$ in 95% yield (eq 1).

$$(np_3)Ni + NCCO_2Et + NaBPh_4 \rightarrow [(np_3)Ni(CO_2Et)]BPh_4 + NaCN \quad (1)$$

Compound $3\cdot BPh_4$ 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 $cm^2\ \Omega^{-1}\ mol^{-1}$).[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 ^1H 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 $3\cdot BPh_4$ 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 $3\cdot BPh_4$ 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 reasonable 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 $cm^2\ \Omega^{-1}\ mol^{-1}$], 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.

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



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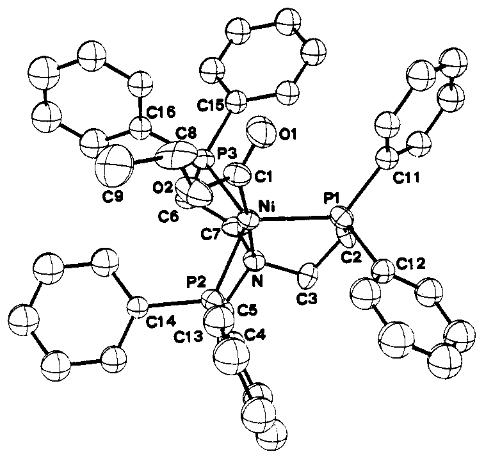

Figure 1. ORTEP drawing of the $[(np_3)Ni(CO_2Et)]^+$ complex cation (3). Hydrogen atoms are omitted for clarity.

Reaction of 2 with $NCCO_2Et$. The ability of the 18-electron species 1 to oxidatively add the CO_2Et group from $NCCO_2Et$ 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 $Ni(PPh_3)_2(C_2H_4)$ with triphos. Ethyl cyanoformate oxidatively adds to 2 according to eq 3 and 4 to give a red-orange complex of formula $(triphos)Ni(CN)(CO_2Et)$ (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 ^1H 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 $NCCO_2Et$. The hydride 5 in THF reacts with neat $NCCO_2Et$ to give the known trigonal-bipyramidal Co(I) cyano complex $(np_3)Co(CN)$ (7) and ethyl formate (eq 5). The formation of HCO_2Et 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 $3\cdot BPh_4$. As shown by an earlier MO analysis[8] the $(np_3)Ni$ fragment has an

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(5) Bianchini, C.; Meli, A.; Scapacci, G. *Organometallics* **1983**, *2*, 1834.

(6) Sacconi, L.; Mani, F. *Transition Met. Chem.* (Weinheim, Ger.) **1982**, *8*, 179.

(7) Bianchini, C.; Innocenti, P.; Meli, A. *J. Chem. Soc., Dalton Trans.* **1983**, 1777.

(8) (a) Ghilardi, C. A.; Mealli, C.; Midollini, S.; Orlandini, A. *Inorg. Chem.* **1985**, *24*, 164. (b) Cecconi, F.; Ghilardi, C. A.; Innocenti, P.; Mealli, C.; Midollini, S.; Orlandini, A. *Inorg. Chem.* **1984**, *23*, 922. (c) Bianchini, C.; Masi, D.; Mealli, C.; Meli, A.; Sabat, M. *Organometallics* **1985**, *4*, 1014.

Table I. Summary of Crystal Structure Data

	$3\cdot BPh_4$	4
formula	$C_{69}H_{67}BNO_2P_3Ni$	$C_{45}H_{44}NO_2P_3Ni$
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	$C2/c$	$Pn2_1a$
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 = 0.71069 Å	
scan type	$\theta/2\theta$	$\theta/2\theta$
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 $I > 3\sigma(I)$	2908	1897
no. of parameters	279	226
R	0.068	0.055
R_w	0.068	0.056
w $1.0[\sigma^2(F) + pF^2]^{-1}$	$p = 0.0005$	$p = 0.001$

axial σ-hybrid that can be utilized in the formation of several stable five-coordinate complexes with various organic fragments. The compound $3\cdot BPh_4$ is an example of the stabilization gained by means of the σ-hybrid. The structure of the $[(np_3)Ni(CO_2Et)]^+$ 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 $Pt(PPh_3)_2(CO_2Et)_2$.[11] Thus, the C=O bond length in $3\cdot BPh_4$ [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 $3\cdot BPh_4$ 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 in the square-pyramidal complex $Ni(CN)_2[P(CH_2OH)Ph_2]_3$[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

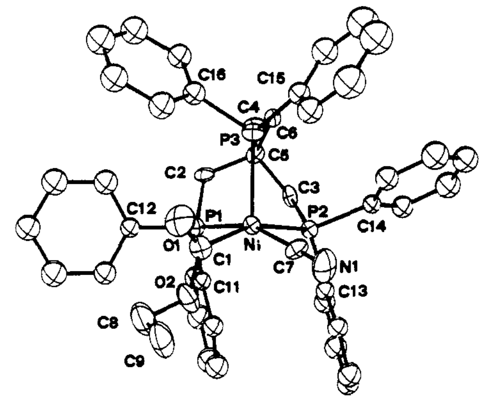

Figure 2. ORTEP drawing of the $(triphos)Ni(CN)(CO_2Et)$ complex molecule (4). Hydrogen atoms have been omitted for clarity.

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[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.

[11] Bellon, P. L.; Manassero, M.; Porta, F.; Sansoni, M. *J. Organomet. Chem.* **1974**, *80*, 139.

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

[13] Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.

[14] (a) Benelli, C.; Di Vaira, M.; Noccioli, G.; Sacconi, L. *Inorg. Chem.* **1977**, *16*, 182. (b) Bianchini, C.; Meli, A. *J. Chem. Soc., Dalton Trans.* **1983**, 2419.

[15] Alyea, E. C.; Meek, D. W. *J. Am. Chem. Soc.* **1969**, *91*, 5761.

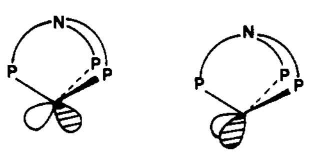
Table II. Positional Parameters (×10⁴) for [(np$_3$)Ni(CO$_2$Et)]BPh$_4$

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

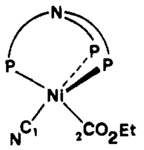
Most likely, eq 1–3 are oxidative-addition reactions. Indeed, 1 can transfer electrons into appropriate empty orbitals of incoming reagents by using either one σ-hybrid (VI) or two π-hybrids (VII).[8] The latter pair of frontier orbitals are attained when the geometry of the d^{10}-(np$_3$)Ni fragment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

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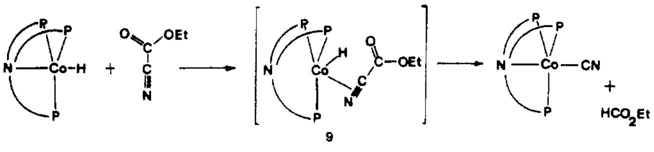
[16] Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006.

Table III. Positional Parameters (×10^4) for (triphos)Ni(CN)(CO$_2$Et)

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)
C1 1	3493 (3)	2834 (7)	7978 (6)
C2 1	3270 (3)	2525 (7)	6867 (6)
C3 1	2921 (3)	1760 (7)	6885 (6)
C4 1	2796 (3)	1303 (7)	8013 (6)
C5 1	3020 (3)	1612 (7)	9124 (6)
C6 1	3368 (3)	2377 (7)	9106 (6)
C1 2	4532 (3)	3135 (6)	7697 (8)
C2 2	4532 (3)	2222 (6)	7083 (8)
C3 2	4977 (3)	1723 (6)	6873 (8)
C4 2	5423 (3)	2137 (6)	7278 (8)
C5 2	5424 (3)	3050 (6)	7893 (8)
C6 2	4978 (3)	3549 (6)	8102 (8)
C1 3	2526 (3)	4434 (6)	7131 (7)
C2 3	2419 (3)	4354 (6)	5857 (7)
C3 3	2034 (3)	3743 (6)	5454 (7)
C4 3	1754 (3)	3211 (6)	6324 (7)
C5 3	1861 (3)	3291 (6)	7597 (7)
C6 3	2246 (3)	3902 (6)	8001 (7)
C1 4	2715 (3)	6455 (6)	7476 (7)
C2 4	2280 (3)	6583 (6)	8162 (7)
C3 4	2049 (3)	7510 (6)	8200 (7)
C4 4	2255 (3)	8308 (6)	7550 (7)
C5 4	2690 (3)	8180 (6)	6864 (7)
C6 4	2920 (3)	7254 (6)	6827 (7)
C1 5	4155 (4)	7554 (7)	7223 (8)
C2 5	4183 (4)	7736 (7)	5940 (8)
C3 5	4147 (4)	8704 (7)	5489 (8)
C4 5	4081 (4)	9491 (7)	6321 (8)
C5 5	4053 (4)	9309 (7)	7604 (8)
C6 5	4090 (4)	8341 (7)	8054 (8)
C1 6	4845 (3)	6123 (7)	8111 (7)
C2 6	5030 (3)	6258 (7)	9318 (7)
C3 6	5534 (3)	6123 (7)	9554 (7)
C4 6	5853 (3)	5853 (7)	8585 (7)
C5 6	5668 (3)	5718 (7)	7378 (7)
C6 6	5164 (3)	5853 (7)	7142 (7)

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 HCO$_2$Et as well.



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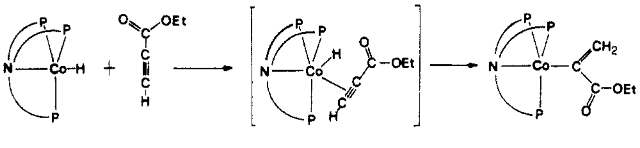
XI

Some support to pathway XI is provided by the reaction of 5 with ethyl propiolate, HC$\equiv$CCO$_2$Et, to give the σ-alkenyl complex [(np$_3$)CoC(CO$_2$et)$\equiv$CH$_2$]$^+$.[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.

Table IV. Bond Distances and Angles for 3•BPh$_4$

(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)



XII

Indeed, the isoelectronic HC$\equiv$CCO$_2$Et and N$\equiv$CCO$_2$Et 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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(17) Bianchini, C.; Innocenti, P.; Masi, D.; Meli, A.; Sabat, M. *Organometallics* **1985**, *5*, 72.

(18) Bianchini, C.; Masi, D.; Mealli, C.; Meli, C.; Sabat, M.; Scapacci, G. *J. Organomet. Chem.* **1984**, *273*, 91.

(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 ia a stream of nitrogen. Triphos and the complexes 1,[4] 5,[4] and $Ni(PPh_3)_2(C_2H_4)$[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 ^{31}P 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 $NCCO_2Et$ with 1. Neat $NCCO_2Et$ (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 $NaBPh_4$ (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**·BPh_4 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 CH_2Cl_2/ethanol. Anal. Calcd for $C_{69}H_{67}BNNiO_2P_3$: 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**·BPh_4 is left standing in its reaction mixture, it slowly transforms into the cyano complex **6**. A complete transformation of **3**·BPh_4 into **6** occurs in 24 h. Anal. Calcd for $C_{67}H_{62}BN_2NiP_3$: 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 $NCCO_2Et$ with $Ni(COD)_2$ and triphos. Neat $NCCO_2Et$ (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 $NCCO_2Et$ with $Ni(PPh_3)_2(C_2H_4)$ and triphos. A solution of $Ni(PPh_3)_2(C_2H_4)$ (0.61 g, 1 mmol) in THF (30 mL) was treated at -10 °C with neat $NCCO_2Et$ (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 $C_{45}H_{44}NNiO_2P_3$: 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 $NCCO_2Et$ with 5. Neat $NCCO_2Et$ (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 $(np_3)CoCN$[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**·BPh_4) and 24 (**4**) randomly oriented reflections. Systematic absences observed for **3**·BPh_4, namely, *hkl*, $h + k = 2n + 1$ and *h*0*l*, $l = 2n + 1$ indicated space groups *Cc* or *C*2/*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 0*kl* with $k + l = 2n + 1$ and *hk*0 with $h = 2n + 1$ were indicative of the space groups $Pn2_1a$ or *Pnma*. The former one which is equivalent to the $a\bar{c}b$ setting of the standard space group $Pna2_1$ (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**·BPh_4 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**·BPh_4 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**·BPh_4 and **4** showed few peaks each ca. 0.5 e/Å^3 high located near phenyl rings. Final atomic coordinates for **3**·BPh_4 and **4** are presented in Tables II and III, respectively.

Registry No. 1, 52633-73-5; 2, 102648-91-9; 3·BPh_4, 95099-93-7; 4, 102648-92-0; 5, 53687-39-1; 6, 102648-94-2; 7, 54353-71-8; $Ni(COD)_2$, 1295-35-8; $Ni(PPh_3)_2(C_2H_4)$, 23777-40-4; $NCCO_2Et$, 623-49-4.

Supplementary Material Available: Tables of thermal parameters and structure factor amplitudes for **3**·BPh_4 and **4** (31 pages). Ordering information is given on any current masthead page.

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[21] Clarke, H. L. *J. Organomet. Chem.* **1974**, *80*, 369.

[22] *International Tables for Crystallography*; D. Reidel: Dordrecht, Holland, 1983; Vol. A., p 57.

[23] Sheldrick, G. M.; SHELX76, Program for Crystal Structure Determination, Univesity of Cambridge, Cambridge, England, 1976.

[24] *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 99.

[25] Reference 24, p 149.