Formation and Crystal Structure of $[\overline{\mathrm{ClPtNMe_2NHCH_2\overline{CHPPh_2CH_2CH_2}PPh_2}}]\mathrm{Cl}$ containing a Novel Tridentate Ylide Ligand formed by Intramolecular Phosphinovinylation

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Treatment of *cis*-$[PtCl_2(PPh_2CH{=}CH_2)_2]$ with Me_2NNH_2 gives the title compound, formed by successive conjugate additions to the vinyl groups, including attack by one P-atom on a vinyl group of an adjacent co-ordinated $PPh_2CH{=}CH_2$ ligand: some reactions of the title compound are described.

We have shown that, when activated by co-ordination to a metal, the vinylidene diphosphine $(Ph_2P)_2C{=}CH_2$ (vdpp), undergoes nucleophilic attack or Michael addition to the activated $CH_2{=}C$ with a variety of nucleophiles.[1—3] One would anticipate that a vinylphosphine such as $Ph_2PCH{=}CH_2$ would be less activated on co-ordination than $(Ph_2P)_2C{=}CH_2$ towards Michael addition. In agreement with this we now find that, although complexes of the type $[M(CO)_4(\text{vdpp-}PP')]$ (M = Mo or W) readily add hydrazines, amines, and thiols,[1] analogous complexes $[M(CO)_{6-x}(Ph_2PCH{=}CH_2)_x]$ ($x = 1$ or 2, M = Mo or W) were recovered unchanged after treatment with these nucleophiles. However, a *cis*-$PtCl_2$ moiety is much more electron attracting than *cis*-$M(CO)_4$[1] and therefore we have studied *cis*-$[PtCl_2(PPh_2CH{=}CH_2)_2]$,† which we made by treating $[PtCl_2(NCPh)_2]$ with $PPh_2CH{=}CH_2$.

We have found previously that Me_2NNH_2 is a particularly good nucleophile for adding to co-ordinated vdpp[1—3] and when we treated *cis*-$[PtCl_2(PPh_2CH{=}CH_2)_2]$ with an excess of Me_2NNH_2 in hot benzene for one hour a white crystalline

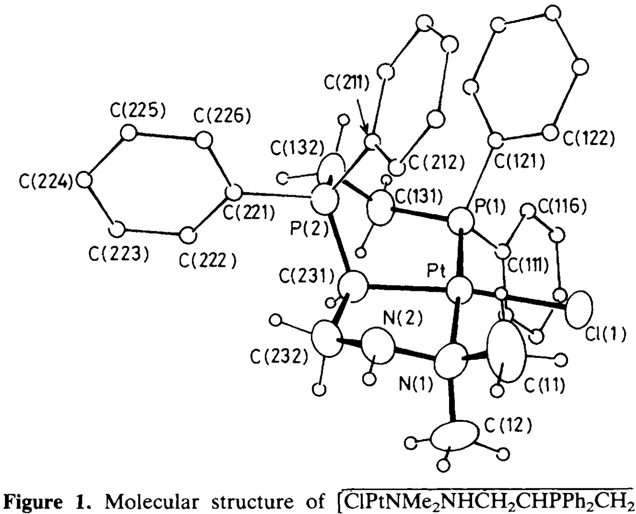

Figure 1. Molecular structure of $[\overline{\mathrm{ClPtNMe_2NHCH_2\overline{CHPPh_2CH_2CH_2}PPh_2}}]\mathrm{Cl}$ (**1**). Selected interatomic distances: Pt–Cl 2.365(4), Pt–P(1) 2.224(4), Pt–N(1) 2.144(9), Pt–C(231) 2.051(9), Pt · · · P(2) 3.141(5) Å. Selected angles: P(1)–Pt–Cl 92.4(2), N(1)–Pt–Cl 91.3(3), C(231)–Pt–N(1) 82.7(4), C(231)–Pt–P(1)°.

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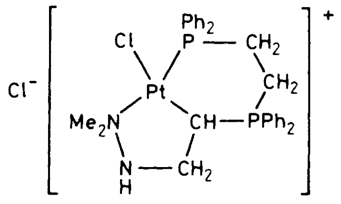
† This and other compounds were characterized by elemental analysis, i.r., and ^1H, $^1H\{^{31}P\}$, and $^{31}P\{^1H\}$ n.m.r. spectroscopy, unless stated otherwise.



(1)

product (adduct) was obtained in *ca.* 95% yield. Elemental analysis established the product to have the composition $PtCl_2(PPh_2C_2H_3)_2 \cdot H_2NNMe_2$ but the electrical conductivity in nitrobenzene showed it to be a 1 : 1 electrolyte *i.e.* a chloride salt, from which the corresponding PF_6 salt was readily made by treatment with NH_4PF_6 in acetone. The complex showed a strong i.r. band at 303 cm^{-1}, due to ν(Pt–Cl) and a band at 3400 cm^{-1}, due to ν(N–H). However, the most interesting feature of this complex was the $^{31}P\{^1H\}$ n.m.r. spectrum (in CD_2Cl_2) which showed that one of the phosphorus atoms (P_B) was no longer co-ordinated to platinum, $\delta(P_A)$ 3.7 p.p.m., $^1J(PtP_A)$ 3530 Hz, $\delta(P_B)$ 31.9 p.p.m.,[2] $J(PtP_B)$ 93, $J(P_AP_B)$ 7 Hz. The $^1H\{^{31}P\}$ was complicated, with a series of resonances 2.5—4.9 p.p.m. but no resonances in the vinyl region. We therefore determined the structure of this complex by *X*-ray diffraction.‡ The structure is shown in Figure 1 with selected data in the caption. The structure, shown diagramatically in (**1**), contains a novel bidentate ylide ligand with a five-membered PtNNCC and a six-membered PtPCCPC ring fused along the Pt–C bond.

We tentatively suggest that Me_2NNH_2 attacks a vinyl C=C of *cis*-$[PtCl_2(PPh_2CH{=}CH_2)_2]$ to give an intermediate, $[ClPt(NMe_2NHCH_2CHPPh_2)(PPh_2CH{=}CH_2)]$, of which the unco-ordinated phosphorus then adds to the adjacent vinyl group to give $[ClPtNMe_2NHCH_2CHPPh_2CH_2CH_2PPh_2]Cl$ (**1**) after picking up a proton.

The chloride ligand in (**1**) is labile, being *trans* to carbon and when treated with NaI or LiBr in acetone the corresponding iodo- or bromo-complexes as bromide or iodide salts were obtained. The chloride salt (**1**) is soluble in water and when an aqueous solution was treated with an aqueous solution of sodium borohydride, an immediate white precipitate of an electrically neutral complex, formed. This product was labile and was not obtained quite pure. However, the $^1H\{^{31}P\}$ and ^1H n.m.r. spectra (in CD_2Cl_2) showed it to be a hydride δ(H) −6.8 p.p.m., ^1J(PtH) 1020, $^2J(P_AH)$ 22, $^3J(P_BH)$ 4 Hz. The $^{31}P\{^1H\}$ n.m.r. data are $\delta(P_A)$ 12.5 p.p.m., $^1J(PtP_A)$ 3652 Hz, $\delta(P_B)$ 27.4 p.p.m., $^2J(PtP_B)$ 37 Hz, $^3J(P_AP_B)$ was too small to resolve. We suggest the complex is $[HPtNMe_2NHCH_2C{=}PPh_2CH_2CH_2PPh_2]$.

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‡ *Crystal data* for (**1**): $C_{30}H_{34}Cl_2N_2P_2Pt$, M = 730.55, monoclinic, space group $C2/c$, a = 3171.1(8), b = 1090.8(2), c = 2558.8(5) pm, β = 136.63(1)°, U = 6.078 nm^3, Z = 8, μ = 46.24 cm^{-1}, $F(000)$ = 2968. Scans running from 0.9° below $K_{\alpha 1}$ to 0.9° above $K_{\alpha 2}$, scan speeds 2.0—29.3° min^{-1}, and $4.0 < 2\theta < 45.0°$. All crystallographic measurements were made on a Nicolet P3/F diffractometer operating in the ω–2θ scan mode using graphite monochromated Mo-K_α radiation following a procedure described elsewhere.[4] The data set was corrected for absorption empirically.[5] The structure was solved by standard heavy atom methods and refined by full-matrix least-squares using SHELX 76.[6] All non-hydrogen atoms were refined anisotropically, all hydrogen atoms were included in calculated positions (C–H = 108 pm) [except for the hydrogen attached to N(2) which was located in a Fourier difference map] and refined with an overall isotropic temperature factor. The weighting scheme $w = [\sigma^2(F_o) + 0.0009(F_o)^2]^{-1}$ was used at the end of refinement. Final R and R_w values are 0.040 and 0.043 (303 parameters, 4020 observed data). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.