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Mixed Palladium–Platinum Complexes with Ph₂PCH₂PPh₂ (dppm)

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The first mixed palladium-platinum complexes with dppm, together with their 'A-frame' adducts with CO. SO_2 , and MeOOCC=CCOOMe, are described.

There has been much recent interest in dipalladium and diplatinum complexes containing the diphosphine, bis-(diphenylphosphino)methane (dppm),¹⁻⁷ e.g. compounds such as (1a) and (1b), containing a metal-metal bond. Such bimetallic compounds can bind small molecules (X) e.g. CO, SO_2 , or acetylenes, sometimes reversibly, to give 'A-frame'

complexes, e.g. (2a).¹ A large number of dipalladium or diplatinum complexes of these and related types have been prepared¹⁻⁷ 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.



We initially found an improved route to the dipalladium(I) complex (1a), which was to use the readily available $Pd(PPh_3)_4$ as the source of palladium(0) and to treat it with the calculated proportions of dppm and [PdCl₂(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 $[Pd(PPh_3)_4]$ and dppm with the labile platinum(II) complex $[PtCl_2(NCBu^{t})_2]$ 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 ${}^{31}P{}^{1}H$ n.m.r. spectrum. Characterizing data for (1c) include ³¹P {¹H} n.m.r. [see (3)] δ 4.5 (P_A) and $-3.95 (P_B)$ p.p.m., ${}^{1}J(Pt-P_A) 2922$ Hz, ${}^{3}J(Pt-P_B) 78$ Hz. (in CDCl₃), and ν (M–Cl) 249 cm⁻¹ (Nujol), this value is the same as that reported for (1a)³ and (1b).⁸ 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 [PdCl₂(dppm)] and [PtCl₂-(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),

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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.3 The platinum analogue loses CO from the solid at 90 °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 SO₂ readily displaces CO from (2b) to give (2c) and that dinitrogen (or argon) displaces SO_2 from (2c) to give (1c) *i.e.* SO_2 'catalyses' the reversible uptake of CO. It has been reported⁴ that electronegative acetylenes such as MeO₂CC=CCO₂Me react with the dipalladium complex (1a) to give an adduct (4a). We similarly find that a dichloromethane solution of (1c) when treated with $MeO_2CC = CCO_2Me$ 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 ${}^{31}P{}^{1}H$, ${}^{1}H$, and ${}^{1}H{}^{31}P{}$ n.m.r. spectroscopy.

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