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FLEXIBLE CIS- OR TRANS- CHELATING BIPHOSPHINE LIGANDS DERIVED FROM αα- OR ββ- TREHALOSE

JOHN M. BROWN, STEPHEN J. COOK AND ALEXANDER G. KENT

The Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY, U.K.

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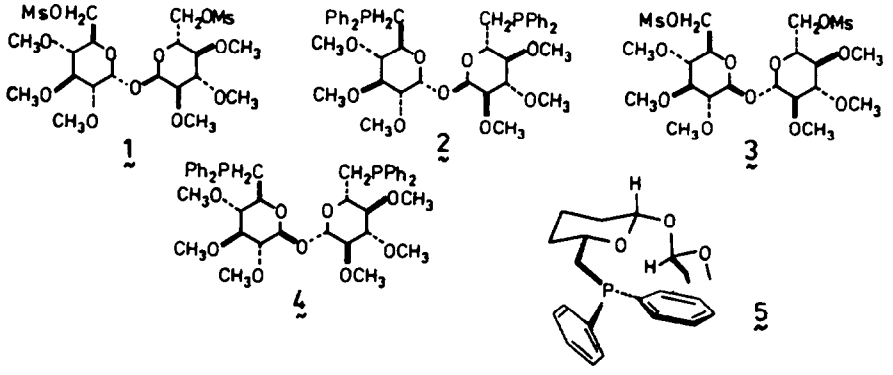
Abstract: The ligands 2,3,4-tri-O-methyl-6-(diphenylphosphino)-α-D-glucopyranosyl-2',3',4'-tri-O-methyl-6'-(diphenyl phosphino)-α-D-glucopyranoside (αα-TREDIP) and the anomer ββ-TREDIP have been prepared from dimesylate precursors. They form a range of rhodium complexes in which the phosphines can be mutually cis or trans, depending on the other ligands present. The αα-anomer shows more propensity for trans-complexation then the ββ-anomer, and this may be explained on conformational grounds.

Hydroformylation of olefins by neutral rhodium complexes occurs under mild conditions and with high regioselectivity. Since it is a reaction of considerable commercial importance, a great deal of effort has been directed towards optimising the selectivity, including the variation of phosphine ligands[1] and involvement of cis-chelating biphosphines.[2] Attendent mechanistic studies demonstrate that two phosphines (normally PPh_3) are coordinated in the catalytic pathway providing highest proportions of linear aldehyde, and they may be cis or trans-related at different stages in the catalytic cycle.[3] Addition of excess phosphine suppresses its displacement by CO and improves the selectivity.[4] On this basis, it seemed to us that a flexible chelating ligand with the capacity for both cisoid and transoid configurations might confer considerable advantages for hydroformylation, since the problems attending dissociation are minimised and the P-Rh-P entity can maintain its integrity thoughout the catalytic cycle. In accompanying papers, the synthesis and structural analysis of ligand precursors, and the successful demonstration of regioselective hydroformylation are described.

Synthesis of αα- and ββ- TREDIP

The protected dimethanesulphonate 1 prepared from αα-trehalose[5] was reacted with lithium diphenylphosphide[6] in thf to give the desired biphosphine 2 in 85% yield as a white solid. Its ^1H N.m.r. spectrum confirmed that anomeric integrity was maintained (δH, = 5.21 p.p.m., $J_{1,2}$ = 3.6Hz), and the compound was fully characterised. It was stored at -30° under argon.

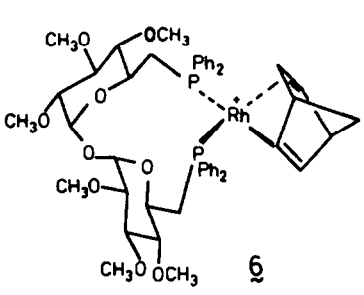
In similar fashion the dimethanesulphonate 3 from ββ-trehalose[5] was reacted with lithium diphenylphosphide in thf to give biphosphine 4 as a microcrystalline solid in 88% yield. The N.m.r. spectrum again indicated anomeric purity (δH, = 4.05 p.p.m., $J_{1,2}$ = 8Hz). The 1.16 p.p.m. chemical shift difference between the anomeric protons in biphosphines 2 and 4 is substantially greater than other trehalose derivatives, where values of 0.4 - 0.6 p.p.m are more usual. The anomaly is in an upfield shift for 4, suggests that a conformation 5 in which the anomeric proton experiences arene ring-current shielding is important.



Complexation studies

Precursors for homogeneous catalysis of hydrogenation[7] or hydroformylation[8] may be prepared from biphosphines and bis bicyclo [2,2,1] heptadienerhodium. Reaction with αα-TREDIP gave a sparingly soluble orange gel which could not be crystallised. This was assumed to be complex 6 (or an oligomeric isomer) on the basis of its ^{31}P N.m.r. which showed a rhodium coupled doublet, δ = 20.0 ppm, J_{Rh-P} = 156Hz, values typical[7] of dienerhodiumbiphosphine complexes. When this complex was suspended in methanol and agitated under H_2, it dissolved with formation of a straw-coloured solution. The ^{31}P N.m.r. spectrum showed a single species. δ = 39.7 p.p.m., J = 116Hz, and a single Rh-H resonance at -17.6 p.p.m. The same species was obtained when reaction was conducted in dichloromethane. These N.m.r. parameters are very typical of solvate rhodium dihydrides in which the phosphines are mutually trans,[7] and the similarity between reactions in CH_3OH and CH_2Cl_2 suggests that oxygen coordination arises from the ligand, presumably O1 and O1'; this presumption is supported by studies described below. Structure 7 is indicated. When the solution of this dihydride was reacted with non-1-ene, hydrogenation occured and the ^{31}P N.m.r. was consistent with solvate 8.

In contrast, the soluble crystalline complex 9 prepared from ββ-TREDIP and bis-bicyclo [2,2,1]heptadienerhodium, δ_p = 11.5 p.p.m, J_{Rh-P} = 159Hz, reacted with H_2 to form solvate 10 directly, without the intervention of an observable dihydride. This complex was also formed in dichloromethane, δ_p = 60.0 p.p.m., J_{Rh-P} = 203Hz, and suggests that the vacant coordination sites in the square plane are occupied by ring oxygens.



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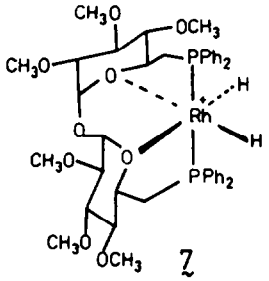

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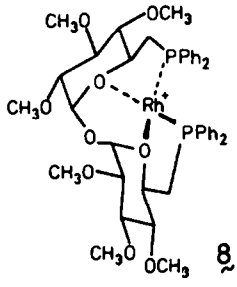

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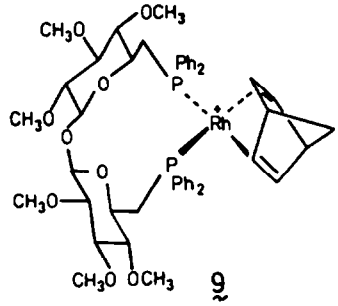

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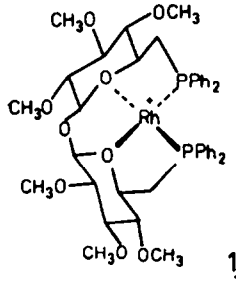

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Further support for the postulated structures stems from a series of related experiments with simpler phosphinoethers in which the number of ether sites available for chelation, and the size of the chelate ring are varied (TABLE 1).

Taking first the simplest phosphinoether 11, hydrogenation of the norbornadiene complex in methanol gives rise to a dihydride with two inequivalent sites in dynamic interchange at room temperature but whose ^1H N.m.r. is well resolved at 253 K. the same pattern of behaviour is observed with the bis (diphenylphosphinomethyl) furan 12, and it is consistent with structure A for the dihydride in both cases. Methanol dissociation gives a five-coordinate intermediate with H_a and H_b equivalent so that recombination may interchange the two sites in A. The two Rh-H chemical shifts are around -19 and -22 p.p.m.,; since the latter is close to the value observed in methanol-solvated dihydrides, the signal at -19 p.p.m. is deemed to be trans to the ligand oxygen. The homologous complex derived from phosphinoether 13 shows more complicated behaviour. Immediately after adding hydrogen to a solution of the rhodium norbornadiene complex in methanol a single Rh-H signal is observed, but a second complex gradually becomes predominant on standing which possesses

inequivalent Rh-H resonances, at 248 K which coalesce at 270 K and are sharp at room temperature. This is ascribed to a B → A type transformation, being consistent with changes observed elsewhere in the ^{1}H N.m.r., and in the ^{31}P N.m.r. spectrum.[9]

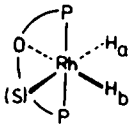
The bis-ether 14 fails to give a dihydride under these conditions, and the spectroscopic properties of the complex formed on hydrogenation are consistent with chelate structure C. In accord with this, the same species is formed in dichloromethane. This behaviour closely resembles that observed with ββ-TREDIP, whilst the αα - forms a dihydride in which the ring oxygens are both coordinated. It is clear that changes in the structure of the ligand backbone can have a marked effect on complexation chemistry.

Table 1. Hydrogenation behaviour of rhodium oxyphosphine complexes.

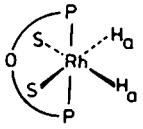
Biphosphine (as Rh NBD$^+$ complex)	Methanol solvate δ_P; J_{PRh}	Dihydride δ_P, J_{PRh}; δ_H, J_{HP}, J_{RhH}, J_{HH}
Ph_2P〜O〜PPh_2 11	——[a]	45.1, 120; -19.2, 14, 27, 14 -21.6
Ph_2P (O) PPh_2 12	——[a]	48.1, 119; -18.7, 13, 26, 13 -21.8
Ph_2P〜O〜〜PPh_2 13	47.9; 204	34.3[b], 118; -22.8, 18, 25, - 31.7 , 118; -21.9, 14, 28, 14 -22.3
Ph_2P〜O〜O〜PPh_2 14	57.8; 205	——[a]
αα - TREDIP 2	56.3; 206	39.7, 116; -17.6, 15, 33 -
ββ - TREDIP 4	60.0; 203	——[a]

[a] Not formed under the reaction conditions.

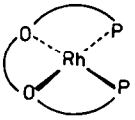
[b] First-formed species. [c] Predominant species at equilibrium.



A



B



C

The ligand αα-TREDIP reacts with $[Rh(CO)_2Cl]_2$ to give a monomeric complex 15 with several unusual features. Firstly, the ^{31}P N.m.r. spectrum is broad at room temperature sharpening at 233 K to a rhodium coupled AB quartet with P-P coupling of 356Hz, typical of inequivalent trans-related phosphorus nuclei.[10] The ^{1}H N.m.r. spectrum is broad at room temperature and sharpens to reveal two inequivalent glucose moieties at 229 K, for which the most striking feature is the anomeric proton separation of 1.85 p.p.m. (δ 4.4 versus 6.25). One set of ring and OCH_3 chemical shifts is similar to the free ligand whilst the other is strongly shifted implying that one O1 atom is involved in coordination to rhodium. This is probably weak, since the molar conductivity Λ_m is 6.93 $\Omega^{-1}M^{-1}cm^2$ in CH_2Cl_2 at 25°; the corresponding value for cationic complex 16 is 54.5. Phosphorus inequivalence arises because planar chirality[11] at rhodium makes the two nuclei diastereotopic, and the pathway of Figure 1 explains the dynamic N.m.r. behaviour.

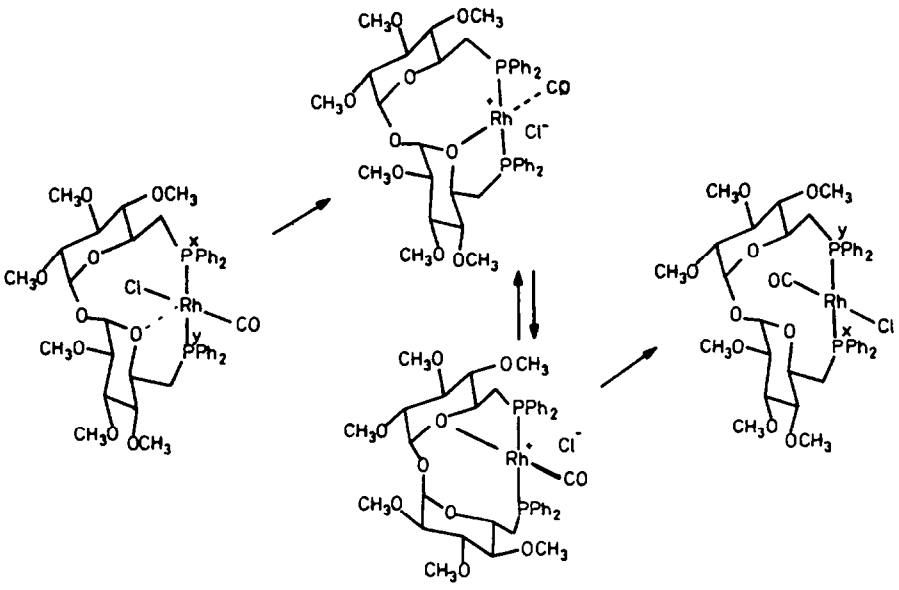
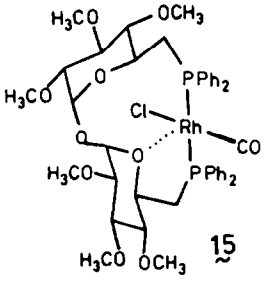


Figure 1 N.m.r. equivalencing of Px and Py.

Addition of $AgBF_4$ to a solution of complex 15 in dichloromethane caused AgCl precipitation and a new complex was observed with one ^{31}P N.m.r. resonance (δ_P = 33.2, J_{PRh} = 99Hz). Addition of methanol modifies the signal the limiting spectrum has δ 30.8, J_{PRh} = 118Hz. These changes are in accord with the formation of complex 17, followed by its conversion into the cation 18.

When the stereoisomeric ββ-TREDIP was reacted with $[Rh(CO)_2Cl]$ the yellow complex 19 may be isolated. This exhibits a ^{31}P N.m.r. spectrum similar to that of 15 but it is sharp at room temperature, J_{pp} = 359Hz. Correspondingly, the complex is non-conducting in solution and the differentiation between diastereotopic protons in the ^1H N.m.r. spectrum is small. Rather unstable complexes related to cations 17 and 18 were produced by successive treatment with $AgBF_4$ and methanol.



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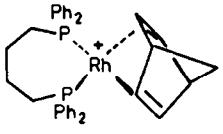

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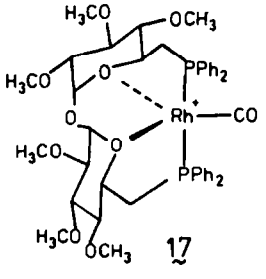

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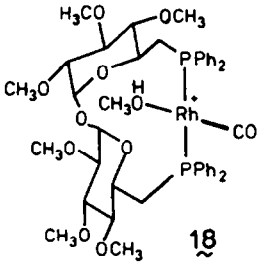

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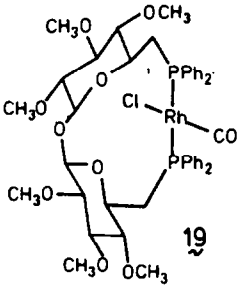

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Structure and conformation of the complexes

These observations reveal that both the αα and ββ anomers of TREDIP may form cis - chelate complexes; when ring ether coordination is involved the ββ anomer does so more readily. The reverse situation applies to trans-complexation. Thus the αα-anomer gives rise to a stable hydride

7 involving coordination of both O1 and O1', and a carbonyl chloride 15 involving weak and reversible coordination of one ring oxygen. For the ββ-anomer no hydride was observed and the carbonyl chloride complex 19 shows no indication of internal O-coordination. These results indicate that the αα-anomer is generally happier than the ββ-anomer in trans-coordination.

Examination of molecular models suggests that the cis-form of the complexed αα-anomer (Figure 2 A) is quite flexible, with anomeric torsion angles[8] typically -120 and + 120°. Coordination of one or both ring oxygens causes considerable angle strain sufficient to make the structure appear an unstable one. In contrast to this the ββ-anomer finds both ring oxygens placed in proximity to the metal on cis-coordination and an essentially strain free form with C_2-symmetry can be obtained where the anomeric torsion angles are about -45, -45° (Figure 2, B). There are in addition strain-free conformations with torsion-angles around -30, -30° in which the ring oxygens remain uncoordinated.

With trans-ligation of the phosphines, a different situation ensues. A strain-free complex may be formed from the αα-anomer with anomeric torsion angles both 180°. Bringing the ring oxygens into coordination (Figure 2, C) gives a further strain-free species with torsion angles of -30° and -30°, with a C_2 symmetry axis maintained. The ββ-anomer is very severely angle-strained when the phosphines are trans-disposed and the oxygens coordinated, but a more favourable structure is obtained when the ring oxygens remain unbound. The modes illustrated in Figure 2, D has torsion angles of +90 and -90°, and no apparent angle strain.

To summarise, it is apparent that both αα and ββ TREDIP are capable of forming chelate rhodium complexes in which the phosphines are cis or trans-disposed, with the possibility of ring oxygen coordination. For the αα-isomer, the trans-isomer is very favourable for ring oxygen chelation but the cis-isomer is rather strained. The opposite situation ensues for the ββ-isomer, where the cis-chelate disposes ring oxygens for coordination without distortion of the backbone, but the trans-chelate only forms readily when ring oxygens are unbound. These conclusions permit the coordination chemistry of the two ligands, described in the previous section, to be rationalised. The stereochemical control of coordination geometry observed here is reminiscent of that described for stereoisomers of linear tetraphosphines.[12]

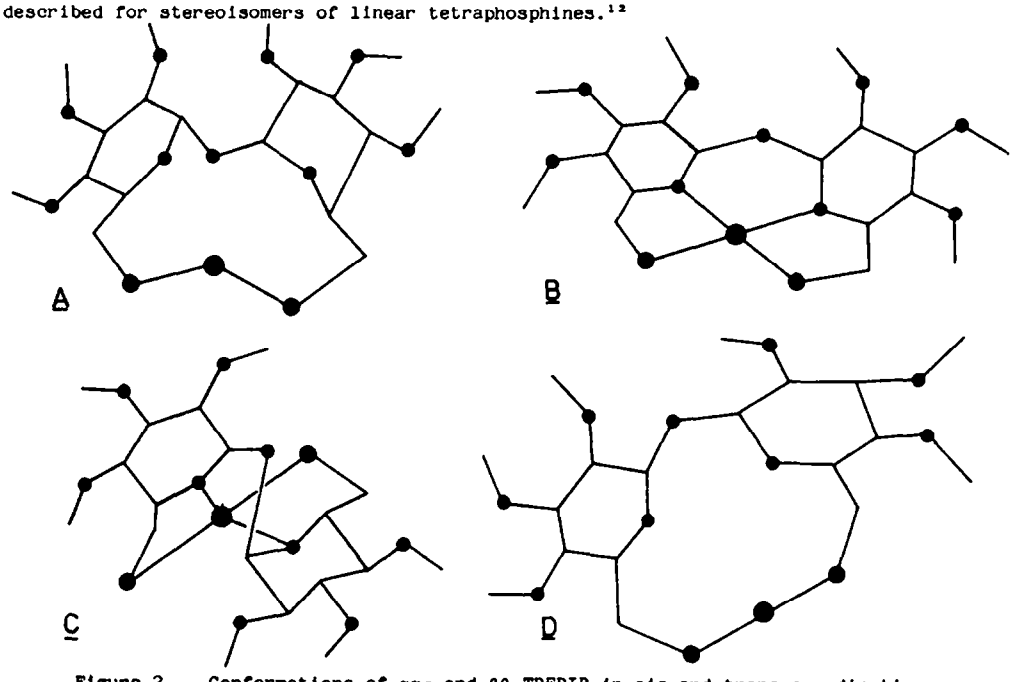

Figure 2. Conformations of αα- and ββ-TREDIP in cis and trans coordination.

Acknowledgement

We thank SERC for support though CASE studentships to SJC (with Tate and Lyle, Ltd.) and AGK (with Johnson-Matthey plc.). Johnson-Matthey kindly provided loans of rhodium salts.

EXPERIMENTAL

All reactions involving phosphines, organometallic complexes and other air-sensitive compounds were conducted under an argon atmosphere using standard vacuum-line techniques and Schlenk glassware. All transfers of liquids and solutions of air- or moisture-sensitive materials were carried out with dried inert gas purged syringes fitted with stainless steel needles or with thin steel tubing. Argon was purified by successive passage through concentrated sulphuric acid and potassium hydroxide pellets.

Commercial solvent were freshly distilled prior to use from an appropriate drying agent according to standard procedures.[17]

2,3,4-Tri-O-methyl-6-(diphenylphosphino)-α-D-glucopyranosyl-2',3',4'-tri-O-methyl-6'-(diphenylphosphino)-α-D-glucopyranoside (αα-TREDIP)

n-Butyllithium (1.5M, 4.3 ml, 6.45 mmol) was added to a degassed solution of diphenylphosphine (0.709 g, 4.24 mmol) in dry ether (20 ml) contained in a Schlenk tube at -78°. On warming to room temperature a yellow solution was formed, which was then concentrated in vacuo. The residue was washed with petroleum ether (3 x 10 ml) at -78° and dried in vacuo to give lithium diphenylphosphide as a yellow solid. Degassed tetrahydrofuran (10 ml) was added and 2,3,4-tri-O-methyl-6-O-methanesulphonyl-α-D-glucopyranosyl-2',3',4'-tri-O-methyl-6'-O-methanesulphonyl-α-D-glucopyranoside (73) (0.711 g, 1.22 mmol) was added in portions at -78° to the red solution. The reaction mixture was then warmed and the colour was almost dissipated after stirring for 15m at room temperature. The solution was stirred for 2h, the solvent was removed in vacuo, the degassed methanol (6 ml) was added, and the solid was filtered off at -78°. The washing process was repeated twice and the white solid was dried in vacuo to give pure 2,3,4-tri-O-methyl-6-(diphenylphosphino)-α-D-glucopyranosyl-2',3',4'-tri-O-methyl-6'-(diphenylphosphino)-α-D-glucopyranoside (0.787 g, 1.032 mmol, 84.5%); m.p. 51-2°; $[\alpha]_D^{\circ}$ + 34.7° (cl. 6.8, CH_3OH); found: C, 65.85; H, 6.72; $C_{42}H_{52}O_9P_2$ requires: C, 66.14; H, 6.82%; ^{1}H-NMR δ (300 MHz, $CDCl_3$) 2.1 (2H, dd, J_{6as} 9.5 Hz, J_{6a6b} 15 Hz, H_{6a}), 2.65 (2H, ddd, J_{6bs} 2.6 Hz, J_{6b6a} 15 Hz, J_{6bP} 4 Hz, H_{6b}), 2.95 (2H, t, $J_{4,3}$ = $J_{4,5}$ 9.5 Hz, H_4), 3.1 (2H, dd $J_{2,3}$ 9.5 Hz, $J_{2,1}$ 3.6 Hz, H_2), 3.1 (6H, s, OMe), 3.45 (6H, s, OMe), 3.5 (6H, s, OMe), 3.55 (2H, m, H_3), 4.0 (2H, dq, $J_{5,6b}$ 2.6 Hz, $J_{5,4}$ = $J_{5,6a}$ = J_{5P} 9.5 Hz, H_5), 5.2 (2H, d, J 3.6 Hz, H_1), 7.2-7.4 (20H, m, Ph); ^{31}P-NMR δ (36.43 MHz, CH_2Cl_2) -20.8 ppm; m/z (field desorption) 762 (M^+).

2,3,4-Tri-O-methyl-6-(diphenylphosphino)-β-D-glucopyranosyl-2',3',4'-tri-O-methyl-6'-(diphenylphosphino)-β-D-glucopyranoside (ββ-TREDIP)

n-Butyllithium (1.5 M, 3.7 ml, 5.55 mmol) was added to a degassed solution of diphenylphosphine (0.74 g, 3.98 mmol) in dry ether (20 ml) at -78° contained in a Schlenk tube. On warming to room temperature a yellow solution was formed, which was then concentrated in vacuo. The residue was washed with petroleum ether (2 x 10 ml) at -78° and dried in vacuo to give lithium diphenylphosphide as a yellow solid. Degassed tetrahydrofuran (10 ml) was added and 2,3,4-tri-O-methyl-6-O-methanesulphonyl-β-D-glucopyranosyl-2'-3'-4'-tri-O-methyl-6'-O-methanesulphonyl-β-D-glucopyranoside (0.74 g, 1.27 mmol) was added in portions at -78° to the red solution. On warming to room temperature the colour was almost dissipated after stirring for 15m. The solution was stirred for 3h, the solvent was removed in vacuo, then degassed methanol 910 ml) was added, and the solid was filtered off at -78°. The washing process was repeated and the white solid was dried in vacuo to give 2,3,4-tri-O-methyl-6-(diphenylphosphino)-β-D-glucopyranosyl-2',3',4'-tri-O-methyl-6'-(diphenylphosphino)-β-D-glucopyranoside (0.852 g, 1.12 mmol, 87.9%); m.p. 114-6°; $[\alpha]_D^{\circ}$ - 12.3 (cl. 4.8, CH_3OH); found: C, 66.03; H, 6.93; $C_{42}H_{52}O_9P_2$ requires: C, 66.14; H, 6.82%; ^{1}H-NMR δ (300 MHz, CD_2Cl_2) 2.25 (2H, dd, J_{6as} 9 Hz, J_{6a6b} 15 Hz, H_{6a}), 2.5 (2H, dt, J_{6bs} = J_{6bp} 2.5 Hz, J_{6b6a} 15 Hz, H_{6b}), 2.92 (2H, m, H_2), 3.0 (4H, m, H_3, H_4), 3.2 (2H, m, H_5), 3.45 (6H, s, OMe), 3.5 (6H, s, OMe), 3.55 (6H, s, OMe), 4.05 (2H, d, J 8 Hz, H_1), 7.25-7.8 (20H, m, Ph); ^{31}P-NMR δ (36.43 MHz, CH_2Cl_2) - 20.2 ppm (s); m/z (field desorption) 762 (M^+).

Bicyclo-(2,2,1)-hepta-2,5-diene[2,3,4-tri-O-methyl-6-(diphenylphosphino)-α-D-glucopyranosyl-2',3',4'-tri-O-methyl-6'-(diphenylphosphino)-α-D-glucopyranoside] rhodium (I) tetrafluoroborate

Bis[bicyclo-(2,2,1)-hepta-2,5-diene] rhodium (I) tetrafluoroborate (97) (51.5 mg, 0.138 mmol) and the biphosphine (105 mg, 0.138 mmol) were mixed in dichloromethane (2 ml) to give an orange gel. The solvent was removed in vacuo, the solid was washed with ether and dried in a stream of argon to give the title compound as an orange solid (101 mg, 0.097 mmol, 70.1%); m.p. 182-5°; ^{31}P-NMR δ (36.43 MHz, CH_2Cl_2) 20.0 ppm (d, J 156 Hz); m/z (fast atom bombardment (957 (M^+ - BF_4), 865 [M^+ - (BF_4 + nbd)].

Addition of hydrogen to a sample of the title compound in an NMR tube gave a mobile straw coloured solution; ^{31}P-NMR δ (36.43 MHz, CH_3OH or CH_2Cl_2) 39.7 ppm (d, J 116 Hz); ^{1}H-NMR δ (300 MHz, CD_3OD or CD_2Cl_2, hydride region) - 17.61 ppm (dt, J_{HRh} 33.9 Hz, J_{HP} = $J_{HP'}$ 15.3 Hz, RhH). The ^{1}H-NMR spectrum was unchanged at - 50°.

Replacement of the hydrogen atmosphere by argon and the addition of excess non-1-ene gave a yellow solution; ^{31}P-NMR δ (36.43 MHz, CH_3OH) 56.3 ppm (d, J 206 Hz).

Bicyclo-(2,2,1)-hepta-2,5-diene[2,3,4-tri-O-methyl-6-(diphenylphosphino)-β-D-glucopyranosyl-2',3',4'-tri-O-methyl-6'-(diphenylphosphino-β-D-glucopyranoside] rhodium (I) tetrafluoroborate

Bis[bicyclo-(2,2,1)-hepta-2,5-diene] rhodium (I) tetrafluoroborate (97) (20.6 mg, 0.055 mmol) and the biphosphine (74) (42 mg, 0.055 mmol) were mixed in dichloromethane (1.5 ml) to give an orange solution which was filtered into petroleum ether. The orange solid was isolated and dried

in vacuo to give bicyclo-(2,2,1)-heptadiene[2,3,4-tri-O-methyl-6-(diphenylphosphino)-β-D-glucopyranosyl-2',3',4'-tri-O-methyl-6'-(diphenylphosphino)-β-D-glucopyranoside] rhodium (I) tetrafluoroborate (96b) (44 mg, 0.042 mmol, 76.4%); m.p. 161-4°; ^{31}P-NMR δ (36.43 MHz, CH_2Cl_2) 11.5 ppm (d, J 158.8 Hz); ^{1}H-NMR δ (300 MHz, CD_2Cl_2) 1.6 (2H, m, nbd, CH_2), 2.65-3.8 (32H, m, H_2, H_3, H_4, H_5, H_6, OMe, nbd CH), 4.0 (2H, m, $=CH_aH_b$), 4.3 (2H, m, $=CH_aH_b$), 5.05 (2H, d, J 7.5 Hz, H_1), 7.15-7.8 (20H, m, Ph); found: C, 56.46; H, 5.59; $C_{49}H_{60}BF_4O_9P_2Rh$ requires: C, 56.34; H, 5.75%; m/z (fast atom bombardment), 957 (M^+ - BF_4), 865 (M^+ - BF_4 - nbd).

Addition of hydrogen to a sample of the title compound dissovled either in CH_3OH or CH_2Cl_2 in an NMR tube gave a yellow-brown coloured solution; ^{31}P-NMR δ (36.43 MHz, CH_3OH) 60.0 ppm (d, J 203 Hz); ^{1}H-NMR δ (300 MHz, CD_3OD) 2.35, 2.8-3.6 (12H, m, H_2, H_3, H_4, H_5, H_6), 3.1 (6H, s, OMe), 3.55 (6H, s, OMe), 3.6 (6H, s, OMe), 5.15 (2H, d, J 8 Hz, H_1), 7.05-7.55 (20H, m. Ph).

Carbonylchloro[2,3,4-tri-O-methyl-6-(diphenylphosphino)-α-D-glucopyranosyl-2',3',4'-tri-O-methyl-6'-(diphenylphosphino)-α-D-glucopyranoside] rhdoium (I) (116)

Tetracarbonyl-μ,μ-dichlorodirhodium (I) (115) (34.7 mg, 0.089 mmol) was added to a solution of the biphosphine (69) (136 mg, 0.178 mmol) in dichloromethane (5 ml). The solution was stirred (45 m), concentrated in vacuo, methanol was added and the resulting yellow solid was isolated and dried in vacuo to give carbonylchloro[2,3,4-tri-O-methyl-6-(diphenylphosphino)-α-D-glucopyranosyl-2',3',4'-tri-O-methyl-6'-(diphenylphosphino)-α-D-glucopyranoside rhodium (I) (116) (145 mg, 0.156 mmol, 88%); m.p. 187.5-9°; found: C, 55.38; H, 5.49; P, 6.74; $C_{43}H_{52}ClO_{10}P_2Rh$ requires C, 55.58; H, 5.60; P, 6.68%; I.R. (KBr disc) 1965 (vs); ^{1}H-NMR δ (300 MHz, CD_2Cl_2, - 44°) 2.2 (1H, t, $J_{3,4}$ = $J_{3,2}$ 9 Hz, H_3), 2.5 (1H, dd, $J_{2,1}$ 3.5 Hz, $J_{2,3}$ 9 Hz, H_2), 2.75 (1H, t, $J_{3',4'}$ = $J_{3',2'}$ 9 Hz, $H_{3'}$), 2.85 (3H, s, OMe), 3.1 (1H, dd, $J_{2',1'}$ 3.5 Hz, $J_{2',3'}$ 9 Hz, $H_{2'}$), 3.25 (6H, 2s, OMe), 3.45 (3H, s, OMe), 3.55 (6H, 2s, OMe), 3.45-3.7 (6H, m, H_4, H_6), 4.1-4.25 (2H, m, H_5), 4.4 (1H, d, J 3.5 Hz, H_1), 6.25 (1H, d, J 3.5 Hz, $H_{1'}$), 7.35-8.2 (20H, m, Ph); ^{31}P-NMR δ (101.2 MHz, CH_2Cl_2, - 40°) 18.6 (dd, $J_{PP'}$ 356 Hz, J_{PRh} 122 Hz), 28.4 ppm (dd, $J_{P'P}$ 356 Hz, $J_{P'Rh}$ 122 Hz); Λ_m (CH_2Cl_2) 6.93 Ω^{-1} M^{-1} cm^2; m/z (fast atom bombardment) 900 (M^+ - CO), 865 [M^+ - (CO + Cl)].

Carbonyl[2,3,4-tri-O-methyl-6-(diphenylphosphino-α-D-glucopyranosyl-2'3'4'-tri-O-methyl-6'-(diphenylphosphino)-α-D-glucopyranoside] rhodium (I) tetrafluoroborate (123)

Excess silver tetrafluoroborate was added to a solution of the above complex (116) (60 mg, 0.064 mmol) in dichloromethane (2 ml). Silver chloride was precipitated and the solution was filtered into hexane (60 ml). The resulting suspension was centrifuged, the solvent decanted off, the solid washed with hexane (30 ml) and dried in a stream of argon to give carbonyl[2,3,4-tri-O-methly-6-(diphenylphosphino)-α-D-glucopyranosyl-2'3'4'-tri-O-methyl-6'-(diphen ylphosphino-α-D-glucopyranoside] rhodium (I) tetrafluoroborate (123) as a pale yellow solid (61 mg, 0.062 mmol, 96%); m.p. 208-10° (dec.); I.R. (KBr disc) 1990 (vs); ^{1}H-NMR δ (300 MHz, CD_2Cl_2) 2.9 (6H, s, OMe), 3.05-3.65 (12H, m, H_2, H_3, H_4, H_5, H_6), 3.7 (6H, s, OMe), 3.8 (6H, s, OMe), 4.45 (2H, d, J 3.5 Hz, H_1), 7.35-8.15 (20H, m, Ph); ^{31}P-NMR δ (36.43 MHz, CH_2Cl_2) 33.2 ppm (d, J 98.5 Hz); ^{31}P-NMR δ (36.43 MHz, CH_3OH) 30.8 ppm (d, J 117.7 Hz).

Carbonylchloro[2,3,4-tri-O-methyl-6-(diphenylphosphino)-β-D-glucopyranosyl-2',3',4'-tri-O-methyl-6'-(diphenylphosphino-β-D-glucopyranoside]rhodium (I) (117)

Reaction of tetracarbonyl-μ,μ-dichlorodirhodium (I) (115) (5.1 mg, 0.013 mmol) and biphosphine (74) (20 mg, 0.026 mmol) by the method of P. 169 gave carbonylchloro[2,3,4-tri-O-methyl-6-(diphenylphosphino-β-D-glucopyranosyl-2',3',4'-tri-O-methyl-6 '-(diphenylphosphino)-β-D-glucopyranoside]rhodium (I) (117) as a yellow powder (22 mg, 0.024 mmol, 91%); m.p. 124-7°; found: C, 55.51; H, 5.82%; $C_{43}H_{52}ClO_{10}P_2Rh$ requires C, 55.58; H, 5.60%; I.R. (KBr disc) 1955 (vs); ^{1}H-NMR δ (300 MHz, CD_2Cl_2) 2.6-3.2 (12H, m, H_2, H_3, H_4, H_5, H_6), 3.34 (3H, s, OMe), 3.44 (3H, s, OMe), 3.52 (3H, s, OMe), 3.54 (3H, s, OMe), 3.60 (3H, s, OMe), 3.62 (3H, s, OMe), 4.85 (2H, d, J 7 Hz, H_1), 7.3-7.55 (16H, m, Ph), 8.0 (4H, m, Ph); ^{31}P-NMR δ (101.2 MHz, CH_2Cl_2) 20.7 (dd, $J_{PP'}$ 359 Hz, J_{PRh} 126.5 Hz), 27.6 ppm (dd, $J_{P'P}$ 359 Hz, $J_{P'Rh}$ 126.5 Hz); Λ_m (CH_2Cl_2) 0.26 Ω^{-1} cm^2; m/z (fast atom bombardment) 900 (M^+ - CO), 865 [M^+ - (CO + Cl)].

Carbonyl[2,3,4-tri-O-methyl-6-(diphenylphosphino)-β-D-glucopyranosyl-2',3',4'-tri-O-methyl-6'-(diphenylphosphino)-β-D-glucopyranoside] rhodium (I) tetrafluoroborate (127)

Excess silver tetrafluoroborate was added to a solution of the above complex (117) (28 mg, 0.030 mmol) in either dichloromethane or methanol (2 ml). The solution was degassed, warmed to room temperature, centrifuged to remove precipitated silver chloride and the title complex (127) was examined by phosphorus NMR; ^{31}P-NMR δ (101.2 MHz, CH_2Cl_2) 18.8 ppm (d, J_{PRh} 106.0 Hz); ^{31}P-NMR δ (101.2 MHz, CH_3OH) 20.8 ppm (d, J_{PRh} 124.0 Hz).

Bicyclo[2.2.1]hepta-2,5-diene-1,7-bis(diphenylphosphino)-4-oxaheptane rhodium(I) tetrafluoroborate (91)

A solution of bis-bicyclo [2.2.1]hepta-2,5-dienerhodium(I) tetrafluoroborate (84) (0.09 g, 0.24 mmol) and 1,7-bis(diphenylphosphino)-4-oxaheptane (64) (0.113 g, 0.24 mmol) in dichloromethane (2 ml) was stirred under argon for 10 min. Addition to ether (25 ml), separation of the precipitate by Craig-tube filtration and washing with ether (3 x 10 ml) yielded 0.17 g (95%) of the complex. Recrystallization from methanol/water gave bicyclo [2.2.1]hepta-2,5-diene-1,7-bis(diphenylphosphino)-4-oxaheptanerhodium(I) tetrafluoroborate dihydrate (91) as red-orange crystals, m.p. (dec.) 144° (Found C, 56.1; H, 5.4; P, 8.1%. $C_{37}H_{40}OP_2RhBF_4$. $2H_2O$ requires: C, 56.4; H, 5.6; P, 7.85%); ^{1}H-NMR δ(CD_2Cl_2) 1.5 (2H, s, CH_2), 1.6 to 2.3 (8H, mult., CH_2CH_2P), 3.1(4H, mult., CH_2O), 4.0(2H, s, CH) and 4.5(4H, s, CH=CH); ^{31}P-NMR δ(CH_2Cl_2) 22.3, $J_{P,Rh}$ 154; m/e (field desorption) 666 (M^+, 100%).

The corresponding rhodium norbornadiene complexes of 1,5-bis (diphenylphosphino)-3-oxapentane, 1,8-bis (diphenylphosphino) 3,6-dioxaoctane and cis-2,5-bis (diphenylphosphinomethyl) tetrahydrofuran were prepared in similar manner.

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