Chelating Diphosphite Complexes of Nickel(0) and Platinum(0): Their Remarkable Stability and Hydrocyanation Activity

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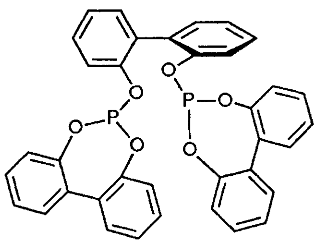
The synthesis, stability and hydrocyanation catalytic activity of nickel(0) complexes of the diphosphite **1** derived from 2,2′-biphenol are described; the X-ray crystal structures of the ligand **1** and its platinum(0) complex **2b** are reported.

Diphosphines are very widely used ligands because the chelate complexes which they form are very stable and they often show catalytic activity, a property which has been particularly valuable in enantioselective catalysis where the rigidity of the chelate is exploited.[1] In contrast, until recently diphosphites were unknown as ligands[2] despite the importance of monophosphite complexes *e.g.* in the nickel–phosphite catalysed hydrocyanation of butadiene.[3] We report here the synthesis of diphosphite **1**, its metal(0) complexes **2a** and **b**, and the hydrocyanation catalytic activity of the nickel complex **2a**. Recently, Union Carbide have reported that rhodium complexes of ligands similar to **1** are very active hydroformylation catalysts.[4]

Ligand **1** is readily made from 2,2′-biphenol and PCl_3 in the presence of Et_3N and then crystallised from CH_2Cl_2–pentane. The X-ray crystal structure† of **1** (see Fig. 1) shows that the ligand is intrinsically chiral because of the twists about the biphenyl C–C linkages [(O)C–C–C–C(O) torsion angles −41.4(4), −61.7(3) and −42.4(4)°]. The diastereoisomer that crystallized has the *RRR* (*SSS*) configuration. The $^{31}P\{^1H\}$ NMR spectrum of **1** at ambient temperatures and at −80 °C is a singlet consistent with only one of the three possible diastereoisomrs being present or, less likely, rapid interconversion of these isomers on the NMR timescale by rotation about the three biphenyl C–C linkages.

The zerovalent nickel and platinum complexes **2a** and **b** are made by treatment of the appropriate $[M(cod)_2]$ (M = Ni or Pt; cod = cycloocta-1,5-diene) with diphosphite **1**. The platinum complex **2b** was crystallized from tetrahydrofuran–pentane solution and the structure of its pentane solvate determined by X-ray diffraction.‡ In the solid state structure of **2b** (which has exact C_2 symmetry) the phosphorus atoms are inequivalent since both of the ligands have an *SRR* configuration (see Fig. 2) with (O)C–C–C–C(O) torsion angles 41.5(11), −106.5(8) and −42.3(13)°. The configuration of the ligand in the solid complex **2b** differs from **1** both in absolute configuration and in the extent of twisting about the central biphenyl C–C linkage [(O)C–C–C–C(O) torsion angles; −106.5(8)° in **2b** and −61.7(3)° in **1**]. The $^{31}P\{^1H\}$ NMR spectrum of **2b** at +30 °C is two singlets (5 : 1 ratio) with ^{195}Pt satellites and at −80 °C two triplets with satellites. The spectrum at low temperature is consistent with the solid state structure of **2b**, *i.e.* an A_2X_2 spin system arising from the inequivalent phosphorus environments; there are twelve possible diastereoisomers of **2b** and it is therefore remarkable that apparently only one of these is present in solution at low



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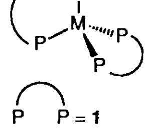
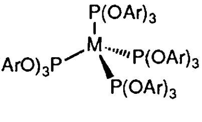


2a M = Ni
2b M = Pt



3 Ar = *p*-MeC_6H_4

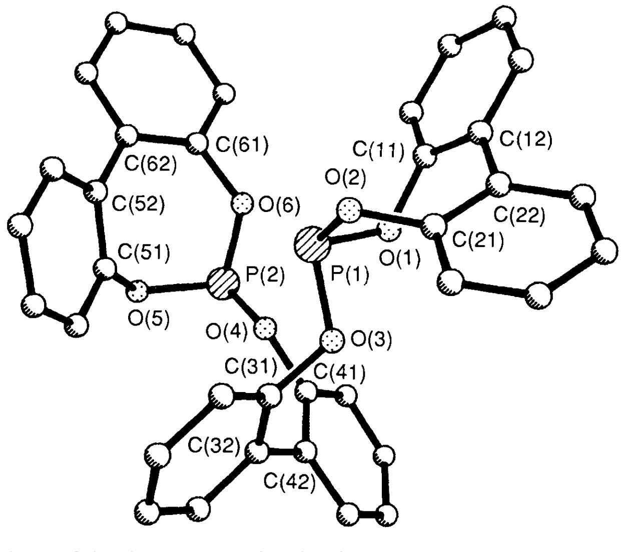


Fig. 1 Molecular struture of **1** showing atom labelling scheme. All hydrogens have been omitted for clarity. Important dimensions include; bond lengths (Å): P(1)–O(1) 1.631(2), P(1)–O(2) 1.635(2), P(1)–O(3) 1.631(2), P(2)–O(4) 1.631(2), P(2)–O(5) 1.613(2), P(2)–O(6) 1.630(2); bond angles (°): O(1)–P(1)–O(2) 99.5(1), O(1)–P(1)–O(3) 91.7(1), O(2)–P(1)–O(3) 101.9(1), O(4)–P(2)–O(5) 102.1(1), O(4)–P(2)–O(6) 92.7(1), O(5)–P(2)–O(6) 100.7(1); torsion angles (°): C(11)–C(12)–C(22)–C(21) −41.4(4), C(31)–C(32)–C(42)–C(41) −61.7(3), C(51)–C(52)–C(62)–C(61) −42.4(4).

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† *Crystal data* for **1**: $C_{36}H_{24}O_6P_2$, M_r = 614.5, triclinic, space group $P\bar{1}$ (No. 2), a = 9.210(2), b = 11.541(3), c = 14.183(4) Å, α = 93.57(2), β = 96.06(2), γ = 100.55(2)°, U = 1468.3(6) Å^3, Z = 2, D_c = 1.39 g cm^{-3}, $\bar{\lambda}$ = 0.71069 Å, μ(Mo-Kα) = 1.89 cm^{-1}, F(000) = 636, T = 293 K. Data were collected on a Nicolet P3m diffractometer for a unique hemisphere of reciprocal space with 3.5 < 2θ < 50°. The structure was solved by direct methods and refined by least-squares to R 0.045 for 3635 unique, observed ($I > 1.5\sigma(I)$), absorption corrected, intensity data.

‡ *Crystal data* for **2b**·$2C_5H_{12}$: $C_{82}H_{72}O_{12}P_4Pt$, M_r = 1568.5, monoclinic, space group $I2/a$ (No. 15), a = 23.094(5), b = 14.044(2), c = 24.164(5) Å, β = 113.53(2)°, U = 7370(2) Å^3, Z = 4, D_c = 1.41 g cm^{-3}, $\bar{\lambda}$ = 0.71069 Å, μ(Mo-Kα) = 20.7 cm^{-1}, F(000) = 3024, T = 293 K. Data were collected on a Nicolet P3m diffractometer for a unique quadrant of reciprocal space with 3.5 < 2θ < 50°. The structure was solved by heavy atom methods and refined by least-squares to R 0.039 for 4245 unique, observed ($I > 1.5\sigma(I)$), absorption corrected, intensity data. For both structures atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

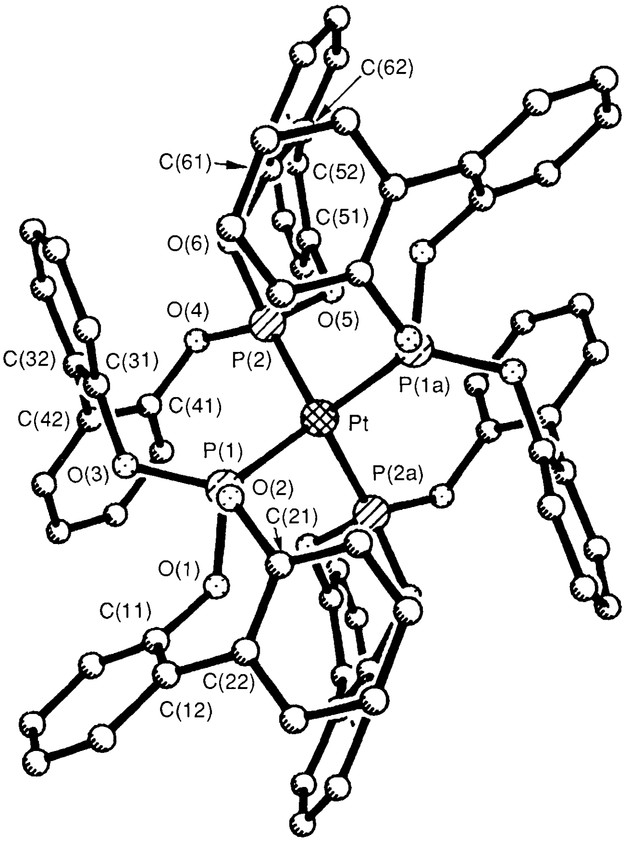

Fig. 2 Molecular structure of **2b** showing atom labelling scheme. All hydrogens have been omitted for clarity. Important dimensions include; bond lengths (Å): Pt-P(1) 2.233(1), Pt-P(2) 2.263(2), P(1)-O(1) 1.609(4), P(1)-O(2) 1.634(4), P(1)-O(3) 1.609(5), P(2)-O(4) 1.608(5), P(2)-O(5) 1.611(4), P(2)-O(6) 1.618(5); bond angles (°): P(1)-Pt-P(2) 115.3(1), P(1)-Pt-P(1a) 114.3(1), P(1)-Pt-P(2a) 102.2(1), P(2)-Pt-P(2a) 107.8(1); torsion angles (°): C(11)-C(12)-C(22)-C(21) 41.5(11), C(31)-C(32)-C(42)-C(41) −106.5(8), C(51)-C(52)-C(62)-C(61) −42.3(13).

temperatures. The phosphorus atoms are equilibrated on the NMR timescale at +30 °C presumably by rapid inversion of the P(biphenoxide) rings giving rise to the major ^{31}P NMR singlet. The $^{195}Pt\{^1H\}$ NMR spectrum at +30 °C shows two quintets (5 : 1 ratio) at similar chemical shift and we therefore conclude that a second diastereoisomer of **2b** is present at ambient temperatures. Similar solution NMR behaviour is observed for the nickel analogue **2a**.

Table 1 Catalytic hydrocyanation of butadiene experiments[a]

Catalyst	Yield of product/g	% Nitriles[b]	% 3PN[c]	Turnover
2a	2.38	61	52	1430
3	2.15	79	69	35
3 + 6L[d]	3.19	75	63	310

[a] Conditions used: butadiene (4 cm^3, 46 mmol) and $Me_2CO{\cdot}HCN$ (3.1 cm^3, 34 mmol) with catalyst (0.088 mmol) in 10 cm^3 metal bomb, stirred for 18 h at 140 °C. Each run was duplicated to ensure consistency; % yields determined by GC. The total number of turnovers for each catalyst was determined by sequentially reducing the amount of catalyst used until the yield of nitriles was seen to drop significantly. [b] The major non-hydrocyanation product is 4-vinyl-1-cyclohexene. [c] Proportion of the nitrile yield that is 3-pentenenitrile rather than 2-methyl-3-butenenitrile. [d] Complex **3** in the presence of 6 equiv. of tris(*p*-tolyl)phosphite.

The Du Pont catalyst $[Ni\{P(OC_6H_4Me\text{-}p)_3\}_4]$ **3** is outstandingly effective for the hydrocyanation of butadiene[5] but the intrinsic instability of the catalyst necessitates the presence of large excesses of phosphite ligand. By contrast the nickel chelate **2a** is a very robust compound, *e.g.* toluene solutions of **2a** when exposed to air for 14 days show no indication of decomposition (by $^{31}P\{^1H\}$ NMR spectroscopy) whereas exposure of similar solutions of **3** to air lead to complete decomposition within 6 hours. The nickel chelate **2a** is a catalyst for the hydrocyanation of butadiene. From the data given in Table 1, it can be seen that **2a**, though less selective than **3**, achieves at least 4 times the number of catalytic turnovers of the commercial catalyst system (**3** + 6 equivalents of ligand[5]) and *40 times* the number of catalytic turnovers of catalyst **3** in the absence of added ligand. It is clear that the high stability of chelating diphosphite complexes gives them great potential as catalysts.

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