Synthesis of some Diplatinum Complexes, including Bis-μ-[bis(diphenylphosphino)methane]-μ-methylene-dichlorodiplatinum, $[Pt_2Cl_2(\mu-CH_2)(\mu-Ph_2PCH_2PPh_2)_2]$, from $[Pt_2Cl_2(\mu-Ph_2PCH_2PPh_2)]$

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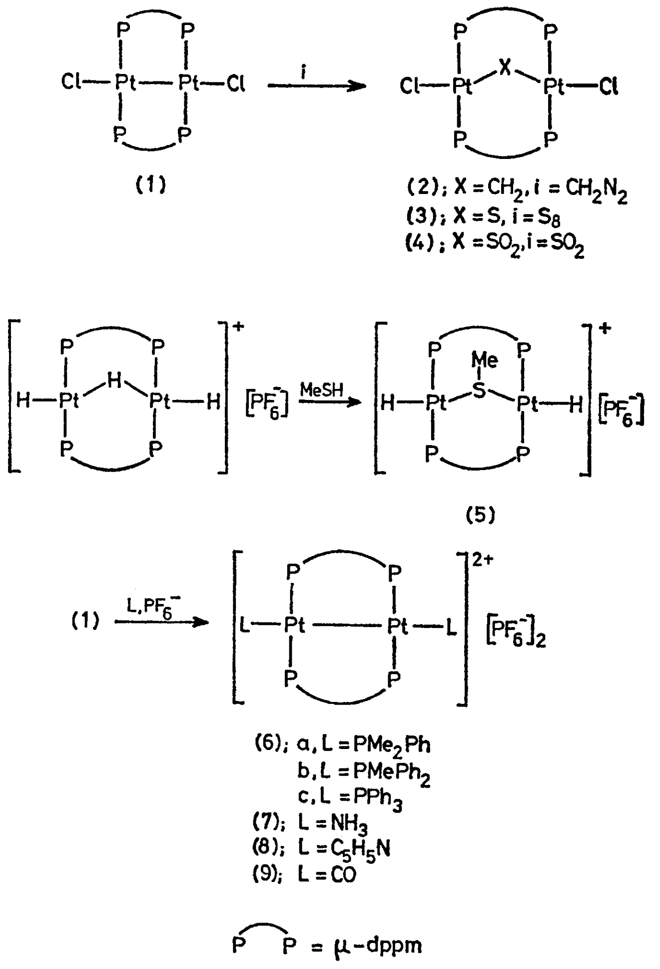
Summary A number of diplatinum complexes including $[Pt_2Cl_2(\mu-CH_2)(\mu-dppm)_2]$ [dppm = bis(diphenylphosphino) methane], the first diplatinum complex containing a bridging CH_2 group, and complexes $[Pt_2Cl_2(\mu-X)(\mu-dppm)_2]$ (X = S and SO_2) and $[Pt_2L_2(\mu-dppm)_2][PF_6]_2$ (L = a monodentate ligand) have been prepared from $[Pt_2Cl_2(\mu-dppm)_2]$.

THE complex $[Pt_2Cl_2(\mu\text{-dppm})_2]$[1,2] [dppm = bis(diphenylphosphino)methane] (**1**) is a potentially useful substrate for the study of reactions[2,3] at a platinum–platinum bond. Favourable factors would appear to be its approximately planar structure[2] allowing ease of attack at platinum, the low formal oxidation state of the two platinum atoms, and the stability conferred on the binuclear unit by the two μ-dppm groups. A number of reactions of (**1**) are reported (Scheme).



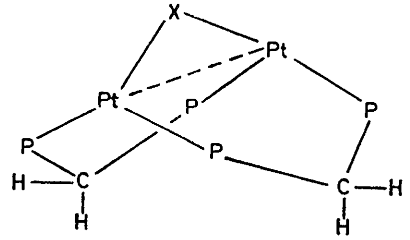
(**1**)
(**2**); $X = CH_2$, $i = CH_2N_2$
(**3**); $X = S$, $i = S_8$
(**4**); $X = SO_2$, $i = SO_2$
(**5**)
(**6**); a, $L = PMe_2Ph$
b, $L = PMePh_2$
c, $L = PPh_3$
(**7**); $L = NH_3$
(**8**); $L = C_5H_5N$
(**9**); $L = CO$
P P = μ-dppm

SCHEME

The CH_2-bridged complex (**2**) [ν(Pt–Cl) 255 cm^{-1}], a lemon-yellow air-stable solid, is readily crystallized (60%) following addition, at 0—20 °C, of an ether solution of CH_2N_2 to (**1**) in CH_2Cl_2. A colourless gas, presumably N_2, is evolved. The presence of a Pt–CH_2–Pt group is shown by a resonance (δ 1·08 in $C_2D_2Cl_4$ at 80 °C) consisting of 13 observable regularly spaced peaks in the ^1H n.m.r. spectrum with relative intensities in good agreement with the calculated values 1 : 2 : 6 : 8 : 8 : 13 : 17 : 13 : 8 : 8 : 6 : 2 : 1. These values (given to the nearest integer) are calculated on the basis of the expected splitting of the CH_2 resonance into a 1 : 4 : 6 : 4 : 1 quintet by four equivalent phosphorus atoms, further splitting into a 1 : 8 : 17 : 8 : 1 pattern[1] by coupling to ^{195}Pt [^2J(Pt–H) 54, ^3J(P–H) 9 Hz], and by taking into account the superposition of some peaks. Four outer peaks are too weak to be observed and their relative intensities are not included in the above values. The overall good agreement between the observed and expected spectra provides strong evidence for the presence of the symmetrical Pt–CH_2–Pt bridge.

The formation of complex (**2**) represents the first reported addition of CH_2 to a Pt–Pt bond in a platinum complex. Only a few other broadly similar reactions of CH_2N_2 are known in transition metal chemistry.[5] Complexes containing $M_2(\mu\text{-}CH_2)$ bridging units are uncommon[6] and (**2**) is the first such platinum complex although related complexes $[Pt_2\{\mu\text{-}C(CF_3)_2\}(cod)_2]$ and $[Pt_2\{\mu\text{-}CH(CF_3)\}(cod)_2]$[7] (cod = cyclo-octadiene) are known.

Treatment of (**1**) in CH_2Cl_2 with a suspension of sulphur (at 20 °C) followed by filtration gives the sulphur-bridged complex (**3**) (80%) [ν(Pt–Cl) 286 cm^{-1}] and with an excess of SO_2 (at 20 °C) (**1**) gives the SO_2-bridged complex (**4**) (95%) [ν(Pt–Cl) 274; ν(SO_2)[4] 1148 and 1024; δ(SO_2) 555 cm^{-1}].† The CH_2 groups of the dppm ligands of (**2**)—(**4**), in contrast to those of (**1**), have two ^1H resonances [δ (CH_2): (**2**), 3·80 and 2·90 in $C_2D_2Cl_4$; (**3**), 4·89 and 2·77 in $C_2D_2Cl_4$; (**4**), 4·24 and 2·84 in CD_2Cl_2–$C_2D_2Cl_4$] with, in some cases, evidence of H–H, P–H, and Pt–H couplings. The non-equivalence of the two H atoms of the CH_2 groups is expected in the presence of an additional bridging group (see A).



(A)

A rather similar, but cationic, (SMe)-bridged hydride (**5**) [ν(Pt–H) 2152 cm^{-1}] is readily prepared (95% yield) from reaction of MeSH with the hydride comples[3] $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+[PF_6^-]$. Unlike the complexes above, (**5**) has two ^{31}P resonances [δ(P), 9·88 and 9·23 p.p.m.] at 40 °C in CD_2Cl_2 indicating that the Me group lies to one side of the $Pt_2(\mu\text{-}S)$ plane, lowering the symmetry and causing the two μ-dppm groups to become non-equivalent. Inversion at sulphur is however sufficiently rapid at 80 °C in $C_2D_2Cl_4$ for only one ^{31}P resonance [δ(P), 10·46 p.p.m.] to be observed (see A; X = SMe). The bridging nature of the SMe group is established by the presence of all five peaks of the 1 : 8 : 17 : 8 : 1 'diplatinum' pattern[1,3] in the ^1H resonance of the Me group [δ 2·38, ^3J(Pt-H) 24·6 Hz] and the Pt–H resonance is also observed [δ − 10·8, ^1J(Pt–H) 1152 Hz].

In contrast to the above reactions of (**1**), in which an additional bridging group is introduced, reactions (in CH_2Cl_2) with phosphines, ammonia, and pyridine yield stable dicationic platinum(I) complexes (**6**)—(**8**) by displacement of chloride ion. The CO complex (**9**) is best prepared indirectly *via* reaction of (**7**) (in CH_2Cl_2) with CO.

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† *Added in proof:* The palladium analogue of this μ-SO_2 complex has now been reported (L. S. Benner, M. M. Olmstead, H. Hope, and A. L. Balch, *J. Organometallic Chem.*, 1978, **153**, C31).

The CH_2 groups in complexes (**6**)—(**9**) have ^1H resonances similar to that of (**1**) and complexes (**7**)—(**9**) have ^{31}P n.m.r. spectra of the expected type, showing that all four phosphorus atoms are equivalent. Analysis of the ^{31}P n.m.r. spectra of complexes (**6**) reveals the presence of two resonances in the expected 1:2 ratio and additional coupling between the phosphorus atoms of the terminal and bridging groups.

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[1] M. P. Brown, R. J. Puddephatt, and M. Rashidi, *Inorg. Chim. Acta*, 1976, **19**, L33; M. P. Brown, R. J. Puddephatt, M. Rashidi, and K. R. Seddon, *J.C.S. Dalton*, 1977, 951.

[2] M. P. Brown, R. J. Puddephatt, M. Rashidi, Lj. Manojlović-Muir, K. W. Muir, T. Solomun, and K. R. Seddon, *Inorg. Chim. Acta*, 1977, **23**, L33.

[3] M. P. Brown, R. J. Puddephatt, M. Rashidi, and K. R. Seddon, *Inorg. Chim. Acta*, 1977, **23**, L27; *J.C.S. Dalton*, 1978, 516; *ibid.*, in the press.

[4] D. M. P. Mingos, *Transition Metal Chem.*, 1978, **3**, 1.

[5] W. A. Herrmann, C. Krüger, R. Goddard, and I. Bernal, *Angew. Chem.*, 1977, **89**, 342; W. A. Herrmann, B. Reiter, and H. Biersack, *J. Organometallic Chem.*, 1975, **97**, 245; R. B. Calvert and J. R. Shapley, *J. Amer. Chem. Soc.*, 1977, **99**, 5225.

[6] R. A. Anderson, R. A. Jones, G. Wilkinson, M. B. Hursthouse, and K. M. Abdul Malik, *J.C.S. Chem. Comm.*, 1977, 865.

[7] M. Green, A. Laguna, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 1010.