Chiral Metal Complexes. Part III.[1] Nickel(0) Complexes containing the Bulky Chiral Ligand Tri[(+)-bornan-2-yl] Phosphite

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Co-ordinatively unsaturated Ni^0 complexes [Ni(tbp)$_2$], [Ni(tbp)$_3$], [Ni(tbp)$_2$L], and [(tbp)$_2$Ni(μ-cod)Ni(tbp)$_2$] {tbp = tri[(+)-bornan-2-yl] phosphite, cod = η-cyclo-octa-1,5-diene, and L = mono-olefin} have been prepared. The cod-bridged complex is versatile in affording a variety of stable nickel complexes, e.g. [NiCl(tbp)$_2$R], [NiCl(tbp)$_2$(COR)], and [Ni(tbp)$_2$L] (R = aryl). The unusual stability of these complexes may be due to the bulkiness of the phosphite ligands. Asymmetric induction has been observed in the formation of complex [Ni(CH$_2$:CH·CO$_2$H·CH$_2$·CF$_3$)(tbp)$_2$].

ASYMMETRIC co-ordination of prochiral olefins to metal atoms [2a] has been the subject of considerable interest for its important bearing on catalytic or non-catalytic asymmetric reactions. Chiral ligands play a key role in asymmetric reactions involving metals.[2b] In many cases of olefin catalysis, transition-metal complexes are used together with phosphorus ligands.[3] However, chiral phosphorus ligands are in general not readily accessible. We are interested in the readily preparable tri[(+)-bornan-2-yl] phosphite (tbp) for its bulkiness and chirality. Indeed some nickel(0) complexes containing this ligand exhibit remarkable features, including asymmetric induction, as reported below.

RESULTS

Four types of co-ordinatively unsaturated Ni^0 complexes, [Ni(tbp)$_2$], [Ni(tbp)$_3$], [Ni(tbp)$_2$L], and [(tbp)$_2$Ni(μ-cod)Ni(tbp)$_2$] (L = mono-olefin and cod = η-cyclo-octa-1,5-diene), were prepared. Freshly prepared, bright orange-red crystals of the complex [Ni(tbp)$_2$] are quite soluble even in n-hexane. The red colour of the solution soon changed at ambient temperature into yellowish orange, an orange-yellow insoluble solid being precipitated. This solid is

complex [Ni(tbp)]$_2$ toward polymerization was apparent. It reacted with CO, Bu^{t}NC, and ethylene affording the complexes [Ni(CO)$_2$(tbp)$_2$], [Ni(CNBu^t)$_2$(tbp)$_2$], and [Ni(η-C$_2$H$_4$)(tbp)$_2$], respectively, but failed to react with cod.

Treatment of [Ni(cod)$_2$] with tbp (3 mol) in n-hexane at ambient temperature produced a mixture containing a small amount of the insoluble yellow complex [(tbp)$_2$Ni(μ-cod)Ni(tbp)$_2$]. A reddish brown three-co-ordinate complex [Ni(tbp)$_3$] was isolated in good yield from the filtered solution. Alternatively, it was prepared by reducing [Ni(pd)$_2$] (pd = pentane-2,4-dionate) with AlMe$_3$ in the presence of tbp (3 mol). When [Ni(cod)$_2$] was treated with tbp (2 mol) in n-hexane, the stirring mixture first became pale yellow and homogeneous but soon turned into a yellow suspension from which [(tbp)$_2$Ni(μ-cod)Ni(tbp)$_2$] and a small amount of [Ni(tbp)$_3$] were isolated. When tbp made from optically inactive borneol was used in the reaction with [Ni(cod)$_2$], yellow precipitates were not formed and [(tbp)$_2$Ni(μ-cod)Ni(tbp)$_2$] was not isolated. Characterization of the latter complex was very difficult. Its poor solubility and extreme air-sensitivity prevent molecular-weight measurement. In addition, the large molecular weight of the phosphite ligand rendered elemental analysis useless for assessment of the molecular formula. The ligand composition of the complex was established by an

Physical properties of the olefin complexes [Ni(tbp)$_2$L]

| L	Colour	M.p., θ_c/°C (decomp.)	α [a]	$\bar{\nu}$(C=O) [b]/cm^{-1}	O–CH$_3$	^{1}H N.m.r. (τ) [e] =CH– or =CH$_2$
H$_2$C:CH$_2$	Pale yellow	190—198	+27·3			d
cis-MeO·OC·HC:CH·CO·OMe	Yellow	175—179	+31·5	1 730 (sh), 1 715, 1 700 (sh)	6·43 (s) 6·46 (s)	6·77 (complex d)
trans-MeO·OC·HC:CH·CO·OMe	Yellow	211—212	−9·3 [e]	1 700	6·52 (s)	6·18 (complex d)
H$_2$C:CH·CO·OMe	Yellow	180—184	−20·2 [f]	1 695	6·45 (s)	7·02 (complex)
H$_2$C:CH·CO·OCH$_2$CF$_3$	Yellow	80—85	−16·1	1 700	g	7·15 (complex)

[a] Measured in benzene at 25 °C and 589 nm. [b] Nujol mull. [c] 60 MHz in C$_6$D$_6$, referred to Me$_4$Si; aliphatic proton signals of tbp have been abbreviated for brevity. [d] Hardly detectable due to a broad multiplet of low intensity. [e] A final steady value was reached, from an initial rotation of −19·4°, after 8 h (an average of two runs). [f] An average final value was reached, from an initial rotation of −35·9°, after 20 min. [g] The expected signal of the –OCH$_2$– group overlapped with a broad complex signal centred at τ 5·15, assignable to the proton of CH–O– in the bornan-2-yl moiety. For the ^{19}F n.m.r. spectrum see the text.

not soluble in n-hexane, but the same composition is maintained. The strong tendency of the two-co-ordinate

[1] Part II, Y. Tatsuno, A. Konishi, A. Nakamura, and S. Otsuka, J.C.S. Chem. Comm., 1974, 588.

[2] (a) See, for example, A. C. Cope, K. Banholzer, H. Keller, B. A. Pawson, J. J. Whang, and J. H. S. Winkler, J. Amer. Chem. Soc., 1965, 87, 3644; A. D. Wrixon, E. Premuzic, and A. I. Scott, Chem. Comm., 1968, 639; E. Benedetti, P. Corradini, and C. Pedone, J. Organometallic Chem., 1969, 18, 203; (b) For a review see B. Bogdanovic, Angew. Chem., 1973, 85, 1013; for some recent interesting examples see B. M. Trost and T. J. Dietsche, J. Amer. Chem. Soc., 1973, 95, 8200; A. De Renzi, R. Palumbo, and G. Paiaro, ibid., 1971, 93, 880.

extensive study of its substitution reactions (see Experimental section) which indicated the cod-bridged dimeric

(A)
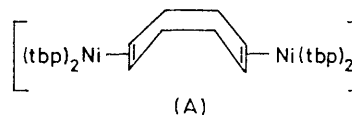
structure (A) as the most probable. Higher polymeric structures would require four or higher co-ordination and

[3] H. B. Kagan and Tuan-Phat Dang, J. Amer. Chem. Soc., 1972, 94, 6429 and refs. therein.

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are unlikely in view of the three-co-ordination realized in the olefin complexes [Ni(tbp)₂L] (Table). The bridged complex proved a versatile material. For example, reactions with an excess of Bu^{t}NC and olefin readily proceeded to give respectively [Ni(CNBu^t)₂(tbp)₂] and [Ni(tbp)₂L] (L = η-ethylene, -propene, -but-1-ene, *etc.*) (Table). Carbon monoxide reacted readily with the complex in the solid state affording [Ni(CO)₂(tbp)₂]. *cis*- or *trans*-But-2-ene did not react with the complex.

Reducing [Ni(pd)₂] with AlEt₃ in the presence of tbp (2 mol) under an ethylene atmosphere produced the pale yellow complex [Ni(η-C₂H₄)(tbp)₂] in practically quantitative yield. This complex showed no indication of dissociation of the ethylene ligand in solution as a sharp singlet peak was not observed in the olefinic proton region of the ¹H n.m.r. spectrum, a behaviour in contrast to that of [Ni(η-C₂H₄)(PPh₃)₂],[4,5] [Ni(η-C₂H₄){P(OC₆H₄Me-*o*)₃}₂],[6] and [Ni(η-C₂H₄){P(OC₆H₄·C₆H₅)₃}₂].[7] The ethylene ligand was replaced with an olefin of stronger acceptor character to give complexes [Ni(tbp)₂L] (L = η-dimethyl maleate, -dimethyl fumarate, and -methyl acrylate). Due to air-sensitivity and to large carbon contents, carbon elemental analyses for some of the olefin complexes were rather unsatisfactory.

Treating the complexes [(tbp)₂Ni(μ-cod)Ni(tbp)₂] and [Ni(η-C₂H₄)(tbp)₂] with a large excess of PhCl resulted in air-stable yellow crystals, the i.r., ¹H n.m.r., and elemental analyses of which conformed to [Ni(Cl)Ph(tbp)₂]. The latter reacted with CO to give an unexpectedly thermally stable acyl derivative, [NiCl(COPh)(tbp)₂], as yellow crystals; this complex was also prepared by oxidative addition of PhCOCl to [(tbp)₂Ni(η-cod)Ni(tbp)₂] or [Ni(η-C₂H₄)(tbp)₂]. Thus these chemical data support the above assignment as a σ-phenyl complex.

The ethylene, but-1-ene, and dimethyl maleate complexes showed specific rotations of comparable degrees (Table). The o.r.d. curve of the but-1-ene complex (α₄₆₄ 0, α₄₉₀ +42°; complex below 464 nm with a maximum α₄₃₈ −31°) resembled that of the ethylene complex (α₄₄₅ 0, α₄₈₂ +27°; complex below 445 nm with a maximum, α₃₇₀ −62°) suggesting the absence of chiral recognition in olefin co-ordination. Olefin dissociation appears not to occur since addition of free but-1-ene to a solution of the but-1-ene complex affected neither the ¹H n.m.r. spectrum nor the specific rotation. The ¹H n.m.r. spectrum of the maleate complex showed a complex doublet of doublets [*J*(HP)(*trans*) 5·4 and *J*(HP)(*cis*) 1·2 Hz] for the olefinic protons and two sharp singlets of nearly equal intensity for methyl protons of the ester groups (Table). The different chemical shifts are presumably due to the influence of the diastereotopic olefinic carbon atoms bonded to the metal. If this view is accepted, the methyl acrylate complex is expected to show one methyl proton signal for each enantiomeric olefinic carbon atom, and two resonances are expected for a racemic mixture. The laevorotatory methyl acrylate complex showed one proton signal for the methyl groups (Table). Shift reagents did not split the resonance. The fumarate complex also showed one sharp singlet peak for

the ester methyl protons and a doublet of doublets [*J*(HP)(*trans*) 3·0 and *J*(HP)(*cis*) 1·5 Hz], typical of the AA′ part in an AA′XX′ system, for the olefinic protons. The coupling with the phosphorus atoms implies a rigid planar molecular structure. The observation of only one methyl proton signal for the acrylate or the fumarate complex may imply either a nearly perfect asymmetric induction for co-ordination of prochiral olefin or fortuitous coincidence of two resonances of the diastereotopic methyl groups. The ¹H n.m.r. spectra provided no measure of the degree of asymmetric induction in these cases. Induction was confirmed in the case of 2,2,2-trifluoroethyl acrylate complex by means of the ¹⁹F n.m.r. spectrum (in C₆H₆). In the absence of a shift reagent, only a complex triplet [*J*(F–H) 8·2 Hz] appeared at δ 4·75 p.p.m. (from CF₃CO₂H). However, in the presence of a shift reagent (europium dipivaloylmethanate) two triplets [*J*(F–H) 8·2 Hz] of 1 : 1·44 intensity ratio were observed with a separation of 0·17 p.p.m. Assuming a linear relation between intensity and composition, the intensity ratio is taken to indicate *ca.* 18% optical purity (o.p.).

DISCUSSION

tbp Displays several interesting features as a ligand stabilizing nickel(0) species. Two, [Ni(tbp)₂], and three co-ordination, [Ni(tbp)₃], can be achieved, though they are not without precedent.[8] The ligand stabilizes olefin co-ordination and σ-aryl– or acyl–metal bonding. Replacement of ethylene in phosphite complexes [Ni(η-C₂H₄)L₂] (L = phosphite) with alkyl-substituted olefins has not been reported; the replacement is possible only when L is an electron-donating phosphine.[7] Hence the successful substitution reaction of the complex [(tbp)₂Ni(μ-cod)Ni(tbp)₂] with propylene or but-1-ene is unique. Remarkably, this complex in powder form reacts readily with gaseous carbon monoxide. It is stable only in the solid state, suggesting significant contribution of the lattice energy to the stability. Bridging co-ordination of cod has been reported previously only for the complex [(cp)(OC)₂Mn(μ-cod)-Mn(CO)₂(cp)] (cp = η-cyclopentadienyl).[9] It is worth noting that a cod-bridged complex analogous to [(tbp)₂Ni(μ-cod)Ni(tbp)₂] could not be prepared by treating [Ni(cod)₂] with bulky phosphines or phosphites, *e.g.* tricyclohexylphosphine, tri(*o*-tolyl) phosphite, and tri(*o*-biphenylyl) phosphite.

The thermal stability and air-insensitivity of [Ni(Cl)Ph(tbp)₂] or [NiCl(COPh)(tbp)₂] is unusual; the latter complex is the first reported example of isolable acylnickel complexes, apart from the recently reported [NiX(COMe)(PMe₃)₂].[10] It is known that the thermal stability of complexes of type [NiX(R)L₂] (R = aryl) is higher with electron-donating ligands than with electron-accepting ones. Accordingly, the electronic property does not provide a rationale for the observed kinetic

⁴ P.-T. Cheng, C. D. Cook, S. C. Nyburg, and K. Y. Wan, *Inorg. Chem.*, 1971, **10**, 2210.
⁵ C. A. Tolman, W. C. Seidel, and D. H. Gerlach, *J. Amer. Chem. Soc.*, 1972, **94**, 2669.
⁶ W. C. Seidel and C. A. Tolman, *Inorg. Chem.*, 1970, **9**, 2354.
⁷ G. Wilke and G. Herrmann, *Angew. Chem.*, 1962, **74**, 693; the ¹H n.m.r. spectrum was measured by the present authors.

⁸ K. Jonas and G. Wilke, *Angew. Chem.*, 1969, **81**, 534; G. Wilke, M. Englert, and D. W. Joley, *ibid.*, 1971, **83**, 84 and refs. therein.
⁹ E. O. Fischer and M. Herberhold, *Experientia*, 1961, **9**, 259; H. P. Fritz and H. Keller, *Chem. Ber.*, 1963, **96**, 1676.
¹⁰ H. F. Klein, *Angew. Chem.*, 1973, **85**, 403.

stability of the above complexes. Apparently the bulk of the phosphite ligand (the corn angle [11] is estimated to
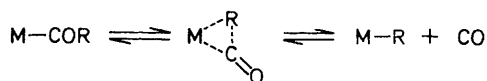
be nearly 180°) is operating to prevent increase in co-ordination number, and hence is responsible for raising the energy barrier to the cyclic transition state requisite for decarbonylation.[12] This effect may be termed an 'inner-steric effect' as distinguished from the usual 'outer-steric effect' of a ligand which contributes to the kinetic stability by preventing approach of attacking reagents. The asymmetric induction observed for co-ordination of the olefin $H_2C{:}CH{\cdot}CO{\cdot}OCH_2CF_3$ is of interest since the chiral centre of tbp is remote from the metal atom.

A novel mutarotation phenomenon (Table) was observed for the laevorotatory complexes [Ni(tbp)$_2$L] (L = η-dimethyl fumarate or -methyl acrylate). Muta-rotation of chiral metal complexes containing olefin ligands is known. Studies on olefinplatinum(II) com-plexes suggest [13] that interconversion between diastereo-isomers takes place through a S_N2 mechanism leading to an optically inactive mixture. Such a mechanism is unlikely in the present complexes since olefin exchange does not occur on addition of the free olefin and P–H coupling in the olefin proton signals remains. There is no significant change in the ^{1}H n.m.r. on dissolution of the complex. It is important to note that the initial specific rotation of the freshly prepared solution is reproduced within experimental errors ($\pm 2°$) when the solid complex (recovered from a solution which achieved constant rotation) is redissolved. A tentative explan-ation for this dismutation is as follows. If the bornan-2-yl groups in the tbp assume a propeller conformation of C_{3v} local symmetry as in PPh$_3$, each P atom should be chiral.[14] A considerable barrier to enantiomer con-version possibly exists in co-ordinated tbp ligands, as is the case for alkyltriphenylphosphonium halides.[14] The conformation of P atoms in the solid complex, if it deviates from C_{3v} symmetry due to crystal packing, would not reflect the solution conformation. Dissolution of the complex thus leads to relaxation of this con-formational heterogeneity.

EXPERIMENTAL

All reactions were carried out under a dinitrogen atmo-sphere. I.r. spectra were measured on Hitachi–Perkin-Elmer 225, ^{1}H n.m.r. (Me$_4$Si internal standard) on Jeol JNM 4H-100 and MH-60HL spectrophotometers, and optical rotation on Jasco automatic polarimeter model DIP-SL.

Crude (+)-borneol containing *ca.* 30% of (−)-*exo*-borneol was treated with a hot methanol solution of sulphuric acid (20 v/v %) to give an optically pure sample,

m.p. 208 °C, α (28 °C, 589 nm) $+36{\cdot}6°$ (*cf.* 9·62° in EtOH) [lit.,[15] α (20 °C, 589 nm) $+37{\cdot}7°$ (*cf.* 5° in EtOH)]. Tri-[(+)-bornan-2-yl] phosphite (tbp) was prepared from phos-phorus trichloride (4·1 g, 30 mmol), (+)-borneol (14·5 g, 95 mmol), and triethylamine (10·1 g, 100 mmol), using benzene (200 cm^3) as solvent, as colourless plates (50% yield), m.p. 238—240 °C, α (26·5 °C, 589 nm) $+0{\cdot}33°$ (*cf.* 5·4° in n-hexane) (Found: C, 73·3; H, 10·3. Calc. for C$_{30}$H$_{54}$O$_3$P: C, 73·45; H, 10·4%). When prepared from crude (+)-borneol, tbp showed α (26 °C, 589 nm) $+16{\cdot}3°$ (*cf.* 9·4° in benzene).

Preparation of Complexes.—Bis{tri[(+)-bornan-2-yl] phos-phite}nickel(0). To a solution of the complex [Ni(pd)$_2$] (pd = pentane-2,4-dionate) (0·38 g, 1·5 mmol) and tbp (1·46 g, 3 mmol) in diethyl ether (60 cm^3) was added a pentane solution (5 cm^3) of AlMe$_3$ (0·58 cm^3, 6 mmol) at −60 °C under an argon atmosphere. On raising the temperature to −30 °C, the initial, almost colourless, mixture changed gradually to orange-red. Bright orange-red crystals appeared in a few hours. The *crystals* were collected, washed with diethyl ether, and dried *in vacuo* at −60 °C (0·7 g, 33%). This complex is stable below −20 °C and soluble in organic solvents such as toluene and n-hexane. However, the solid changed gradually to an in-soluble orange-yellow powder, m.p. 165—167° (decomp.) (Found: C, 69·95; H, 10·4. Calc. for C$_{60}$H$_{102}$NiO$_6$P$_2$: C, 69·3; H, 9·80%).

Tris{tri[(+)-bornan-2-yl] phosphite}nickel(0) A mixture of the complex [Ni(cod)$_2$] (cod = η-cyclo-octa-1,5-diene) (0·26 g, 0·95 mmol) and tbp (1·85 g, 3·80 mmol) was stirred at room temperature for 2 h in n-hexane (20 cm^3). After a trace amount of yellow powder (*ca.* 100 mg) was filtered off, the red-brown filtrate was concentrated to give red-brown *microcrystals* (880 mg, 60%), m.p. 201 °C (decomp.) (Found: C, 70·05; H, 9·95. Calc. for C$_{90}$H$_{162}$NiO$_9$P$_3$: C, 70·65; H, 10·0%).

μ-(1—2-η:5—6-η-*Cyclo-octa*-1,5-*diene*)-*bis[bis{tri[(+)-born-an-2-yl] phosphite}nickel*(0)]. A mixture of bis(cyclo-octa-1,5-diene)nickel (0·80 g, 3·1 mmol) and tbp (3·1 g, 6·2 mmol) in n-hexane (20 cm^3) was stirred at room temperature for 24 h to give a yellow suspension. The yellow *precipitates* were filtered off, washed with n-hexane and subsequently with benzene, and dried *in vacuo* (2·7 g, 77%), m.p. 50 °C (decomp.) (Found: C, 70·0; H, 9·60. Calc. for C$_{128}$H$_{216}$Ni$_2$O$_{12}$P$_4$: C, 70·25; H, 9·90%). The complex is very unstable in air and practically insoluble in organic solvents. The cod liberated by treating the complex with CO was nearly one mole per two nickel atoms as determined by g.l.c. G.l.c. analysis of a solution obtained by dissolving the complex in carbon disulphide determined the mole ratio cod : tbp to be 1 : 4.

(η-*Ethylene*)*bis{tri[(+)-bornan-2-yl] phosphite}nickel*(0). To a mixture of the complex [Ni(pd)$_2$] (0·54 g, 2·1 mmol) and tbp (2·1 g, 4·2 mmol) in toluene (30 cm^3) saturated with ethylene was added AlEt$_3$ (0·7 cm^3) at −50 °C. The mixture was allowed to reach room temperature with occasional shaking. After 3 h stirring at room tem-perature, the resulting pale yellow solution was filtered and concentrated to *ca.* 15 cm^3 under vacuum. Methanol

[11] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 2956.
[12] S. Otsuka, A. Nakamura, T. Yoshida, M. Naturo, and K. Ataka, *J. Amer. Chem. Soc.*, 1973, **95**, 3180.
[13] G. Paiaro and A. Panunzi, *Ricerca sci.*, 1964, **4**, 601; K. Konya, J. Fujita, H. Kido, and K. Saito, *Bull. Chem. Soc. Japan*, 1972, **45**, 2161.
[14] J. M. Brown and K. Mertis, *J. Organometallic Chem.*, 1973, **47**, C5.
[15] Merk Index.

saturated with ethylene (*ca.* 20 cm³) was added to the concentrate to give pale yellow *crystals*, which were washed with methanol and dried *in vacuo* (1·9 g, 85%), m.p. 190—198 °C (decomp.) (Found: C, 69·8; H, 10·3. Calc. for $C_{62}H_{106}NiO_6P_2$: C, 69·7; H, 10·0%). The complex was also obtained in good yield from the reaction of [(tbp)₂Ni(μ-cod)Ni(tbp)₂] with ethylene. Similarly obtained from the latter were (*η-propene*)*bis*{*tri*[(+)-*bornan-2-yl*] *phosphite*}-*nickel*(0), yellow crystals (18% yield), m.p. 180—186 °C (decomp.) (Found: C, 68·15; H, 9·80. Calc. for $C_{63}H_{110}NiO_6P_2$: C, 69·9; H, 10·05%) and (*η-but-1-ene*)-*bis*{*tri*[(+)-*bornan-2-yl*] *phosphite*}*nickel*(0), yellow crystals (62% yield), m.p. 176 °C (decomp.), α (27 °C, 589 nm) +31·3° (*cf.* 3·72°, benzene) (Found: C, 69·75; H, 10·15. Calc. for $C_{64}H_{112}NiO_6P_2$: C, 70·15; H, 10·0%).

(*η-Dimethyl maleate*)*bis*{*tri*[(+)-*bornan-2-yl*]*phosphite*}-*nickel*(0). To a toluene solution (5 cm³) of the complex [Ni(η-C₂H₄)(tbp)₂] (0·44 g, 0·41 mmol) was added dimethyl maleate (0·07 g, 0·42 mmol) at room temperature. After overnight stirring at room temperature, methanol (20 cm³) was added to the solution giving yellow *crystals* (0·34 g, 70%) (Found: C, 65·55; H, 9·35. Calc. for $C_{66}H_{110}NiO_{10}P_2$: C, 66·95; H, 9·35%). Similarly obtained were (*η-dimethyl fumarate*)*bis*{*tri*[(+)-*bornan-2-yl*]*phosphite*}*nickel*(0) (Found: C, 67·45; H, 9·55. Calc. for $C_{66}H_{110}NiO_{10}P_2$: C, 66·95; H, 9·35%) (*η-methyl acrylate*)*bis*{*tri*[(+)-*bornan-2-yl*] *phosphite*}*nickel*(0) (Found: C, 67·5; H, 9·75. Calc. for $C_{64}H_{108}NiO_8P_2$: C, 68·25; H, 9·65%), and *bis*{*tri*[(+)-*bornan-2-yl*] *phosphite*}(η-2,2,2-trifluoroethyl acrylate)nickel(0), ν(C–F) (Nujol) at 1 165 cm⁻¹ (Found: C, 65·6; H, 9·05. Calc. for $C_{65}H_{107}F_3NiO_8P_2$: C, 65·35; H, 9·05%).

Reactions of the Complex [(tbp)₂Ni(μ-cod)Ni(tbp)₂].— (a) *With carbon monoxide.* On introduction of carbon monoxide over the yellow solid, the complex changed rapidly to a colourless powder. Recrystallization from benzene–ethanol gave colourless crystals, m.p. 152 °C (decomp.), α (26·5 °C, 589 nm) +7·5° (*cf.* 1·53°, benzene), ν(C=O) (Nujol) at 1 995ds and 1 940vs cm⁻¹ (Found: C, 67·75; H, 9·30. Calc. for $C_{62}H_{108}NiO_8P_2$: C, 67·75; H, 9·30%).

(b) *With t-butyl isocyanide.* To a stirred suspension of the complex (390 mg, 0·18 mmol) in n-hexane (5 cm³) was added BuᵗNC (100 mg) to give, after the usual work-up and recrystallization from benzene–ethanol, colourless crystals (220 mg, 50%), m.p. 205 °C (decomp.), ν(C≡N) (Nujol) at 2 050 (sh) and 2 000vs cm⁻¹ (Found: C, 68·8; H, 10·0; N, 2·30. Calc. for $C_{70}H_{126}N_2NiO_6P_2$: C, 69·7; H, 9·95; N, 2·30%).

(c) *With chlorobenzene.* The complex (0·64 g, 0·29 mmol) was dissolved in chlorobenzene (20 cm³) at room temperature. The reaction mixture was then filtered and the yellow filtrate concentrated to *ca.* 10 cm³ and cooled to −20 °C, affording [Ni(Cl)Ph(tbp)₂] as yellow *crystals* (0·58 g, 90%), m.p. 174 °C (decomp.), $v_{max.}$ (Nujol) at 1 560, 720, and 690 (Ph bands), and 345 cm⁻¹ [ν(Ni–Cl)] (Found: C, 68·8; H, 9·25; Cl, 3·35. Calc. for $C_{66}H_{109}ClNiO_6P_2$: C, 68·8; H, 9·30; Cl, 3·80%).

(d) *With benzoyl chloride.* A mixture of the complex (100 mg, 0·045 mmol) and benzoyl chloride (0·2 cm³) in diethyl ether (2 cm³) was stirred at room temperature resulting in a yellow solution. After removal of the solvent, recrystallization of the residue from n-hexane gave [NiCl(COPh)(tbp)₂] as yellow needles (10 mg, 10%), m.p. 179—181 °C (decomp.), ν(C=O) (Nujol) 1 645 cm⁻¹ (Found: C, 68·85; H, 9·30; Cl, 3·05. Calc. for $C_{67}H_{109}ClNiO_7P_2$: C, 68·15; H, 9·05; Cl, 3·05%). Alternatively this was prepared by treating a benzene solution of the complex [Ni(Cl)Ph(tbp)₂] with gaseous carbon monoxide at room temperature.