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Preliminary communication

OLEFIN DISPLACEMENT FROM 4,5-BIS(DIPHENYLPHOSPHINOMETHYL)-2,2-DIMETHYL-1,3-DIOXOLAN ETHYLENEPLATINUM(0) UNDER MILD CONDITIONS

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Summary

The compound 4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolan ethyleneplatinum(0) is readily prepared and its ethylene moiety may be displaced by, for example, allene or CO.

Platinum complexes find increasing application in catalysis, particularly of hydroformylation. It is known that chelate diphosphines provide the most reactive catalysts and the dependence of reactivity on a ring-size is substantial, with bis(diarylphosphino)butane derivatives superior to shorter-chain analogues. Asymmetric hydroformylation can be achieved [2] through catalysis by platinum complexes of 4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolan [DIOP] [1] or better its phosphole analogue, in the presence of $SnCl_2$. Little is known about the true catalytic intermediates in these reactions [3], which necessarily involve platinum alkyls and acyls where the carbon ligand is *trans* to a phosphine. Most biphosphine platinum acyl complexes have a *trans*-disposition of the two phosphines [4] which are then *cis* to the acyl group), one of the few exceptions being formed under very mild conditions [5].

For these reasons we sought a chiral platinum biphosphine complex with an easily displaced ligand. It was earlier found that reaction of bis(cyclooctadiene)platinum [6] with the biphosphine DIOP led to disproportionation and the formation of $(DIOP)_2Pt$ [7]. Since ethylene bis(triphenylphosphine)-platinum has recently been prepared [8] by $NaBH_4$ reduction of $(PPh_3)_2PtCl_2$ [9] under a C_2H_4 atmosphere, this reaction was adapted. The complex [4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolan]-platinum dichloride was dissolved in $CH_2Cl_2/EtOH$, cooled to −78°C and stirred under an ethylene atmosphere whilst a 5 *M* excess of $NaBH_4$ was added. After allowing to warm to room temperature and stirring under ethylene for

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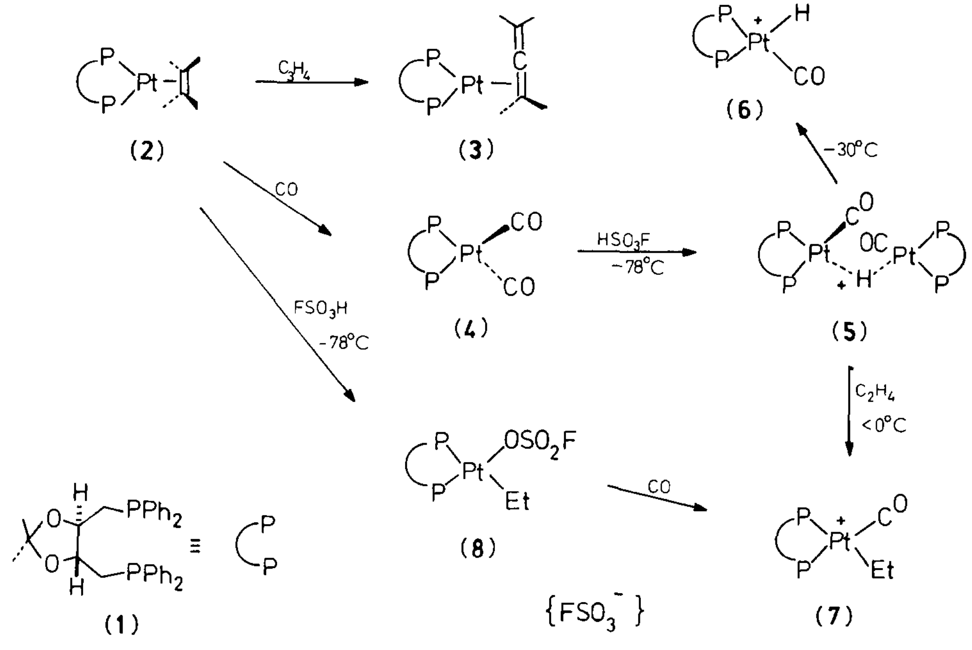
a further 2 h, complex 2, m.p. > 170°C (dec.) was isolated in 78% yield as an analytically pure cream solid. The ^1H NMR showed two multiplets with platinum satellites (^2J(Pt—H) 56 Hz) at 1.8 and 2.0 ppm due to the two pairs of *trans*-related diastereotopic olefin protons, and three complex adsorbances at 2.4, 3.55 and 3.9 ppm due to the protons of the chelate ring [10].

Ethylene was cleanly and quantitatively displaced from the complex by a variety of added ligands. Addition of excess propadiene to the solution of complex 2 in CH_2Cl_2 leads to the η^2-mononuclear complex 3 [11] with distinct ^1H NMR for the bound (δ 1.9, 2.0, ^2J(Pt—H) 70 Hz) and free (δ 4.65, ^3J(Pt—H) 75; 6.05, ^3J(Pt—H) 105 Hz) olefinic protons.

Reaction with carbon monoxide in CH_2Cl_2 gave the dicarbonyl complex 4, unstable in the absence of CO. It was characterised in solution by IR (CH_2Cl_2), 1980, 1935 cm^{-1}, ^1H and ^{13}C NMR (CD_2Cl_2, —50°C, ^{13}CO labelled), 182.8 ppm (J(CP) 22, J(CPt) 1850 Hz). The ^{31}P NMR spectrum of ^{13}C-labelled complex 4 shows the expected triplet structure at low temperatures, but broadens by dissociative exchange, with coalescence at +5°C ($\Delta G^\dagger \approx 14$ kcal mol^{-1}). On addition of an equivalent of FSO_3H to a solution of complex 4 in CH_2Cl_2 at —78°C, a single hydride-bridged complex [12] was produced whose spectroscopic properties were consistent with structure 5. The ^1H NMR spectrum at —35°C in CD_2Cl_2 showed a characteristic 1/8/18/8/1 quintet structure (δ — 1.8 ppm, ^2J(HP) 32, ^1J(HPt) = ^1J(HPt′) = 442 Hz). The CO is labile, even at low temperature, and C—P coupling could not be observed in the ^{31}P or ^{13}C NMR spectra. The former was first-order and showed no evidence for Pt—Pt or long-range Pt—P coupling. On warming to —30°C for a few hours, decomposition occurred, and a small proportion of the mononuclear cation 6 was produced (^1H NMR, CD_2Cl_2, —58°C, δ —3.3 ppm, ^2J(HP) = B (*cis*),



SCHEME 1

160 (*trans*) ^1J(HPt) 844 Hz). Under a C_2H_4 atmosphere, a clean transformation to the ethylcarbonyl cation 7 occurred below 0°C demonstrating the reactivity of the bridging hydride towards free olefin. The same complex could be prepared by protonating the ethylene complex with HSO_3F under an argon atmosphere at −78°C and then treating the labile fluorosulphonate 8 with CO. The reactions are summarised in Scheme 1.

The ethylene complex 1 provides a convenient precursor for studies of platinum-catalysed allylic alkylation [13], and of intermediates in cross-coupling reactions [14], a detailed account of which will be provided later.

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