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Preliminary communication

Deprotonation and metallation of an olefinic tertiary phosphine by planar d^8 divalent metal complexes; the crystal structure of [PtCl(o-$Ph_2PC_6H_4C{=}CHC_6H_4PPh_2$-$o$)]

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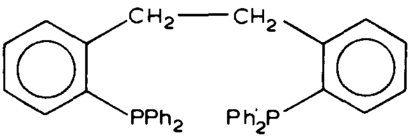
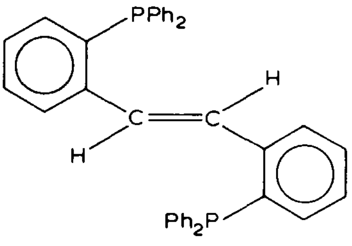
SUMMARY

The reaction of 2,2′-bis (diphenylphosphino)stilbene with halide salts or complexes of Ni^{II}, Pd^{II}, or Pt^{II} results in the elimination of hydrogen halide and the formation of complexes [MCl(o-$Ph_2PC_6H_4C{=}CHC_6H_4PPh_2$-$o$)] in which the tridentate phosphine ligand is bonded to the metal via two M–P σ-bonds and one M–C σ-bond.

We have recently reported that the ligand 2,2′-bis (diphenylphosphino)bibenzyl (I) loses two benzylic hydrogen atoms on reaction with rhodium(I) chloro-complexes or with rhodium(III) chloride, to give a chlororhodium(I) complex of the corresponding tridentate *trans*-stilbene ligand o-$Ph_2PC_6H_4CH{=}CHC_6H_4PPh_2$-$o$ (II)[2]. We now find that on reaction with palladium(II) and platinum(II) complexes [*e.g.*, $MCl_2(PhCN)_2$, K_2MBr_4 (M = Pd or Pt), $PdI_2(PPh_3)_2$, or $PtI_2(1,5\text{-}C_8H_{12})$] in refluxing 2-methoxyethanol, the ligand I loses one equivalent of hydrogen halide to give yellow (Pd) or cream (Pt) planar σ-bonded de-



(I)



(II)

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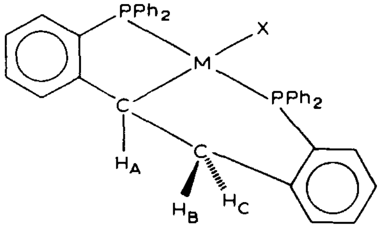
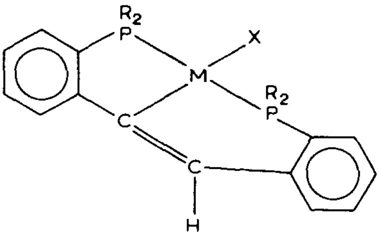
rivatives which are assigned structure III. The 100 MHz ^{1}H NMR spectra of the palladium(II) complexes III show an ABC pattern arising from the three protons of the aliphatic chain (*e.g.*, for [$PdCl(o\text{-}Ph_2PC_6H_4CHCH_2C_6H_4PPh_2\text{-}o)$] in $CDCl_3$, δ_A 3.84, δ_B 3.15, δ_C 3.53 ppm; J_{AB} 1.0, J_{AC} 9.5, J_{BC} 17.0 Hz).



(III)

M = Pd , Pt ; X = Cl, Br, I



(IV)

M = Ni , Pd, Pt ; X = Cl, Br, I
R = C_6H_5 , $o\text{-}CH_3C_6H_4$

The ^{31}P NMR spectrum of the same complex shows an AB pattern (δ_A −14.5; δ_B −43.5 ppm; ^2J(P–P) 410 Hz)[*], the large value of ^2J(P–P) is typical of mutually *trans* phosphorus atoms in a planar d^8 metal complex.

The stilbene ligand II, and its di-*o*-tolylphosphino analogue [$(o\text{-}MeC_6H_4)_2PC_6H_4CH{=}CHC_6H_4P(C_6H_4Me\text{-}o)_2$]^2, react under similar conditions with salts or complexes of Ni^{II}, Pd^{II}, or Pt^{II}, with elimination of hydrogen halide, to give air-stable yellow or pale yellow (Pd, Pt) or red (Ni) σ-bonded complexes of structure IV. In the nickel complexes, the olefinic proton appears as a singlet (*e.g.*, for [$NiCl(o\text{-}MeC_6H_4)_2PC_6H_4C{=}CHC_6H_4P(C_6H_4Me\text{-}o)_2$] in CD_2Cl_2 (100 MHz), δ (=CH) is 6.10 ppm), but in the palladium and platinum complexes, the olefinic proton resonance is not observed, presumably because it is buried beneath the aromatic proton resonances.

The structural assignment IV is confirmed by the three-dimensional X-ray structural analysis of [$PtCl(o\text{-}Ph_2PC_6H_4C{=}CHC_6H_4PPh_2\text{-}o)$], crystals of which are monoclinic, space group $P2_1$, with a = 10.633, b = 16.934, c = 9.947 Å, β = 119.02°, Z = 2. The 4669 independent reflections, with $I/\sigma(I) \geqslant 3.0$, were collected on a Picker FACS-I fully automatic diffractometer using graphite-crystal monochromated Mo-K_α radiation. With anisotropic thermal parameters for all non-hydrogen atoms, refinement has converged to a conventional R-factor of 0.049. Corrections for anomalous scattering have been included in the structure factor calculation; for the structure of inverse absolute configuration, least-squares refinement converged with R = 0.065. Data have yet to be corrected for absorption effects, and hydrogen atom contributions have not, as yet, been included in the scattering model.

The overall stereochemistry of the molecule, which is essentially square-planar about the central platinum atom, is shown in Fig. 1. The maximum deviation from the

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[*] The negative sign indicates ppm downfield of 85% H_3PO_4.

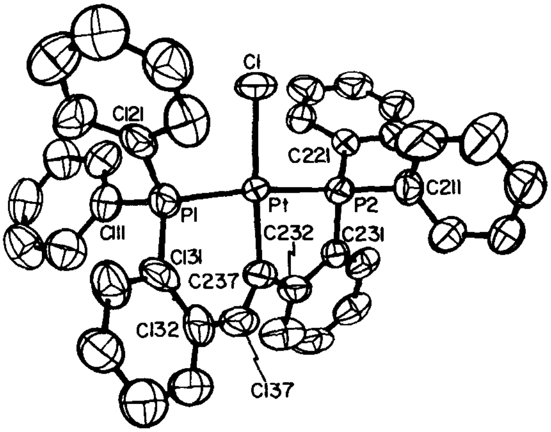

Fig. 1. The overall stereochemistry of [PtCl(o-$Ph_2PC_6H_4C$=$CHC_6H_4PPh_2$-o)].

weighted least-squares plane through Pt, Cl, P(1), P(2), and C(237) is 0.06 Å [at C (237); "below" the coordination plane]. In contrast, C(137) is 0.46 Å "above" this plane.

The Pt—P distances [Pt—P(1), 2.266(3); Pt—P(2), 2.269(3) Å] are equal within experimental error.

The Pt—C σ-bond distance [Pt—C(237), 2.01(1) Å] is significantly shorter than the Pt—C σ-bond distances in *trans*-[$PtCl(CH_2SiMe_3)(PMe_2Ph)_2$] [2.08(1) Å]^3, and *trans*-[$PtClMe(PMePh_2)_2$] [2.07(1) Å]^4. The apparent contraction (of ca. 0.06 Å) of the Pt—Cl σ-bond is larger than can be accounted for solely in terms of the differing σ-bond radii of sp^2 and sp^3 hybridized carbon atoms, and it may result, in part, from the chelate effect.

As expected, there is a strong structural *trans* effect^5. The Pt—Cl distance [2.371(3) Å] is very much longer than the Pt—Cl distance in *trans*-[$PtCl_2(PEt_3)_2$] [2.294(9) Å]^6, but it is only slightly shorter than the Pt—Cl distance (*trans* to σ-bonded methyl) in [$PtClMe(PMePh_2)_2$] [2.411(2) Å]^4.

The olefinic distance [C(137) - C(237), 1.340(16) Å] is within experimental error of the value normally expected for simple carbon—carbon double bonds [1.335 Å]^7, but it is significantly shorter than the value of 1.45(1) Å found for the coordinated olefin distance in the related rhodium(I) complex [RhCl(o-$Ph_2PC_6H_4CH$=$CHC_6H_4PPh_2$-o)]^1.

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