

## Mixed Palladium–Platinum Complexes with $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm)

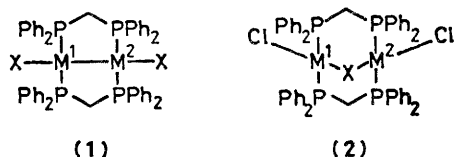
Paul G. Pringle and Bernard L. Shaw\*

*School of Chemistry, The University of Leeds, Leeds LS2 9JT, U.K.*

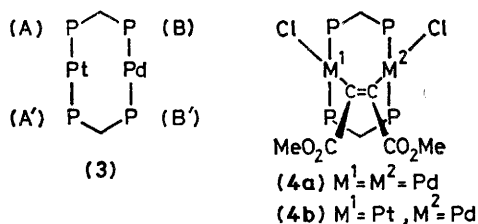
The first mixed palladium–platinum complexes with dppm, together with their ‘A-frame’ adducts with CO,  $\text{SO}_2$ , and  $\text{MeOCC}\equiv\text{CCOOMe}$ , are described.

There has been much recent interest in dipalladium and diplatinum complexes containing the diphosphine, bis-(diphenylphosphino)methane (dppm),<sup>1–7</sup> *e.g.* compounds such as (**1a**) and (**1b**), containing a metal–metal bond. Such bimetallic compounds can bind small molecules (X) *e.g.* CO,  $\text{SO}_2$ , or acetylenes, sometimes reversibly, to give ‘A-frame’

complexes, *e.g.* (**2a**).<sup>1</sup> A large number of dipalladium or diplatinum complexes of these and related types have been prepared<sup>1–7</sup> but, hitherto, mixed complexes containing one palladium and one platinum have not been described. We now report such compounds, which are remarkably stable to disproportionation.



- a;  $M^1 = M^2 = \text{Pd}$ ,  $X = \text{Cl}$       a;  $M^1 = M^2 = \text{Pt}$ ,  $X = \text{CO}$   
 b;  $M^1 = M^2 = \text{Pt}$ ,  $X = \text{Cl}$       b;  $M^1 = \text{Pt}$ ,  $M^2 = \text{Pd}$ ,  $X = \text{CO}$   
 c;  $M^1 = \text{Pt}$ ,  $M^2 = \text{Pd}$ ,  $X = \text{Cl}$     c;  $M^1 = \text{Pt}$ ,  $M^2 = \text{Pd}$ ,  $X = \text{SO}_2$   
 d;  $M^1 = \text{Pt}$ ,  $M^2 = \text{Pd}$ ,  $X = \text{Br}$       d;  $M^1 = \text{Pt}$ ,  $M^2 = \text{Pd}$ ,  
 e;  $M^1 = \text{Pt}$ ,  $M^2 = \text{Pd}$ ,  $X = \text{I}$          $X = \text{MeOCC}=\text{CCO}_2\text{Me}$   
 f;  $M^1 = \text{Pt}$ ,  $M^2 = \text{Pd}$ ,  $X = \text{SCN}$



We initially found an improved route to the dipalladium(I) complex (**1a**), which was to use the readily available  $\text{Pd}(\text{PPh}_3)_4$  as the source of palladium(0) and to treat it with the calculated proportions of dppm and  $[\text{PdCl}_2(\text{PhCN})_2]$  in benzene. This gave (**1a**) so readily (and in 80–90% yield), that it led us to attempt to make a mixed palladium–platinum complex. We therefore treated the deep-red benzene solution formed from  $[\text{Pd}(\text{PPh}_3)_4]$  and dppm with the labile platinum(II) complex  $[\text{PtCl}_2(\text{NCBu}^t)_2]$  in the calculated proportions. The mixed Pd–Pt complex (**1c**) crystallized out of the reaction mixture in excellent (90–95%) yield as orange microcrystals of the benzene solvate. Remarkably, this procedure gave the product in an analytically pure condition free from (**1a**) or (**1b**), as evidenced by the  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. spectrum. Characterizing data for (**1c**) include  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. [see (3)]  $\delta$  4.5 ( $P_A$ ) and  $-3.95$  ( $P_B$ ) p.p.m.,  $^1J(\text{Pt}-P_A)$  2922 Hz,  $^3J(\text{Pt}-P_B)$  78 Hz (in  $\text{CDCl}_3$ ), and  $\nu(\text{M}-\text{Cl})$   $249\text{ cm}^{-1}$  (Nujol), this value is the same as that reported for (**1a**)<sup>3</sup> and (**1b**).<sup>8</sup> Complex (**1c**) could be recrystallized from dichloromethane–hexane without disproportionation and is stable in dichloromethane solution for days at room temperature: in dichloromethane–ethanol solution it gradually decomposes to  $[\text{PdCl}_2(\text{dppm})]$  and  $[\text{PtCl}_2(\text{dppm})]$ . The terminal chlorines in (**1c**) are readily exchanged by metathesis with alkali-metal salts in acetone or acetonitrile giving the dibromide (**1d**), di-iodide (**1e**), and dithiocyanate (**1f**),

respectively, again without disproportionation. When carbon monoxide or sulphur dioxide was bubbled through a chloroform or dichloromethane solution of (**1c**), the adducts (**2b**) and (**2c**) were rapidly formed and readily isolated. Carbon monoxide is more strongly bound by (**1c**) than by the dipalladium analogue (**1a**) which loses its CO at ambient temperatures.<sup>3</sup> The platinum analogue loses CO from the solid at  $90^\circ\text{C}$  *in vacuo*. The mixed adduct (**2b**) loses CO to give (**1c**) on prolonged heating in chloroform and this is accompanied by some decomposition. However, we found that  $\text{SO}_2$  readily displaces CO from (**2b**) to give (**2c**) and that dinitrogen (or argon) displaces  $\text{SO}_2$  from (**2c**) to give (**1c**) *i.e.*  $\text{SO}_2$  ‘catalyses’ the reversible uptake of CO. It has been reported<sup>4</sup> that electronegative acetylenes such as  $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$  react with the dipalladium complex (**1a**) to give an adduct (**4a**). We similarly find that a dichloromethane solution of (**1c**) when treated with  $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$  gives the mixed adduct (**4b**), as a yellow microcrystalline precipitate, in 65% yield. We have been unable to make a hydride from (**1c**) and treatment with elemental sulphur gives a complex mixture of products.

The mixed Pd–Pt–dppm complexes discussed in this communication were characterized by elemental analysis (C, H, N, and halogen), molecular weight determination, i.r. spectroscopy, and particularly by  $^{31}\text{P}\{^1\text{H}\}$ ,  $^1\text{H}$ , and  $^1\text{H}\{^{31}\text{P}\}$  n.m.r. spectroscopy.

We thank Johnson Matthey Ltd. for the generous loan of platinum salts and the S.E.R.C. for support.

Received, 23rd October 1981; Com. 1246

## References

- M. P. Brown, R. J. Puddephatt, M. Rashidi, and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 1978, 1540.
- M. P. Brown, S. J. Cooper, A. A. Frew, L. Manojlović-Muir, K. W. Muir, R. J. Puddephatt, K. R. Seddon, and M. A. Thompson, *Inorg. Chem.*, 1981, **20**, 1500, and references therein.
- L. S. Benner and A. L. Balch, *J. Am. Chem. Soc.*, 1978, **100**, 6099.
- A. L. Balch, C. L. Lee, C. H. Lindsay, and M. M. Olmstead, *J. Organomet. Chem.*, 1979, **177**, C22.
- A. L. Balch, C. T. Hunt, C. L. Lee, M. M. Olmstead, and J. P. Farr, *J. Am. Chem. Soc.*, 1981, **103**, 3764.
- C. T. Hunt and A. L. Balch, *Inorg. Chem.*, 1981, **20**, 2267, and references therein.
- T. S. Cameron, P. A. Gardner, and K. R. Grundy, *J. Organomet. Chem.*, 1981, **212**, C19.
- M. P. Brown, R. J. Puddephatt, M. Rashidi, and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 1977, 951.