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Bimetallic complexes supported by bis(diphenylphosphino)methane anti and syn to the Mn-Pd bonds

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We dedicate this paper to Prof. Pierre Braunstein for his pioneering contributions to the development of heterometallic science. His chemistry provided an inspiration for the work described in this paper

Abstract

Redox condensation of PPN[Mn₂(μ -PPh₂)(CO)₈] and PdCl₂(η^2 -dppm) gives bimetallic PdMn(μ -PPh₂)(μ -dppm)(CO)₃(PPh₃) (1) with an unexpected formation of PPh₃. The latter can be displaced when 1 reacts with free diphosphines (dppm, dppe, dppf) giving PdMn(μ -PPh₂)(μ -dppm)(CO)₃(Ph₂P-X-P(=O)Ph₂) (2, X=CH₂ (2a), C₂H₄ (2b), C₅H₄FeC₅H₄ (2c)) and [PdMn(CO)₃(μ -PPh₂)(μ -dppm)]₂(μ -Ph₂P-X-PPh₂) (3a). Complexes 2 are "A-frame"-type bimetallic complexes with an *syn*-dppm bridging the Mn-Pd bond. In contrast, complex 3a is a "double A-frame" *anti*-bridged by dppm. As a result, the latter is *trans* to the Mn-Pd bonds. Both types of dppm bridges are substitutionally inert. Either bridging role is best served by dppm (and not dppe or dppf). The structures of the complexes were derived from NMR analyses of all complexes and X-ray single-crystal diffraction analyses of 1, 2a and 2b. The common and stable "A-frame"-type core in these bimetallics provides a thermodynamic driving force for the opposite transmetallation migration of phosphide and phosphine (dppm) when 1 is formed. © 2003 Elsevier Science B.V. All rights reserved.

Keywords: Palladium; Manganese; Bimetallic; Heterometallic; Phosphine; Phosphide; Carbonyl; A-frame

1. Introduction

Considerable interest in heterometallic clusters is promoted by their potential applications in areas such as nanotechnology [1] and catalysis [2]. When two or more metal sites with different electronic properties are brought into a single entity, the synergic effect could lead to enhanced performance, e.g., in bifunctional catalysis [3]. A simple way to lock two metals within close proximity, with or without active M–M interaction, is through a diphosphine such as bis(diphenylphosphino)methane (dppm), e.g., in A-frame-type complexes with the [MM'(μ -dppm)₂] core [4]. The demonstrated catalytic activity of some Pd–dppm com-

plexes in the fixation of CO₂ in water-gas shift reaction [8] also provides an added impetus. Similar use of anionic bridges like phosphide $(-Ph_2P^-)$ is also effective [5]. Our interest and success in the cooperative use of these bridges are found in the assembly of some multimetallic complexes, e.g., [AuMn₂(CO)₈(µ-PPh₂)]₂-(μ -dppf), (P–P)AuMn₂(CO)₇(μ -PPh₂) (P–P = dppm, dppe, dppp, dppb, dppf) [6] and PdMn(µ-PPh₂)(CO)₄- $(\eta^2 - P - P)$ (P-P = dppm, dppe, dppf), Mn₂Pd₂Ag(μ -Cl) $(\mu$ -PPh₂)₂ $(\mu$ -dppm)(CO)₈ [7]. In this paper, we shall extend these ideas to examine the unique properties of dppm compared with other ligands in this family and subtle relationship of syn or anti bridging with respect to the M-M' bond. The syn dppm bridge strengthens the MM' entity whereas the anti one brings together two dimetal units in a process that marks the birth of a heterometal-metal bonded coordination polymer.

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2. Experimental

2.1. General procedures and materials

All reactions were performed under pure nitrogen using standard Schlenk techniques. $Mn_2(CO)_8(\mu-H)(\mu-PPh_2)$ [9] and $PPN[Mn_2(CO)_8(\mu-PPh_2)]$ [10] were prepared by literature methods. $PdCl_2(\eta^2-dppm)$ was prepared from $PdCl_2(CH_3CN)_2$ and dppm in CH_2Cl_2 . All other reagents were commercial products and were used as received. FT-IR spectra were recorded on a Perkin– Elmer 1600 spectrometer. All NMR spectra were recorded in CDCl₃ solution on a Bruker ACF 300 MHz spectrometer. ³¹P NMR chemical shifts were externally referenced to 85% H₃PO₄. Elemental analyses were performed by the analytic service of this department. Pre-coated silica TLC plates of layer thickness 0.25 mm were obtained from Merck or Baker.

2.2. X-ray crystallography

The diffraction experiments for samples 1, 2a and 2b were carried out on a Bruker AXS CCD diffractometer with a Mo K α ($\lambda = 0.71073$ Å). The program SMART [11] was used for collection of data frames, indexing reflection and determination of lattice parameters, SAINT [11] for integration of intensity of reflection and scaling, SADABS [12] for absorption correction and SHELXTL [13] for space group, and structure determination and refinements. In 2a, the dangling phosphine (P5) was partially oxidized with occupancy of oxygen (O4) fixed at 0.5. Complex 2b crystallized with half a molecule of acetone and half a molecule of water in the crystal lattice. Crystal data and refinement details are given in Tables 1 and 2.

2.3. Syntheses and characterization

2.3.1. $PdMn(\mu - PPh_2)(\mu - dppm)(CO)_3(PPh_3)$ (1)

To a suspension of $PdCl_2(\eta^2-dppm)$ (0.318 g, 0.56 mmol) in toluene (150 ml) was added PPN[Mn₂(CO)₈(μ -PPh₂)] (0.300 g, 0.28 mmol). The mixture was refluxed with vigorous stirring for 4 h, filtered, and stripped of solvent to give a reddish-brown residue, which was dissolved in a minimum amount of acetone, loaded onto silica TLC plates and eluted with acetone/hexane (3:7, v v⁻¹). The first major red band was removed and extracted with acetone to give 1 (yield: 31%). Careful recrystallization from acetone/hexane gave good crystals of **1**.

Anal. Calc. for 1: C, 64.67; H, 4.40. Found: C, 64.11; H, 4.33%. ³¹P NMR (δ): 12.3, 12.4, 13.2, 13.3, 14.0, 14.1, 14.8, 14.9 (ddd, P_C, trans ²J_{P-P_A} = 204 Hz, ²J_{P-P_D} = 101 Hz, cis ²J_{P-P_B} = 15 Hz); 15.9, 16.0, 16.1, 16.2, 16.4, 16.5 (ddd, P_B, cis ²J_{P-P_A} = 38 Hz, cis ²J_{P-P_C} = 15 Hz, ²J_{P-P_D} = 15 Hz); 69.8, 70.6 (d, br, P_D , $J_{P-P} = 95$ Hz); 186.5, 188.0 (d, br, P_A , $J_{P-P} = 209$ Hz). IR (CO, cm⁻¹): 1963 s, 1884 vs, 1723 s (solid KBr).

2.3.2. $PdMn(\mu - PPh_2)(\mu - dppm)(CO)_3(Ph_2PCH_2P(= O)Ph_2)$ (2a) and $[PdMn(\mu - PPh_2)(\mu - dppm)(CO)_3]_2(\mu - ppm)$ (3a)

To a red solution of $PdMn(\mu-PPh_2)(\mu-dppm)(CO)_3$ -(PPh₃) (**1**, 0.067 g, 0.062 mmol) in toluene (60 ml) was added dppm (0.012 g, 0.031 mmol). The mixture was then refluxed for 24 h. After filtration and removal of solvent under vacuum, the residue was coated onto TLC plates and eluted with acetone/hexane (3:7). The first red band was **1**. The following two bands were [PdMn(μ -PPh₂)(μ -dppm)(CO)₃]₂(μ -dppm) (**3a**) (yield: 41%) and PdMn(μ -PPh₂)(μ -dppm)(CO)₃(Ph₂PCH₂P(=O)Ph₂) (**2a**) (yield: 23%). Good red crystals of **2a** were grown in acetone/hexane mixture.

Anal. Calc. for **2a**: C, 64.24; H, 4.48. Found: C, 64.52; H, 4.57%. ³¹P NMR (δ): 3.5, 3.7, 3.8, 4.0, 4.1, 4.3 (ddd, P_D, *cis* ²J_{P-P_C} = 15 Hz, ²J_{P-P_E} = 30 Hz, *cis* ²J_{P-P_A} = 47 Hz); 12.6, 12.7, 13.4, 13.5, 14.2, 14.3, 15.1, 15.2 (ddd, P_C, *cis* ²J_{P-P_D} = 15 Hz, ²J_{P-P_B} = 103 Hz, *trans* ²J_{P-P_A} = 202 Hz); 23.8, 24.0 (d, P_E, ²J_{P-P_D} = 24 Hz); 71.0, 71.8 (d, br, P_B, J_{P-P} = 107 Hz); 184.7, 184.9, 186.2, 186.5 (dd, P_A, J_{P-P} = 35 Hz, *trans* ²J_{P-P_C} = 194 Hz). IR (CO, cm⁻¹): 1965 s, 1880 vs, 1858 vs.

Anal. Calc. for **3a**: C, 62.61; H, 4.30. Found: C, 63.41 H, 4.35%. ³¹P NMR (δ): -9.8 (s, P_D); 12.7, 13.5, 14.3, 15.2 (dd, P_C, J_{P-P} = 103 Hz, trans ²J_{P-P_A} = 202 Hz); 71.3, 72.1 (d, br, P_B, J_{P-P} = 100 Hz); 185.9, 187.6 (d, P_A, J_{P-P} = 206 Hz). IR (CO, cm⁻¹): 1964 s, 1890 vs, 1858 vs.

2.3.3. $PdMn(\mu - PPh_2)(\mu - dppm)(CO)_3(Ph_2PC_2H_4P(=O)Ph_2)$ (2b)

A similar procedure as in **2a** using $PdMn(\mu-PPh_2)(\mu-dppm)(CO)_3(PPh_3)$ (**1**, 0.116 g, 0.108 mmol) and dppe (0.022 g, 0.054 mmol) gave $PdMn(\mu-PPh_2)(\mu-dppm)(CO)_3(Ph_2PC_2H_4P(=O)Ph_2)$ (**2b**, yield: 46%). Good red crystals of **2b** were grown from $CH_2Cl_2/hexane mixture$.

Anal. Calc. for **2b**: C, 64.48; H, 4.59. Found: C, 64.52; H, 4.67%. ³¹P NMR (δ): 8.6, 8.8, 8.9, 9.0, 9.2, 9.3 (ddd, P_D, cis ²J_{P-P_C} = 19 Hz, ²J_{P-P_E} = 29 Hz, cis ²J_{P-P_A} = 45 Hz); 12.5, 13.4, 14.2, 15.0 (dd, P_C, J_{P-P} = 105 Hz, trans ²J_{P-P_A} = 200 Hz); 31.5, 31.9 (d, P_E, ²J_{P-P_D} = 53 Hz); 70.1, 70.8 (d, br, P_B, J_{P-P} = 95 Hz); 185.9, 187.7 (d, br, P_A, J_{P-P} = 213). IR (CO, cm⁻¹): 1963 s, 1882 vs, 1861 vs (solid KBr).

2.3.4. $PdMn(\mu - PPh_2)(\mu - dppm)(CO)_3(Ph_2PC_5H_4 - FeC_5H_4P(=O)Ph_2)$ (2c)

A similar procedure as in 2a using $PdMn(\mu-PPh_2)-(\mu-dppm)(CO)_3(PPh_3)$ (1, 0.054 g, 0.050 mmol) and

Table 1

Data collection and structure refinement of $PdMn(PPh_3)(CO)_3(\mu-PPh_2)(\mu-dppm)$ (1), $PdMn(Ph_2PCH_2P(=O)Ph_2)(CO)_3(\mu-PPh_2)(\mu-dppm)$ (2a) and $PdMn(Ph_2PC_2H_4P(=O)Ph_2)(CO)_3(\mu-PPh_2)(\mu-dppm)$ (2b)

	1 2a		$\mathbf{2b} \cdot [(CH_3)_2 CO]_{0.5} [H_2 O]_{0.5}$
Empirical formula	C ₅₈ H ₄₇ MnO ₃ P ₄ Pd	C ₆₅ H ₅₄ MnO _{3.5} P ₅ Pd	C _{67.5} H ₆₀ MnO ₅ P ₅ Pd
Formula weight	1077.18	1207.27	1267.34
Temperature (K)	223(2)	223(2)	223(2)
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/c$	Pbca	$P2_1/c$
Unit cell dimensions			
a (Å)	12.319(3)	11.9379(18)	14.6600(9)
b (Å)	22.284(5)	24.190(4)	17.6585(12)
c (Å)	18.065(4)	39.297(6)	25.2702(16)
α (°)	90	90	90
β (°)	92.765(6)	90	99.839(2)
γ (°)	90	90	90
V (Å ³)	4953.4(18)	11348(3)	6445.6(7)
Ζ	4	8	4
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.444	1.413	1.306
Absorption coefficient (mm^{-1})	0.792	0.728	0.646
Reflections collected	28598	63840	36951
Independent reflections	$8736 [R_{int} = 0.0688]$	9994 [$R_{\rm int} = 0.1112$]	11343 $[R_{int} = 0.0347]$
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0494, wR_2 = 0.1075$	$R_1 = 0.0495, wR_2 = 0.0970$	$R_1 = 0.0404, wR_2 = 0.1287$
R indices (all data)	$R_1 = 0.0837, wR_2 = 0.1196$	$R_1 = 0.0872, wR_2 = 0.1086$	$R_1 = 0.0494, wR_2 = 0.1346$

dppf (0.014 g, 0.025 mmol) gave $PdMn(\mu-PPh_2)-(\mu-dppm)(CO)_3(Ph_2PCH_2P(=O)Ph_2)$ (2c, yield: 38%).

Anal. Calc. for **2c**: C, 64.91; H, 4.42. Found: C, 65.17; H, 4.52%. ³¹P NMR (*δ*): 4.2, 4.6 (d, P_D, *J*_{P-P} = 38 Hz,);

11.9, 12.8, 13.6, 14.5 (dd, P_C , $J_{P-P} = 103$ Hz, *trans* ${}^{2}J_{P-P_A} = 204$ Hz); 28.6, 29.2 (d, P_E , ${}^{2}J_{P-P_D} = 73$ Hz); 69.2, 70.0 (d, br, P_B , $J_{P-P} = 96$ Hz); 185.6, 187.3 (d, br, P_A , $J_{P-P} = 206$). IR (CO, cm⁻¹): 1971 s, 1882 vs, 1869 vs (solid KBr).

Table 2

Selected bond length (Å) and angles (°) for 1, 2a and 2b

$MnPd(\mu-PPh_2)(\mu-dppm)(CO)_3(PPh_3), 1$								
Mn(1)-Pd(1)	2.7068(8)	Pd(1)-P(2)	2.3384(13)	Mn(1)-C (average)	1.803			
Mn(1) - P(1)	2.2224(14)	Pd(1)-P(3)	2.3056(13)					
Pd(1)-P(1)	2.2959(12)	Mn(1) - P(4)	2.2533(14)					
Mn(1) - P(1) - Pd(1)	73.59(4)	P(3)-Pd(1)-P(2)	105.14(5)	P(4)-Mn(1)-Pd(1)	97.44(4)			
Pd(1)-Mn(1)-P(1)	54.45(3)	P(1)-Pd(1)-P(2)	114.16(5)	P(1)-Mn(1)-P(4)	151.88(5)			
Mn(1) - Pd(1) - P(1)	51.96(4)	P(1)-Pd(1)-P(3)	140.65(5)	P(3)-C(12)-P(4)	109.3(2)			
Mn(1)-Pd(1)-P(3)	89.46(4)	Mn(1)-Pd(1)-P(2)	163.57(4)					
$MnPd(u-PPh_2)(u-dppm)(CO)_3(Ph_2PCH_2P(=O)Ph_3), 2a$								
Mn(1)-Pd(1)	2.6670(7)	Pd(1) - P(4)	2.3234(11)	Mn(1)-C (average)	1.814			
Mn(1)-P(1)	2.2166(13)	Pd(1)-P(3)	2.3031(11)	P(5)-O(4)	1.362(8)			
Pd(1) - P(1)	2.2958(11)	Mn(1) - P(2)	2.2361(13)					
Mn(1) - P(1) - Pd(1)	72.44(3)	P(3)-Pd(1)-P(4)	105.67(4)	P(2)-Mn(1)-Pd(1)	98.15(4)			
Pd(1)-Mn(1)-P(1)	55.15(3)	P(1)-Pd(1)-P(4)	111.59(4)	P(1)-Mn(1)-P(2)	153.18(5)			
Mn(1) - Pd(1) - P(1)	52.41(3)	P(1)-Pd(1)-P(3)	142.73(4)	P(3)-C(5)-P(2)	113.0(2)			
Mn(1)-Pd(1)-P(3)	91.20(3)	Mn(1) - Pd(1) - P(4)	158.94(3)					
$MnPd(u-PPh_2)(u-dppm)(CO)_3(Ph_2PC_2H_4P(=O)Ph_2), 2b$								
Mn(1)-Pd(1)	2.6610(5)	Pd(1) - P(4)	2.3202(8)	Mn(1)-C (average)	1.803			
Mn(1) - P(1)	2.2100(10)	Pd(1) - P(3)	2.3152(9)	P(5)-O(4)	1.482(3)			
Pd(1) - P(1)	2.2920(8)	Mn(1) - P(2)	2.2415(10)					
Mn(1) - P(1) - Pd(1)	72.44(3)	P(3)-Pd(1)-P(4)	104.40(3)	P(2)-Mn(1)-Pd(1)	97.92(3)			
Pd(1)-Mn(1)-P(1)	55.20(2)	P(1)-Pd(1)-P(4)	110.91(3)	P(1)-Mn(1)-P(2)	152.99(4)			
Mn(1) - Pd(1) - P(1)	52.36(2)	P(1)-Pd(1)-P(3)	144.56(3)	P(3)-C(6)-P(2)	112.63(18)			
Mn(1) - Pd(1) - P(3)	92.41(2)	Mn(1)-Pd(1)-P(4)	160.16(3)					

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3. Results and discussion

The decarbonylative condensation of $PdCl_2(\eta^2-dppm)$ and $PPN^+[Mn_2(CO)_8(\mu-PPh_2)]^-$ (2:1) in hot toluene gave a dinuclear bimetallic complex analyzed as $MnPd(CO)_3(PPh_3)(\mu-PPh_2)(\mu-dppm)$ (1) in 31% yield. Its ³¹P NMR spectrum (Fig. 1) is consistent with a dimetal structure that has a low symmetry; it shows four discrete resonances, corresponding to bridging phosphide (P_A), heterometallic-bridging phosphorus (P_D and P_C) and the Pd-bound phosphine (P_B). The magnitude of the *J*(PP) coupling of the two high-field resonances supports a *transoid* P_C-Pd-(μ -P_A) arrangement, with P_B *cis* to Pd-P_{A/C} bonds.

This reaction has three unusual features: (1) the condensation is not a simple cluster build-up process that results in a trinuclear $[PdMn_2]$ core even though there is a pre-existing Mn–Mn bond; (2) the phosphide has migrated from an Mn–Mn bridge to an Mn–Pd bridge, although the driving force is not obvious; (3) this is most surprising—there is a new PPh₃ ligand on Pd,

although there is no free or coordinated PPh_3 in the substrates or reaction system. These can be understood from the structural and mechanistic standpoints given below.

Formation of 1 is largely driven by the thermodynamic stability of its A-frame structure. During the process (Scheme 1), dppm and phosphide have swapped their metal hosts and, in doing so, release presumably a $[MnCl(CO)_4]$ entity. This oxidation of Mn from OS = 0to +1 serves as an internal reducing source for the reduction of Pd from formally +2 [in PdCl₂(dppm)] to +1 (in 1). This intramolecular redox behavior provides a driving force for the reaction and its product formation. Upon losing a dppm arm, the unsaturated Pd center regains its stability through the acquisition of a 2e donor ligand, which is best served by a ligand like PPh₃ [14]. We have discounted the possibility that PPN^+ is the source of PPh₃. Not only that PPh₃ on PPN^+ is kinetically stable, we also obtained 1 when $Na^{+}[Mn_{2}(CO)_{8}(\mu-PPh_{2})]^{-}$ was used as the substrate. The unexpected PPh₃ is hence traced to phosphide (-



Fig. 1. ${}^{31}P{}^{1}H$ NMR spectra of the title bimetallic complexes (1, 2a, 2b, 2c and 3a), illustrating the lack of symmetry and presence of chemically different phosphorus nuclei.



Scheme 1. Formation pathway of Pd-Mn bimetallic complexes by redox condensation.

PPh₂-), through a complex phenyl scrambling that is yet to be identified. The formation process could also lead to a by-product MnPd(μ -PPh₂)(CO)₄(η^2 -P-P) (1a), which we have described, albeit in low yield, in a condensation reaction between $PdCl_2(\eta^2-dppm)$ and $[Mn_2(CO)_8(PPh_2)]^-$ in the presence of AgNO₃ [7]. Complexes 1 and 1a are isoelectronic but not isostructural, since dppm is chelating in 1a but bridging in 1. Although it seems reasonable to suggest that 1 and 1a are synthetically interconvertible, we could not convert 1 to **1a** even upon heating and in the presence of excess CO. Nevertheless, the independent isolation of these two structural relatives in two different but related reactions suggests that the {MnPd} dimetal core is a thermodynamic sink in this type of condensation and that dppm has sufficient flexibility to stabilize even a much less stable "coordination isomer" (1a). When dppm is replaced by dppe or dppf, i.e., when $PdCl_2(\eta^2-dppe)$ or $PdCl_2(\eta^2-dppf)$ is the substrate in this condensation reaction, the major product is the dppe or dppf analogue of 1a. This illustrates further not only that dppe or dppf is more suited as a chelating ligand in this environment, but also the need to form PPh₃ to stabilize the Pd center is related to the departure of a phosphine arm on it.

Phosphine (PPh₃) displacement reactions of **1** with free diphosphines give the phosphine-oxide complexes $MnPd(\mu-PPh_2)(\mu-dppm)(CO)_3(Ph_2P-X-P(=O)Ph_2)$ $(X=CH_2$ (**2a**), C_2H_4 (**2b**), $C_5H_4FeC_5H_4$ (**2c**)) and an *anti*-bridged product, viz. [PdMn(μ -PPh_2)(μ -dppm)-(CO)_3]_2(μ -dppm) (**3a**) when the diphosphine used is dppm (Scheme 2). Complexes **2** are direct substitution products, but the dangling terminal phosphine is easily oxidized. Such easy oxidation for a dangling end of a monodentate diphosphine is known [15]. It is notable that the *anti*-bridged tetrametallic structure is only isolated when dppm is used as a ligand. This again shows that dppm is a particularly suitable bridge in multimetallic coordination network.

 31 P NMR spectra of **2** (Fig. 1) invariably show five discrete resonances, suggesting that all the phosphorus centers are chemically inequivalent. The downfield bridging phosphide resonance is broadened by neighbourse is



Scheme 2. Formation of *syn*-bridged bimetallic complexes 1 and 2a-2c, and *anti*-bridged 3a.

boring ⁵⁵Mn quadrupolar nucleus. The dppm bridge over the Mn–Pd bond occurs at ~70 ppm (P_B) and ~14 ppm (P_C). The diphosphine oxides contribute to the high-field resonances (P_D and P_E). Their coupling patterns are consistent with the proposed structures and length of the diphosphine backbone. ³¹P NMR spectrum of the *anti*-bridged product [PdMn(μ -PPh₂)(μ dppm)(CO)₃]₂(μ -dppm) (**3a**) shows four resonances (Fig. 1). Its P_{A/B/C} resonances are very similar to those of **1** and **2**, thus suggesting the retention of the [PdMn(μ -PPh₂)(μ -dppm)] core. The uniquely high-field P_D singlet points to the unique *anti*- and inter-M₂ role played by dppm in this inter-bridge arrangement. These signals are consistent with the structure proposed.

X-ray single-crystal diffractometric analyses of 1 (Fig. 2), **2a** (Fig. 3) and **2b** (Fig. 4) suggest that the solid-state structures are consistent with the solution structures proposed above. Essentially, they contain a heterometallic A-frame core with bridging dppm and phosphide,



Fig. 2. Molecular structure of $MnPd(\mu-PPh_2)(\mu-dppm)(CO)_3(PPh_3)$ (1) (ellipsoids at 50% probability level).

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Fig. 3. Molecular structure of $MnPd(\mu-PPh_2)(\mu-dppm)(CO)_3$ -(Ph₂PCH₂P(=O)Ph₂) (2a) (ellipsoids at 50% probability level).

phosphine on Pd and carbonyls on Mn. Both *anti*- and *syn*-bridges can be served only by dppm, which is not substitutionally labile, whereas the monodentate diphosphine is less sensitive towards the length of the backbone in diphosphine. The stability of this A-frame underpins the formation of all the complexes described. The length of the Mn-Pd bond [2.7068(8) Å in 1, 2.6670(7) Å in 2a and 2.6610(5) Å in 2b] is in agreement with other typical Mn-Pd bonds [16].

When the condensation of $PdCl_2(\eta^2-dppm)$ and $PPN[Mn_2(CO)_8(\mu-PPh_2)]$ is done in the presence of free diphosphines, the relative abundance of the bime-tallic species depends on the nature of the diphosphine. In the case of dppm, $PdMn(\mu-PPh_2)(\mu-dppm)(CO)_3$ -($Ph_2PCH_2P(=O)Ph_2$) (2a) and $[PdMn(\mu-PPh_2)(\mu-dpph_2)(\mu-d$

dppm)(CO)₃]₂(µ-ppm) (3a) are the only bimetallics obtained. The absence of 1 is understood since there is no longer a need to create a stabilizing source (PPh₃) when free dppm is present. In fact, excess dppm also could not result in the analogue of 1, viz. $MnPd(CO)_3(\eta^1-dppm)(\mu-PPh_2)(\mu-dppm)$, since such species would easily convert to 3a, which is isolated. Reaction with free dppe gives $MnPd(\mu-PPh_2)(CO)_4(\eta^2-\eta^2)$ dppe) [7] (major), which is the analogue of **1a**, as well as $PdMn(\mu-PPh_2)(\mu-dppm)(CO)_3(Ph_2PCH_2P(=O)Ph_2)$ (2a, major), and PdMn(µ-PPh₂)(µ-dppm)(CO)₃(Ph₂PC₂H₄P-(=O)Ph₂) (2b, major). Formation of the former highlights that dppe is more adapted than dppm as a chelating ligand in this environment. For dppf, $PdMn(\mu-PPh_2)(\mu-dppm)(CO)_3(Ph_3P)$ (1, minor), MnPd- $(\mu$ -PPh₂)(CO)₄(η ²-dppf) [7] (major), PdMn(μ -PPh₂)(μ $dppm)(CO)_3(Ph_2PCH_2P(=O)Ph_2)$ (2a, major), and $PdMn(\mu-PPh_2)(\mu-dppm)(CO)_3(Ph_2PC_5H_4FeC_5H_4P(=$ O)Ph₂) (2c, major) could be obtained. These consistently suggest that both syn and anti bridging positions are best served by dppm and that it is not substitutionally labile. The other diphosphines could, however, force their way to the chelating end or as monodentate diphosphine oxide.

The loss of a $[Mn(CO)_4]$ fragment, presumably in form of MnCl(CO)₄ or its derivative during the formation of **1**, is a blessing in disguise. Its departure is undesirable in a cluster build-up reaction, but it provides an internal mechanism for a redox condensation, which is the key to the formation of **1** and subsequently **2** and **3**. Eventually, this leads to the formation of a stable heterometallic Mn⁰-Pd¹ A-frame. This cleavage and departure of the Mn fragment was not observed in our similar work with the Au¹/Mn⁰ system. We attribute this



Fig. 4. Molecular structure of MnPd(µ-PPh₂)(µ-dppm)(CO)₃(Ph₂PC₂H₄P(=O)Ph₂) (2b) (ellipsoids at 50% probability level).

to the ease of reduction from Pd(II) to Pd(I), the stability of Pd(I)-based A-frame and the difficulty in the stabilization of Au(0)-Mn(0) systems. Our next venture is to test these ideas in the use of Pd(I) as starting substrates. They may behave very differently from the current Pd(II) substrate since reduction of Pd(I) to Pd(0) may not be achievable or desirable and the implication is that Mn cleavage may not be necessary. These could pave an alternative pathway for the formation of a different series of Pd–Mn clusters.

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