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Synthetic and Mechanistic Aspects of Palladium-Catalyzed Asymmetric Hydrocyanation of Alkenes: Crystal Structure and Reactions of (η^2-Ethene)(diop)palladium

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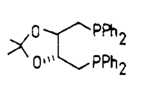
The asymmetric hydrocyanation of norbornene, catalyzed by chiral palladium diphosphine complexes, gives the exo nitrile with up to 40% enantiomeric excess. The mechanism has been studied by using (diop)PdC_2H_4 (**6b**) as a convenient precursor complex, whose crystal structure is reported. The crystals are monoclinic, space group $P2_1$, with two molecules in a unit cell of dimensions a = 10.664 (3) Å, b = 11.023 (4) Å, c = 13.926 (2) Å, β = 109.41 (2)°; R = 0.034 for 2220 observed reflections. Principal dimensions include Pd—C(olefin) = 2.119 (8) and 2.122 (9) Å, Pd—P = 2.289 (2) Å, and C═C = 1.366 (11) Å. Intermediates in the catalytic cycle have been detected by NMR, including a hydrido cyanide and an alkyl cyanide.

Introduction

The metal-catalyzed addition of hydrogen cyanide to alkenes has been studied in detail in recent years. In particular synthetic and mechanistic aspects of the nickel-catalyzed hydrocyanation of butadiene[1] have been examined, in view of the importance of the Du Pont adiponitrile process. More recently the palladium-catalyzed asymmetric addition of hydrogen cyanide to alkenes has been studied[2] and some previous results revised in view of a reappraisal of product enantiomeric purity.[3] Apart from a demonstration that addition of hydrogen cyanide is stereospecifically cis,[4,5] the mechanism of the palladium-catalyzed route has not been examined in detail. Indeed an understanding of the timing and nature of the fundamental steps is still lacking, although some obvious correlations have been drawn with related addition reactions such as hydroformylation.[5] On the basis of established precedents, mechanisms have been suggested for the palladium-catalyzed route,[6] but the detection of key intermediates has not been reported. To a certain extent this lack of information may be related to the unavailability of a suitable precursor palladium complex. The catalyst $(diop)_2Pd$ only reacts directly with some electron-poor alkenes,[7] and suitable palladium alkene complexes of mono- and diphosphines have previously been considered to be very unstable.[8]

In this paper, the palladium-catalyzed addition of hydrogen cyanide to norbornene is described by using the chiral diphosphines (RR)-"diop" (1), (SS)-"BPPM" (2), and (R)-"BINAP" (3). [diop is 4,5-bis((diphenylphosphino)methyl)-2,2-dimethyl-1,3-dioxolane. BPPM is *tert*-butyoxycarbonyl-4-(diphenylphosphino)-2-((diphenylphosphino)methyl)pyrrolidine. BINAP is 2,2′-bis(diphenylphosphino)-1,1′-binaphthalene.] Product enantiomeric purities have been measured by using both chiroptical and ^1H NMR methods, leading to a revision of previously reported data.[2,5] The complex (η^2-ethene)(diop)palladium(0) has been prepared and characterized by X-ray crystallography, and some of its olefin displacement and oxidative addition reactions are defined. It is a convenient precursor for a preliminary study of the mechanism of palladium-catalyzed hydrocyanations. A preliminary account of this work has appeared.[3,9]



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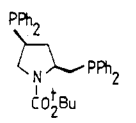

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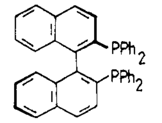

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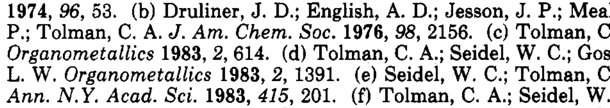
Results and Discussion

Hydrocyanation Reactions. The addition of hydrogen cyanide to norbornene, catalyzed by $Pd(diop)_2$, was effected in benzene and gave *exo*-bicyclo[2.2.1]heptane-2-carbonitrile stereoselectively. Acidic hydrolysis (6 M HCl, 110 °C, 3 h) of the nitrile afforded the *exo*-norbornanecarboxylic acid (eq 1), whose enantiomeric purity was measured by independent methods. The optical rotation of the enantiomerically pure (1R,2R,4S)-(−)-acid 4 is $[\alpha]^{20}_D$ −27.8° (c 1, EtOH)[10] and not $[\alpha]^{20}_D$ −10.7° as has been



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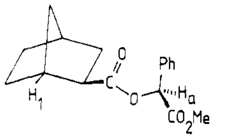
assumed previously.[2,5] With use of this value, the enantiomeric purity of the (−)-4 derived from the Pd(diop)$_2$-catalyzed hydrocyanation of norbornene was 10% (*R*). *Confirmation of the enantiomeric purity of this sample of* (−)-acid was obtained by esterifying it with enantiomerically pure (*S*)-methyl mandelate under nonracemizing conditions to give the diastereoisomeric esters **5a** and **5b**.



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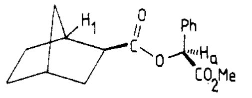


5b

The diastereoisomeric mandelate esters of chiral acids have previously been shown to exhibit anisochronous resonances in their ^1H NMR spectra for both the mandelate C*H* resonance and the acid moiety resonances.[11] Integration of the separated anisochronous resonances permits a direct measure of the enantiomeric purity, and (*S*)-methyl mandelate has proved to be a versatile chiral derivatizing agent for such NMR analyses.[11] Proton NMR analysis of the diastereoisomeric mixture **5a** and **5b** showed separate anisochronous resonances for the bridgehead norbornyl proton H-1 ($\Delta\delta$ = 0.33 ppm, C_6D_6, 298 K) and for the mandelate proton H_a ($\Delta\delta$ = 0.01 ppm). Integration of these resonances gave values for the enantiomeric purity of 4 in accord (±1%) with the chiroptical data. The values reported earlier for the asymmetric hydrocyanation of norbornene are therefore 2.6 times too high.[2,5a–c] Furthermore, the enantiomeric purity of *exo*-bicyclo[2.2.1]heptane-2-carboxaldehyde recently prepared by the asymmetric hydroformylation of norbornene is 23.4% and not 60.7% as reported recently.[5d]

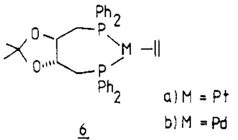
Table I. Palladium-Catalyzed Asymmetric Hydrocyanations of Norbornene in Benzene[f]

phosphine (L) used in PdL$_2$	isolated yield of exo nitrile (%)	enantiomeric excess[a,c] (% ee) (±1%)	reactn temp (°C)
(*RR*)-diop	60	10*R*	120
(*SS*)-diop	94	13*S*[b]	80
(*SS*)-diop[d]	6	14*S*[b]	35
(*RR*)-diop[e]	86	9*R*	120
(*SS*)-BPPM	68	20*R*	120
(*SS*)-BPPM	13	25*R*	80
(*R*)-BINAP	6	40*R*	120

[a] Referring to the purity of (1*R*,2*R*,4*S*)-*exo*-2-cyanonorbornane. [b] The 1*S*,2*S*,4*R* enantiomer. [c] Values obtained were deduced by measuring the rotation of the product nitrile (homogeneous by GLC) and comparing to $[\alpha]^{20}_D$ −29.6 (*c* 1, EtOH), for enantiomerically pure (1*R*,2*R*,4*S*)-*exo*-2-cyanonorbornane. In three independent cases, these values were confirmed by ^1H NMR analysis (see Discussion). [d] Corrected data taken from reported rotation.[2b] [e] In tetrahydrofuran. [f] Using an in situ catalyst generated from bis(dibenzylideneacetone) (0.02 mmol), phosphine (0.2 mmol), norbornene (28 mmol), and HCN (14 mmol).

The hydrocyanations were typically carried out in benzene in a sealed tube immersed in a bath at a temperature of 120 °C. The catalyst used either was an isolated palladium bis(diphosphine) complex of 1–3 or was generated in situ by reaction of bis(dibenzylideneacetone)palladium(0) with excess phosphine. In each case an eightfold excess of the diphosphine to the diphosphine palladium complex was used. The chemical and optical yields obtained were similar using either the preformed or the "in situ generated" catalyst. Results are summarized in Table I. The lowest product enantiomeric purities, at 120 °C, were obtained with (diop)$_2$Pd, while (BINAP)$_2$Pd gave the best optical yield, but with an inferior isolated chemical yield. Yields quoted in Table I have not been optimized and represent average values. The enantiomeric purity of the product depends on the reaction temperature but did not vary using benzene, toluene, or tetrahydrofuran as solvent. Lowering the temperature improves the optical yield but results in a much slower rate of reaction, as noted previously.[2,5] Each of the ligands used in this study gives a seven-membered chelate complex with palladium. Complexes of palladium with five-ring chelate diphosphines [e.g. (1*R*,2*R*)-1,2-dimethyl-1,2-bis(diphenylphosphino)ethane (chiraphos) and prophos ((2*R*)-2-methylbis(diphenylphosphino)ethane)] do not act as catalysts for this reaction.[2,5] This behavior may be compared with the improved enantioselectivity but lower reactivity observed with five-ring chelate rhodium complexes in asymmetric hydrogenation reactions.[12] The dramatic effects of the interligand angle (chelate bite angle) ∠PMP on the reactivity of d^{10} M(L-L) species has been noted previously.[13] It may be ascribed to the sensitivity of the relative energy of the HOMO of the 14-electron fragment M(L-L) (a filled $2b_1$ orbital for a bent ML_2 species) to the chelate bite angle. As the chelate bite angle diminishes, the M(L-L) fragment becomes more nucleophilic. The relative energy of the LUMO of the alkene is also important in determining the reactivity of the alkene substrate to addition of hydrogen cyanide. Addition of hydrogen cyanide to vinyl acetate, *N*-vinylacetamide, and (*E*)- or (*Z*)-1,2-diphenylethene catalyzed by (diop)$_2$Pd gave less than 5% of hydrocyanated product, under the standard conditions described herein.

Mechanistic Studies. In order to probe the mechanism of palladium-catalyzed hydrocyanation, a convenient palladium diphosphine precursor complex was required. The complex (diop)$_2$Pd does react with certain electron-deficient alkenes to give palladium alkene complexes observable by ^{31}P NMR,[7] but it neither reacts with norbornene nor hydrogen cyanide. The stable ethene complex (η^2-ethene)(diop)platinum(0) (**6a**) has been reported, and the ethene ligand may be displaced by other η^2-donors and is sensitive to oxidative addition reactions.[14] The corresponding ethene complex **6b** was prepared accordingly by reduction of (diop)PdCl$_2$ with sodium borohydride in dichloromethane–ethanol solvent (1:5) at −40 °C. Smokey-gray crystals of the complex may be isolated from the reaction mixture in reasonable yield (70%). The structure of **6b**, constituting the first reported X-ray analysis of a palladium ethene complex, has been determined by X-ray crystallography and a diagram of the molecule is shown in Figure 1.[9] Tables II and III give bond length and bond angle information, respectively, and key molecular dimensions are summarized in **7**.



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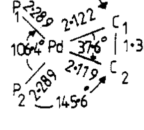

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Table II. Bond Lengths in 6b (Å)[a]

Pd–P1	2.289 (2)	C12–C13	1.387 (14)
Pd–P2	2.289 (2)	C13–C14	1.345 (14)
Pd–C1	2.122 (9)	C14–C15	1.317 (13)
Pd–C2	2.119 (8)	C15–C16	1.386 (13)
P1–C3	1.840 (8)	C21–C22	1.367 (11)
P1–C11	1.831 (8)	C21–C26	1.380 (10)
P1–C21	1.828 (5)	C22–C23	1.392 (9)
P2–C6	1.843 (7)	C23–C24	1.349 (14)
P2–C31	1.828 (5)	C24–C25	1.369 (14)
P2–C41	1.834 (7)	C25–C26	1.404 (10)
O1–C4	1.407 (9)	C31–C32	1.386 (9)
O1–C7	1.423 (9)	C31–C36	1.379 (10)
O2–C5	1.407 (9)	C32–C33	1.381 (12)
O2–C7	1.402 (10)	C33–C34	1.368 (14)
C1–C2	1.366 (11)	C34–C35	1.332 (12)
C3–C4	1.528 (10)	C35–C36	1.399 (10)
C4–C5	1.529 (8)	C41–C42	1.376 (12)
C5–C6	1.511 (9)	C41–C46	1.366 (12)
C7–C8	1.502 (11)	C42–C43	1.372 (13)
C7–C9	1.480 (13)	C43–C44	1.377 (16)
C11–C12	1.369 (11)	C44–C45	1.301 (19)
C11–C16	1.378 (11)	C45–C46	1.396 (13)

[a] Estimated standard deviations are given in parentheses.

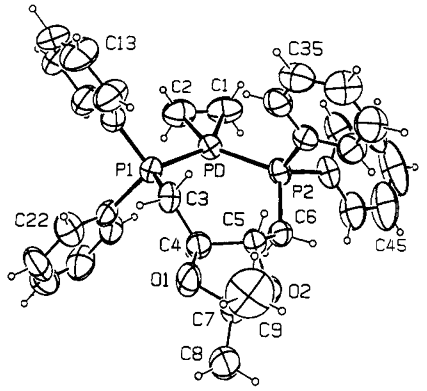

Figure 1. A view of **6b** showing the crystallographic numbering scheme. Ellipsoids are at the 50% level. Phenyl ring carbon atoms are labeled C*i*1–C*i*6 (*i* = 1–4).

Table III. Bond Angles in 6b (deg)[a]

P1–Pd–P2	106.41 (7)	O2–C7–C9	110.9 (6)
P1–Pd–C1	145.2 (2)	C8–C7–C9	113.1 (9)
P1–Pd–C2	108.0 (2)	P1–C11–C12	125.0 (6)
P2–Pd–C1	108.1 (2)	P1–C11–C16	116.9 (6)
P2–Pd–C2	145.6 (2)	C12–C11–C16	118.0 (8)
C1–Pd–C2	37.6 (3)	C11–C12–C13	119.8 (8)
Pd–P1–C3	117.0 (2)	C12–C13–C14	120.9 (8)
Pd–P1–C11	111.6 (2)	C13–C14–C15	120.1 (9)
Pd–P1–C21	120.5 (3)	C14–C15–C16	121.0 (8)
C3–P1–C11	103.6 (3)	C11–C16–C15	120.2 (8)
C3–P1–C21	100.3 (3)	P1–C21–C22	122.4 (5)
C11–P1–C21	101.3 (3)	P1–C21–C26	113.3 (5)
Pd–P2–C6	115.0 (2)	C22–C21–C26	119.3 (6)
Pd–P2–C31	117.8 (2)	C21–C22–C23	120.4 (8)
Pd–P2–C41	116.9 (2)	C22–C23–C24	121.0 (9)
C6–P2–C31	100.5 (3)	C23–C24–C25	119.3 (7)
C6–P2–C41	102.1 (3)	C24–C25–C26	120.8 (8)
C31–P2–C41	101.9 (3)	C21–C26–C25	119.1 (7)
C4–O1–C7	110.3 (6)	P2–C31–C32	121.6 (6)
C5–O2–C7	107.1 (5)	P2–C31–C36	120.0 (5)
Pd–C1–C2	71.1 (5)	C32–C31–C36	118.2 (7)
Pd–C2–C1	71.3 (5)	C31–C32–C33	120.4 (9)
P1–C2–C4	112.4 (5)	C32–C33–C34	121.1 (8)
O1–C4–C3	108.6 (6)	C33–C34–C35	118.7 (7)
O1–C4–C5	102.2 (5)	C34–C35–C36	122.3 (8)
C3–C4–C5	118.6 (5)	C31–C36–C35	119.4 (7)
O2–C5–C4	102.1 (5)	P2–C41–C42	117.0 (6)
O2–C5–C6	106.3 (6)	P2–C41–C46	124.9 (6)
C4–C5–C6	118.9 (5)	C42–C41–C46	118.1 (7)
P2–C6–C5	114.9 (5)	C41–C42–C43	121.8 (9)
O1–C7–O2	105.3 (6)	C42–C43–C44	119.1 (10)
O1–C7–C8	109.5 (5)	C43–C44–C45	118.9 (9)
O1–C7–C9	109.6 (8)	C44–C45–C46	123.8 (11)
O2–C7–C8	108.2 (8)	C41–C46–C45	118.2 (9)

[a] Estimated standard deviations are given in parentheses.

The carbon–carbon bond in **6b** is 1.366 (11) Å, which may be compared to 1.337 (2) Å for free ethene and 1.43 Å for the isostructural ethene complexes $(PPh_3)_2NiC_2H_4$[15] and $(PPh_3)_2PtC_2H_4$.[16] The shortness of the carbon–carbon bond in the coordinated ethene accords with the relatively poor π-donor ability of the d^{10} palladium species. This π-donor ability has been related[17] to the relative order of the promotion energy from the $(n-1)d^{10}$ state to the $(n-1)d^9$ np state which increases in the order 1.72, 3.28, and 4.23 eV for nickel, platinum, and palladium, respectively.[18] The strength of the metal–olefin bond in this triad will depend primarily on π-donation from the metal to the LUMO of the ethylene ligand. Accordingly the metal with the greatest electron availability may be expected to form the most stable alkene complex. The palladium–carbon bond lengths of 2.12 Å are rather long compared to the values found for $(PPh_3)_2NiC_2H_4$ (2.00 Å) and $(PPh_3)_2PtC_2H_4$ (2.11), given the larger covalent radius of platinum compared to palladium. Similarly the C1–Pd–C2 bond angle of 37.6 (3)° is rather acute in comparison to that found in $(PPh_3)_2NiC_2H_4$ (42.1°). The coordination geometry about the palladium center is approximately planar and trigonal, and the torsional angles P1–Pd–C1–C2 and P2–Pd–C1–C2 are −9.9 and 176.9°, respectively. Similar such geometries for "tricoordinate" zerovalent nickel, palladium, and platinum complexes have been observed previously.[15,16,19] The chelate bite angle in **6b** is 106.41 (7)° and is more obtuse compared to the PMP angle of 96° in the d^8 complex $(diop)PdCl_2$.[20]

The exchange of bound ethene in **6a** and **6b** has been studied by ^1H NMR. The ethene ligand in **6a** does not dissociate in solution (C_6D_6 or CD_2Cl_2) as suggested earlier,[14] and a limit for the dissociation constant of 2×10^{-6} M may be deduced from the behavior of the spectra in the absence and presence of free C_2H_4.[21] The bound ethene signals at 1.8 and 2.0 ppm are due to the pairs of diastereotopic alkene protons,[14] and these signals do not broaden in the presence of an approximately 10 M excess of free ethene in solution. The free ethene signal in this latter experiment also remained sharp, so that if associative exchange does occur, as seems likely from previous work with d^{10} platinum ethene complexes,[17] it is slow on the NMR time scale.[7] Solutions of **6b** in C_6D_6 or CD_2Cl_2 quickly turn orange-red (unlike **6a** which forms colorless solutions) which darken further in the absence of added ethene. Such observations are in accord with an irreversible decomposition (oxidation) of the complex, which may be obviated by addition of excess ethene. In the ^1H NMR spectrum of **6b**, carefully obtained under argon (CD_2Cl_2, 298 K), resonances due to the pairs of diaste-

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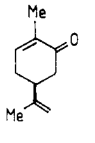
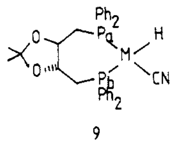
(21) In a 0.02 M solution of the complex, we estimate that 2×10^{-4} M of free ethene could have been detected, so that an upper limit for K_d is 2×10^{-6} M.

reotopic bound ethene protons may be observed centered at 2.59 and 2.83 ppm. As soon as any decomposition occurs (manifested by the appearance of diop oxide signals in the ^{31}P and ^{1}H NMR spectra), free ethene is liberated and an exchange broadened signal for ethene is observed centered at 5.2 ppm. This broad ethene resonance sharpens upon addition of further ethene (e.g. $w_{1/2}$ = 20 Hz with an approximately 40 M excess of ethene in CD_2Cl_2), and separate resonances due to bound ethene are not observed. A rapid exchange between free and bound ethene is occurring in solution, presumably via an associative exchange mechanism.

Some simple alkene displacement and oxidative reactions of **6b** have been monitored by ^{31}P NMR. The ethene complex **6b** generally reacts sluggishly at room temperature with other alkenes in both coordinating (e.g. THF) and noncoordinating solvents (C_6H_6 or CH_2Cl_2). Indeed it does not react with a 100 M excess of cyclopentene or cyclohexene (298 K, CH_2Cl_2), although a 20 M excess of norbornene cleanly displaces bound ethene and gives one stereoisomer only (δ_P + 6.2), consistent with the expected selective binding of the exo face of this strained alkene. It also reacts rapidly with other alkenes with a low-lying LUMO. Reaction with tetracyanoethene displaces ethene rapidly, while enantiomerically, pure (−)-carvone (**8**) is bound regioselectively by the conjugated alkene and stereoselectively by the *si-si* face so that only one diastereoisomer is observed.

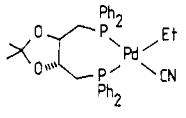


8



9

a) M = Pt
b) M = Pd



10

Complex **6b** is much more sensitive to oxidative addition reactions. Addition of allyl acetate proceeds rapidly to give the cationic η^3-allyl complex, presumably via an S_N2 pathway. This simple reaction is of direct relevance to the reaction pathway in the palladium(0)-catalyzed asymmetric alkylation of allyl substrates.[22] Allyl chloride and allyl bromide react differently, to give η^1-allyl halide complexes together with diopPdX_2. Now given that **6b** reacts quantitatively with $CHCl_3$ or CCl_4 to form (diop)$PdCl_2$, it seems most likely that these reactions proceed via a direct halogen abstraction to give a 15-electron [(diop)PdX] radical intermediate. Similar single electron-transfer mechanisms have been identified in the reactions of d^8[23a] and d^{10} systems.[23b–d] When the reaction of **6b** with allyl chloride was effected in the presence of 5 mol % duroquinone—a radical inhibitor—only the formation of the η^1-allyl complex was suppressed, and formation of (diop)$PdCl_2$ was observed. This behavior suggests that (diop)$PdCl_2$ may be formed via competitive interception of the radical cage pair by further allyl chloride or that there is competition between halogen abstraction by $[(\text{diop})\text{PdCl}]^\bullet$ and its reaction to form a σ-bond with additional allyl chloride. Aryl iodides also react rapidly with **6b** to form σ-alkyl halide complexes in which electron transfer probably precedes covalent bond formation. Such complexes, which are sensitive to CO insertion, are also plausible intermediates in palladium diphosphine catalyzed aryl-coupling reactions.[23d,24] Phosphorus-31 NMR data for these complexes are summarized in Table IV.

Table IV. ^{31}**P NMR Data of (diop)Pd Complexes**[a]

compd	δ_P	δ_{P_a}	δ_{P_b}	$J_{P_aP_b}$ (Hz)
(diop)PdC_2H_4	+6.8			
$(\text{diop})_2$Pd	−1.21			
(diop)$PdCl_2$	+16.1			
(diop)Pd(norbornene)	+6.2			
[(diop)Pd(η^3-allyl)]$^+$OAc	+8.1			
(diop)Pd(TCNE)	+9.2			
(diop)Pd(η^1-allyl)Cl		+20.8	+2.0	40
(diop)Pd(η^1-Ph)I		+13.2	−3.2	41
(diop)PdHCN		+4.0	−6.3	13
(diop)Pd(Et)CN		18.2	−1.4	40

[a] In CD_2Cl_2 at 198 K (101 MHz); shifts are relative to 85% H_3PO_4.

The reaction of the (diop)Pd(norbornene) complex with HCN (C_6D_6, 298 K) leads to formation of one complex selectively, **9b**, (δ_{P_a} +4.0, δ_{P_b} −6.3, $J_{P_aP_b}$ = 13 Hz) with displacement of norbornene. A similar reaction is observed between (diop)Pt(norbornene) and HCN even in the presence of a 50 M excess of norbornene. The product in this case (δ_{P_a} 11.5, J_{PtP_a} = 2840 Hz; δ_{P_b} 9.69, J_{PtP_b} = 1725, $J_{P_aP_b}$ = 15 Hz) is a platinum(II) hydrido cyanide, **9a**, in which P_a is trans to the cyano group and P_b trans to the bound hydride.[25] Confirmation of this bound hydride was furnished by examination of the ^{1}H NMR which showed a sharp hydride multiplet at −3.99 ppm [J_{PtH} = 967, J_{PH} = 187 (trans), J_{PH} = 16 (cis) Hz]. The hydride resonance in **9b** was observed at −4.9 ppm, although at 298 K in C_6D_6 it was broad and broadened further upon addition of more HCN. This information clearly suggests that in the palladium-catalyzed hydrocyanation of norbornene, the olefin binds subsequent to the formation of the hydrido cyanide complex **9b**. Indeed reaction of **9b** and **9a** with excess norbornene is slow and may be rate-determining; competitive formation of $(\text{diop})\text{Pd}(\text{CN})_2$ is observed in the case of the palladium complex. Formation of this inert palladium(II) complex may be associated with catalyst deactivation and partly explains the low catalytic activity of this system.

In the nickel-catalyzed hydrocyanation of alkenes, the propensity of ethene to form an observable nickel ethyl complex has been noted.[1] Similar behavior was observed in the direct reaction of **6b** (but not **6a**) with hydrogen cyanide in the presence of excess ethene. With **6b**, two major complexes were observed by ^{31}P NMR—one of which was **9b**. The other species had spectral data (δ_{P_a} +18.2, δ_{P_b} −1.4, $J_{P_aP_b}$ = 40 Hz) which suggested that it may be the η^1-ethyl cyanide **10** (Table IV, viz., the η^1-allyl chloride), from which the product nitrile may be derived by reductive elimination. In the absence of free ethene, reaction of hydrogen cyanide with **6b** was monitored by ^{1}H NMR (CD_2Cl_2, 298 K). A sharp signal due to free ethene (δ 5.2) was observed, and the diop CMe_2 resonances appeared as two closely spaced singlets consistent with a loss of C_2 symmetry in the product. A broadened hydride

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resonance was observed at δ −4.9, consistent with formation of **9b**. Reaction of **6a** with hydrogen cyanide gave **9a** as the major species (≥90%, C_6D_6, 298 K) observed by ^{31}P NMR.

The relative importance of the characterization of these reaction intermediates should await a more detailed kinetic analysis of their behavior before firm conclusions are drawn regarding the mechanism of asymmetric hydrocyanation. It is appropriate, however, to summarize the more pertinent data: complexation of norbornene to the palladium(0) center occurs stereoselectively via the exo face in accord with the selective formation of the exo nitrile (eq 1). The plausible reaction intermediates (diop)Pd(norbornene) and the hydrido cyanide **9b** have been characterized by NMR, and it appears that oxidative addition of hydrogen cyanide to the Pd(0) center may precede olefin binding and β-cis hydride transfer. Given the weakness of palladium alkene bonds—as manifested by the structural analysis of the ethene complex **6b**—it seems likely that alkene binding is rate-limiting.

Experimental Section

Reactions were carried out under an argon atmosphere by using standard Schlenk techniques. Melting points were determined by using a Reichert Kofler block and are uncorrected. Microanalyses were carried out by M. Cocks, University of Durham. ^1H and ^{31}P spectra were recorded on a Bruker AC250 spectrometer operating at 250.1 and 101 MHz, respectively. ^1H shifts are given in parts per million to higher frequency of Me_4Si, and ^{31}P shifts are given in parts per million to higher frequency (positive) of external 85% H_3PO_4. Mass spectra were recorded on a VG7070E spectrometer, and infrared spectra were recorded as Nujol mulls or KBr disks using a Perkin-Elmer 497 spectrophotometer. Optical rotations were measured on a Perkin-Elmer 141 polarimeter.

The chiral phosphines "diop" and "binap" were obtained from the Aldrich Chemical Co. and Fluka, respectively and were used as received. The chiral ligand "BPPM" was prepared by using minor modifications to the literature method,[28] involving reaction of the precursor ditosylate with potassium diphenylphosphide (generated in situ by cleavage of triphenylphosphine with sodium/potassium alloy[29]) in dioxane: mp 104–105 °C (lit.[27] 105–106 °C); $[\alpha]^{24}_D$ −23.0° (*c* 0.4, C_6H_6) (lit.[27] $[\alpha]^{20}_D$ −23°). Hydrogen cyanide was generated by reaction of glacial acetic acid with potassium cyanide and was stored at −15 °C over phosphorus pentoxide in order to inhibit polymerization. It was distilled prior to use. Bis(dibenzylideneacetone)palladium(0) was prepared from dibenzylideneacetone and sodium tetrachloropalladate according to the method of Takahashi.[30] Bicyclo[2.2.1]heptene was distilled from sodium prior to use, and benzene was distilled from sodium–benzophenone ketyl. The zerovalent diphosphine complexes $(diop)_2Pd$ and $(BPPM)_2Pd$ were prepared following established literature methods,[2] and $(diop)PtC_2H_4$ was prepared following the published procedure.[14]

Typical Hydrocyanation of Norbornene. A Carius tube was charged with bis(dibenzylideneacetone)palladium (13.6 mg, 0.024 mmol) (2*S*,4*S*)-*tert*-butoxycarbonyl-4-(diphenylphosphino)-2-((diphenylphosphino)methyl)pyrrolidine (112 mg, 0.203 mmol) and a solution of bicyclo[2.2.1]heptene (2.68 g, 28.6 mmol) in benzene (5 cm^3). Hydrogen cyanide (385 mg, 14.3 mmol) was distilled into the tube, and a further addition of benzene (7 cm^3) was made. The tube was sealed under argon (500 mmHg) and heated to 120 °C for 18 hours. Unreacted hydrogen cyanide, excess norbornene, and benzene were removed by distillation at atmospheric pressure, and the residue was distilled to yield a colorless oil, bp 80 °C (6 mmHg), which solidified to a colorless wax at room temperature [1.175 g, 68% (based on HCN)]; $[\alpha]^{20}_D$ −5.8 (*c* 0.9, $CHCl_3$). The product was confirmed to be pure bicyclo[2.2.1]heptane-*exo*-carbonitrile by gas chromatography, by comparison to authentic samples of a mixture of the exo and endo diastereoisomers and of the exo isomer. Acidic hydrolysis (6 M HCl, 110 °C, 3 h) of the nitrile according to the published procedure[2] gave the corresponding acid as a colorless solid that was purified by sublimation (60 °C, 0.1 mmHg) to give bicyclo[2.2.1]heptene-*exo*-2-carboxylic acid (1.0 g) as a colorless solid: mp 57–58 °C (lit.[31] 58–58.5 °C), $[\alpha]^{20}_D$ −5.45° (*c* 1.0, EtOH). The enantiomeric purity of this acid was determined independently by ^1H NMR analysis of the (*S*)-methyl mandelate ester.[11] To a solution of the *exo*-2-norbornanecarboxylic acid (140 mg, 1.0 mmol) in dichloromethane (5 cm^3) at −10 °C was added (*S*)-methyl mandelate (183 mg, 1.1 mmol), 4-(dimethylamino)pyridine (2.5 mg), and dicyclohexylcarbodimide (206 mg, 1.0 mmol). After the mixture was stirred at −10 °C for 3 h, the dicyclohexylurea was removed by filtration, solvent removed under reduced pressure, and the residue purified by preparative thin-layer chromatography [SiO_2, EtOAc/hexane (1:1)] to yield the desired ester as a homogeneous colorless oil: δ_H (C_6D_6) 7.46 (2 H, d, ortho arom), 7.09 (3 H, mult), 6.077 + 0.066 (1 H, s + s, CHOCO), 3.19 (3 H, s, CO_2CH_3), 2.87 + 2.54 (1 H, br s + br s, H-1), 2.38 (1 H, mult, H-2), 2.09 (2 H, mult, H-3), 1.61 (1 H, dd, H-4), 1.39–1.01 (6 H, mult, H-5, H-6, H-7). Integration of the resonances at 6.077/6.061 and 2.87/2.54 ppm gave ratios of 60:40 and 40.5:59.5 (±1%), respectively, in agreement with the chiroptical data (20% ee). Other hydrocyanations were effected in a similar manner.

Table V. Summary of Crystal Data, Intensity Collection, and Refinement Details for $(diop)PdC_2H_4$ (6b)

fw	633.00
formula	$C_{33}H_{36}O_2P_2Pd$
space group	$P2_1$ or $P2_1/m$ from systematic absences (ōko, $k = 2n + 1$), $P2_1$ assumed and confirmed by successful analysis
Z	2
cell parameters	
a, Å	10.664 (3)
b, Å	11.023 (4)
c, Å	13.926 (2)
β, deg	109.41 (2)
V, $Å^3$	1544 (1)
ρ(calcd), g cm^{-3}	1.36
temp, °C	23
radiatn	Mo Kα (λ = 0.71073 Å, graphite monochromated)
cryst size, mm	0.15 × 0.22 × 0.33
scan width, deg	$0.6 + 0.350 \tan \theta$
max 2θ, deg	54
range of indices	h, 0–13, k, 0–14, l, 17 to 17
μ, cm^{-1}	7.2
range of transmissn coeffs	0.856 to 0.902, mean 0.881
unique data collected	3549
unique data used	2220 ($I > 3\sigma(I)$)
final no. of parameters refined	342
error in observn of unit weight	1.16
R	0.034
R_w	0.037

(η^2-Ethene)[4,5-bis((diphenylphosphino)methyl)-2,2-dimethyl-1,3-dioxolane]palladium(0) (6b). To a solution of $(diop)PdCl_2$ (160 mg, 0.24 mmol) in dry ethanol (1.5 cm^3) and dichloromethane (3.6 cm^3), cooled to −78 °C, was passed ethene gas (15 mm). To this solution was added a cold solution (ca. −40 °C) of sodium borohydride (22 mg, 0.6 mmol) in ethanol (2.5 cm^3) over a period of 5 minutes, maintaining the ethene atmosphere throughout. The mixture was allowed to warm slowly to room temperature, and the color of solution was observed to change from an opaque white to red and finally pale brown, over a period of 20 min. While an ethene flow was maintained through the

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Table VI. Final Fractional Coordinates for Non-Hydrogen Atoms in 6b with Estimated Standard Deviations in Parentheses[a]

atom	*x*	*y*	*z*	*B*, Å^2
Pd	0.11790 (4)	0.25[b]	0.23417 (3)	3.652 (8)
P1	0.1627 (2)	0.0717 (2)	0.3234 (1)	3.56 (4)
P2	−0.0935 (2)	0.3043 (2)	0.2236 (1)	3.67 (4)
O1	−0.0688 (5)	0.0081 (5)	0.4886 (4)	6.7 (1)
O2	−0.2065 (4)	0.1684 (5)	0.4505 (3)	4.6 (1)
C1	0.1874 (8)	0.3770 (8)	0.1489 (5)	6.1 (2)
C2	0.2870 (7)	0.2967 (9)	0.1943 (5)	6.2 (2)
C3	0.0252 (6)	0.0013 (6)	0.3554 (5)	4.1 (2)
C4	−0.0265 (6)	0.0823 (7)	0.4230 (5)	4.0 (2)
C5	−0.1495 (6)	0.1603 (6)	0.3730 (4)	3.4 (1)
C6	−0.1311 (6)	0.2891 (6)	0.3430 (4)	4.0 (2)
C7	−0.1864 (6)	0.0563 (8)	0.5008 (5)	5.3 (2)
C8	−0.1630 (8)	0.0791 (12)	0.6117 (6)	9.0 (3)
C9	−0.2992 (11)	−0.0267 (11)	0.4538 (9)	10.3 (3)
C11	0.2147 (6)	−0.0471 (7)	0.2529 (5)	4.0 (2)
C12	0.1399 (8)	−0.1460 (9)	0.2089 (6)	6.7 (2)
C13	0.1889 (9)	−0.2287 (8)	0.1552 (6)	7.9 (3)
C14	0.3083 (8)	−0.2122 (9)	0.1441 (5)	7.3 (2)
C15	0.3820 (7)	−0.1181 (9)	0.1866 (6)	6.7 (2)
C16	0.3378 (7)	−0.0339 (9)	0.2420 (6)	5.8 (2)
C21	0.2947 n6)	0.0640 (7)	0.4471 (5)	4.0 (2)
C22	0.3241 (7)	−0.0404 (8)	0.5031 (6)	5.7 (2)
C23	0.4210 (8)	−0.0405 (10)	0.5991 (6)	7.1 (2)
C24	0.4894 (8)	0.0611 (10)	0.6380 (6)	6.8 (2)
C25	0.4644 (8)	0.1653 (9)	0.5813 (7)	7.0 (2)
C26	0.3679 (7)	0.1674 (7)	0.4838 (6)	5.1 (2)
C31	−0.2315 (6)	0.2185 (5)	0.1366 (4)	3.6 (2)
C32	−0.3627 (6)	0.2508 (12)	0.1197 (5)	5.2 (2)
C33	−0.4650 (7)	0.1779 (10)	0.0612 (6)	6.8 (2)
C34	−0.4395 (7)	0.0739 (8)	0.0173 (6)	6.0 (2)
C35	−0.3135 (8)	0.0436 (7)	0.0323 (5)	5.7 (2)
C36	−0.2067 (7)	0.1141 (7)	0.0914 (5)	5.0 (2)
C41	−0.1436 (6)	0.4612 (6)	0.1865 (5)	4.3 (2)
C42	−0.1361 (9)	0.5000 (8)	0.0947 (7)	6.7 (2)
C43	−0.1640 (10)	0.6176 (9)	0.0621 (8)	9.2 (3)
C44	−0.2012 (10)	0.6989 (8)	0.1228 (9)	10.9 (4)
C45	−0.2088 (10)	0.6617 (9)	0.2093 (10)	9.5 (4)
C46	−0.1823 (8)	0.5429 (7)	0.2449 (7)	6.2 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$. [b] The *y* coordinate of Pd was fixed to define the origin.

solution, highly reflective crystals were deposited over a period of 2 h. The supernatant liquid was removed by syringe, and the colorless crystals were washed with cold ethene-saturated ethanol (3 × 1 cm^3). The crystals were dried in vacuo (0.01 mmHg) and were stored at −15 °C under ethene, as a precaution (104 mg, 61%): mp 80 °C dec; δ_P +6.8 (CD_2Cl_2); δ_H (CD_2Cl_2) 7.8–7.2 (20 H, mult, Ar), 3.98 (2 H, mult, CHO), 3.07 (2 H, mult, CHP), 2.83 (2 H, mult, olefin CH), 2.59 (2 H, mult, olefin CH), 2.36 (2 H, dd, CHP), 1.30 (6 H, s, CMe_2). Anal. Calcd for $C_{33}H_{36}O_2P_2Pd$: P, 9.8; Pd, 16.8; C, 62.6; H, 5.7. Found: P, 10.0; Pd, 16.8, Cl, absent; C, 63.0, H, 5.4.

X-ray Data Collection. A smoky-gray plate crystal of (diop)PdC_2H_4 was isolated from the reaction mixture. Accurate cell parameters were determined on a CAD-4 diffractometer by a least-squares treatment of the setting angles of 25 reflections in the range $8 < \theta < 13°$. Relevant data are in Table V. The intensities of three reflections measured every 2 h showed no evidence of crystal decay. A total of 3812 reflections were measured, 3549 of which were unique and 2220 of these with $I > 3\sigma(I)$ were labeled observed and after correction for Lorentz, polarization, and absorption effects were used in structure solution and refinement.

Structure Solution and Refinement. The coordinates of the palladium atom were determined from an analysis of the three-dimensional Patterson function, and the coordinates of the remaining non-hydrogen atoms were found via the heavy-atom method. Refinement was by full-matrix least-squares calculations, initially with isotropic and then with anisotropic thermal parameters. At an intermediate stage in the refinement, difference maps showed maxima in positions consistent with the expected locations of the hydrogen atoms; in the final rounds of calculations, the hydrogen atoms were positioned on geometrical grounds (C–H, 0.95 Å), and included (as riding atoms) in the structure factor calculations with an overall B_{iso} of 5 Å^2.

The final cycle of refinement included 342 variable parameters and converged to $R = 0.034$ and $R_w = 0.037$. A final difference map showed no significant features. Scattering factors and anomalous dispersion corrections were taken from Cromer's tables.[26] As **6b** is optically active, we performed refinement calculations with models of opposite hand. The model corresponding to the (known) absolute stereochemistry had a *R* factor that was lower by one percentage point than its enantiomer. The coordinates and molecular diagram refer to this correct absolute stereochemistry. All calculations were performed on a PDP 11/73 computer with SDP-Plus programs.[27] Final fractional coordinates are given in Table VI. Lists of structure factors, thermal parameters, calculated hydrogen coordinates, mean plane data, and torsion angles have been deposited with the Cambridge Crystallographic Data Centre (see ref 9).

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