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Synthesis and Reactivity of Dinuclear Complexes Containing η^2-Phenyl−Metal Interactions. Crystal Structures of $[NBu_4][(C_6F_5)_3Pt\{\mu\text{-}Ph_2PCH_2PPh(\eta^2\text{-}Ph)\}Pt(C_6F_5)_2]$ and $[NBu_4][(C_6F_5)_3Pt(\mu\text{-}dppm)Pt(C_6F_5)_2(CO)]$

José M. Casas, Juan Forniés,* Francisco Martínez, Angel J. Rueda, and Milagros Tomás

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón,
Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain

Alan J. Welch

Department of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, U.K.

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Reaction between $[NBu_4][Pt(C_6F_5)_3(dppm\text{-}\kappa^1P)]$ and *cis*-$[M(C_6X_5)_2(thf)_2]$ (M = Pt, Pd; X = F, Cl; thf = tetrahydrofuran) leads to dinuclear derivatives with dppm ligands bridging two metal centers: $[NBu_4][(C_6F_5)_3Pt\{\mu\text{-}Ph_2PCH_2PPh(\eta^2\text{-}Ph)\}M(C_6X_5)_2]$ [X = F, M = Pt (**1**), M = Pd (**2**); X = Cl, M = Pt (**3**), M = Pd (**4**)]. The structural characterization of complex **1** by single-crystal X-ray diffraction (orthorhombic system, space group *Fdd*2, with $a = 26.520(7)$ Å, $b = 83.69(3)$ Å, $c = 13.835(5)$ Å, $V = 30706(11)$ Å^3, and $Z = 16$) reveals two square-planar platinum(II) fragments sharing a dppm ligand with a η^2-phenyl−platinum interaction between a phenyl ring of the dppm ligand and one platinum center. This weak η^2-phenyl−platinum interaction can be easily displaced by addition of ligands such as CO (giving complex **5**), PPh_3 (**6**), or *p*-toluidine (**7**). The structure of **5** was determined by single-crystal X-ray diffraction. It crystallizes in the monoclinic system, space group *Pn*, with $a = 12.259(2)$ Å, $b = 16.375(3)$ Å, $c = 18.851(4)$ Å, $\beta = 100.99(3)°$, $V = 3714.8$ Å^3, and $Z = 2$. The complex consists of two square-planar platinum(II) fragments with the dppm ligand acting as a conventional bridge.

Introduction

Bis(diphenylphosphino)methane (dppm) is a much-used ligand, mainly because of its ability to facilitate the synthesis of homo- or heterometallic polynuclear bridged complexes. The structure and flexibility of this phosphine make it adequately suited to bridge two metal centers which are involved in metal−metal bonds, although there exists a large number of complexes in which the dppm ligand bridges metal centers not involved in metal−metal interactions or acts as a chelating or monodentate ligand.[1−3]

In the course of our current research we are studying the basic properties of pentafluorophenyl-containing platinate complexes toward metal complexes or metal salts (M = Ag, Pb, Tl, Hg)[4] which should allow the formation of polynuclear complexes with Pt→M (donor−acceptor) bonds. In this context we considered it of interest to study the reaction between $[NBu_4][Pt(C_6F_5)_3(dppm\text{-}\kappa^1P)]$ and *cis*-$[M(C_6F_5)_2(thf)_2]$ with the aim of preparing binuclear complexes with Pt→M bonds based on the following ideas:

(a) $[NBu_4][Pt(C_6F_5)_3(dppm\text{-}\kappa^1P)]$ can function as a bidentate metalloligand with the P and Pt atoms acting as donors.

(b) *cis*-$[M(C_6X_5)_2(thf)_2]$ (M = Pt, Pd; X = F, Cl) are appropriate substrates with which to utilize the bidentate behavior of the above anionic platinum complex because of the well-documented lability of both thf ligands.[5] Assuming that both reagents react as expected, the reaction should give (eq 1) the dinuclear compounds having perpendicular metal coordination planes and a Pt→M donor−acceptor bond.[6]

This paper reports the results of such reactions. Binuclear compounds of the expected stoichiometry are produced, but without a Pt→M bond. Instead, a η^2-phenyl−Pt interaction results.

Experimental Section

General Methods. C, H, and N analyses were carried out with a Perkin-Elmer 240B microanalyzer. IR spectra were recorded over the 4000−200 cm^{-1} range on a Perkin-Elmer 883 spectrophotometer using Nujol mulls between polyethylene sheets. ^{1}H, ^{19}F, and ^{31}P NMR spectra

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at room temperature were recorded on a Varian XL-200 or a Unity-300 spectrometer in $CDCl_3$ or HDA solutions. ^1H, ^{19}F, and ^{31}P NMR spectra at low and variable temperature were recorded in CD_2Cl_2 solutions on a Brüker ARX-300 spectrometer, also the ^1H NMR and the COSY experiments at −40 °C were recorded on a Brüker DMX-500 spectrometer. Negative ion FAB mass spectra were recorded on a VG-Autospec spectrometer operating at ca. 30 kV, using the standard cesium ion FAB gun and 3-nitrobenzyl alcohol as matrix. $[NBu_4][Pt(C_6F_5)_3(dppm\text{-}\kappa^1P)]$,[7] *cis*-$[M(C_6F_5)_2(thf)_2]$ (M = Pd, Pt),[8] and dppm[9] were prepared as described elsewhere.

$[NBu_4][(C_6F_5)_3Pt\{\mu\text{-}Ph_2PCH_2PPh(\eta^2\text{-}Ph)\}Pt(C_6F_5)_2]$ (1). To a solution of $[NBu_4][Pt(C_6F_5)_3(dppm\text{-}\kappa^1P)]$ (0.400 g, 0.302 mmol) in CH_2Cl_2 (30 mL) was added *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (0.203 g, 0.302 mmol) (molar ratio 1:1). After 10 min stirring at room temperature, the solution was evaporated to dryness and the residue was treated with $CHCl_3$ (5 mL) and evaporated to dryness again. Upon addition of *n*-hexane (20 mL) and after 30 min of stirring a white solid (**1**) was obtained, which was filtered off and washed with *n*-hexane. Yield: 71%. Anal. Found (Calcd for $C_{71}H_{58}F_{25}N_1P_2Pt_2$): C, 45.19 (46.03); H, 3.11 (3.15); N, 0.72 (0.75).

FAB$^-$ MS: *m/z* 1609 $[Pt_2(C_6F_5)_5(dppm)]^-$. IR (cm^{-1}): C_6F_5 X-sensitive mode,[10] 804 m, 773 m; others, 1635 w, 1607 w, 1499 vs, 1058 s, 958 s; dppm: 696 m, 535 m, 513 m, 493 w. ^1H NMR room temperature ($CDCl_3$): δ 7.3 (br, 20H, aromatic), 3.6 (m, 2H, CH_2).^1H NMR (CD_2Cl_2, −40 °C): δ 9.48 (dd, 2H, *o*-H, Ph-b), 8.00 (dd, 2H, *o*-H, Ph-c), 7.86 (t-br, 1H, *m*-H, Ph-**a**), 7.74 (t, 1H, *p*-H, Ph-b), 7.64 (m, 5H, -*m*-H, Ph-b- and -*m*-H, Ph-c- and -*p*-H, Ph-c-), 7.17 (t, 1H, *p*-H, Ph-d), 7.12 (t, 1H, *o*-H, Ph-**a**), 6.83 (t, 2H, *m*-H, Ph-d), 6.77 (t, 1H, *o*-H, Ph-**a**), 6.74 (t, 1H, *o*-H, Ph-**a**), 6.13 (t, 1H, *m*-H, Ph-**a**), 6.08 (dd, 2H, *o*-H, Ph-d), 3.51 (m, 1H, $CH_{2)}$), 3.30 (m, 1H, CH_2). ^{19}F NMR ($CDCl_3$): δ −115.4 (m_c, 10F, *o*-F), −164.6 (br, 4F, *m*-F), −165.4 (br, 4F, *m*-F), −166.5 (br, 2F, *m*-F), −162.3 (t, 1F, *p*-F), −163.2 (t, 1F, *p*-F), −165.7 (m_c, 2F, *p*-F), −166.0 (t, 1F, *p*-F). ^{31}P NMR ($CDCl_3$): δ 22.4 [$^1J(^{195}Pt2,P2)$ = 2648 Hz], 26.2 [$^1J(^{195}Pt1,P1)$ = 2379 Hz].

$[NBu_4][(C_6F_5)_3Pt\{\mu\text{-}Ph_2PCH_2PPh(\eta^2\text{-}Ph)\}Pd(C_6F_5)_2]$ (2). To a solution of $[NBu_4][Pt(C_6F_5)_3(dppm\text{-}\kappa^1P)]$ (0.200 g, 0.151 mmol) in CH_2Cl_2 (15 mL) was added *cis*-$[Pd(C_6F_5)_2(thf)_2]$ (0.088 g, 0.151 mmol) (molar ratio 1:1). After 25 min of stirring at room temperature, the solution was evaporated to dryness and the residue was treated with $CHCl_3$ (5 mL) and evaporated to dryness again. Upon addition of *n*-hexane (20 mL) a white solid (**2**) was obtained, filtered off, and washed with *n*-hexane. Yield: 86%. Anal. Found (Calcd for $C_{71}H_{58}F_{25}N_1P_2PdPt$ with a $CHCl_3$ molecule): C, 45.27 (45.93); H, 3.14 (3.08); N, 0.74 (0.74).

FAB$^-$ MS: *m/z* 1521 $[PtPd(C_6F_5)_5(dppm)]^-$. IR (cm^{-1}): C_6F_5 X-sensitive mode,[10] 848 m, 800 m, 791 m; others, 1606 w, 1467 s, 1055 m, 958 s; dppm: 696 m, 535 m, 513 m, 493 w. ^1H NMR (CD_2Cl_2): δ 7.3 (br, 20H, aromatic), 3.4 (m, 2H, CH_2). ^{19}F NMR (CD_2Cl_2): δ −113.1 (br, 2F, *o*-F), −114.0 (br, 6F, *o*-F), −115.0 (br, 2F, *o*-F), −158.9 (t, 1F, *p*-F), −161.0 (t, 1F, *p*-F), −161.3 (m_c, 2F, *m*-F), −162.5 (m_c, 2F, *m*-F), −164.5 (br, 9F, 6 *m*-F + 3 *p*-F). ^{31}P NMR (CD_2Cl_2): δ 20.4 [$^1J(^{195}Pt,P)$ = 2648 Hz], 23.8.

$[NBu_4][(C_6F_5)_3Pt\{\mu\text{-}Ph_2PCH_2PPh(\eta^2\text{-}Ph)\}Pt(C_6Cl_5)_2]$ (3). To a solution of $[NBu_4][Pt(C_6F_5)_3(dppm\text{-}\kappa^1P)]$ (0.400 g, 0.302 mmol) in CH_2Cl_2 (30 mL) was added *cis*-$[Pt(C_6Cl_5)_2(thf)_2]$ (0.253 g, 0.302 mmol) (molar ratio 1:1). The solution quickly turned pale yellow. After 5 min stirring at room temperature, the solution was evaporated to dryness and the residue was treated with $CHCl_3$ (5 mL) and evaporated to dryness again. Upon addition of *n*-hexane and after 30 min of stirring (20 mL) a pale yellow solid (**3**) was obtained, filtered off, and washed with *n*-hexane. Yield: 94%. Anal. Found (Calcd for $C_{71}H_{58}Cl_{10}F_{15}N_1P_2Pt_2$): C, 42.65 (42.30); H, 2.72 (2.90); N, 0.69 (0.70).

FAB$^-$ MS: *m/z* 1773 $[Pt_2(C_6F_5)_3(C_6Cl_5)_2(dppm)]^-$. IR ($cm^{-1}$): C_6F_5 X-sensitive mode,[10] 835 m, 803 m; others, 1633 w, 1465 vs, 1057 s, 956 s; dppm, 694 m, 534 m, 516 m, 484 m. ^1H NMR ($CDCl_3$): δ 7.2 (br, 20H, aromatic), 3.2 (m, 2H, CH_2). ^{19}F NMR ($CDCl_3$): δ −116.2 (m_c, 6F, *o*-F), −166.4 (br, 9F, 6 *m*-F + 3 *p*-F). ^{31}P NMR ($CDCl_3$): δ 18.8 [$^1J(^{195}Pt,P)$ = 2685 Hz], 24.7 [$^1J(^{195}Pt,P)$ = 2195 Hz].

$[NBu_4][(C_6F_5)_3Pt\{\mu\text{-}Ph_2PCH_2PPh(\eta^2\text{-}Ph)\}Pd(C_6Cl_5)_2]$ (4). To a solution of $[NBu_4][Pt(C_6F_5)_3(dppm\text{-}\kappa^1P)]$ (0.200 g, 0.151 mmol) in CH_2Cl_2 (15 mL) was added *cis*-$[Pd(C_6Cl_5)_2(thf)_2]$ (0.113 g, 0.151 mmol) (molar ratio 1:1). After 5 min stirring at room temperature, the solution was evaporated to dryness and the residue was treated with $CHCl_3$ (5 mL) and evaporated to dryness again. Upon addition of *n*-hexane (20 mL) a pale yellow solid (**4**) was obtained, filtered off, and washed with *n*-hexane. Yield: 76%. Anal. Found (Calcd for $C_{71}H_{58}Cl_{10}F_{15}N_1P_2PdPt$): C, 44.07 (44.24); H, 2.93 (3.01); N, 0.75 (0.73).

IR (cm^{-1}): C_6F_5 X-sensitive mode,[10] 840 m, 823 m; others, 1633 w, 1467 vs, 1055 s, 957 s; dppm, 693 m, 536 w, 511 w, 485 w. ^1H NMR ($CDCl_3$): δ 7.2 (br, 20H, aromatic), 2.9 (m, 2H, CH_2). ^{19}F NMR ($CDCl_3$): δ −115.9 (br, 6F, *o*-F), −166.2 (br, 9F, 6 *m*-F + 3 *p*-F). ^{31}P NMR ($CDCl_3$): δ 20.2, 11.2 [$^1J(^{195}Pt,P)$ = 2602 Hz].

$[NBu_4][(C_6F_5)_3Pt(\mu\text{-}dppm)Pt(C_6F_5)_2(CO)]$ (5). A CH_2Cl_2 solution of $[NBu_4][Pt_2(C_6F_5)_5(dppm)]$ (**1**, 0.150 g, 0.081 mmol) was reacted with carbon monoxide. After 5 min of stirring at room temperature under a carbon monoxide atmosphere, the solution was evaporated to dryness and the residue was treated with *n*-hexane (20 mL) to render a white solid (**5**), which was filtered off. Yield: 79%. Anal. Found (Calcd for $C_{72}H_{58}F_{25}N_1O_1P_2Pt_2$): C, 45.80 (45.99); H, 3.20 (3.08); N, 0.90 (0.74).

FAB$^-$ MS: *m/z* 1637 $[Pt_2(C_6F_5)_5(dppm)(CO)]^-$. IR ($cm^{-1}$): C_6F_5 X-sensitive mode,[10] 794 m; others, 1636 w, 1607 w, 1498 s, 1465 vs, 1064 s, 956 s; dppm, 693 m, 534 m, 515 m, 483 m; ν(CO), 2109 s. ^1H NMR (acetone-d_6): δ 7.7 (m_c, 4H, aromatic), 7.3 (m_c, 4H, aromatic), 7.2 (m_c, 8H, aromatic), 7.0 (m_c, 4H, aromatic), 3.8 (m, 2H, CH_2). ^{19}F NMR (acetone-d_6): δ −116.2 [m_c, $^3J(^{195}Pt,F)$ = 332.1 Hz, 4F, *o*-F], −117.1 (br, 2F, *o*-F), −118.5 [m_c, $^3J(^{195}Pt,F)$ = 322.4 Hz, 2F, *o*-F], −119.5 [m_c, $^3J(^{195}Pt,F)$ = 349.8 Hz, 2F, *o*-F], −162.0 (m_c, 1F, *p*-F), −163.7 (m_c, 1F, *p*-F), −165.5 (m_c, 2F, *m*-F), −166.0 (m_c, 2F, *m*-F), −168.0 (m_c, 6F, 2 *p*-F + 4 *m*-F), −168.3 (m_c, 1F, *p*-F), −168.7 (m_c, 2F, *m*-F). ^{31}P NMR (acetone-d_6): δ 7.6 [$^1J(^{195}Pt,P)$ = 2611 Hz], 3.0 [$^1J(^{195}Pt,P)$ = 2194 Hz].

$[NBu_4][(C_6F_5)_3Pt(\mu\text{-}dppm)Pt(C_6F_5)_2(PPh_3)]$ (6). To a solution of $[NBu_4][Pt_2(C_6F_5)_5(dppm)]$ (**1**, 0.150 g, 0.081 mmol) in CH_2Cl_2 (30 mL) was added PPh_3 (0.021 g, 0.081 mmol) (molar ratio 1:1). After 15 min of stirring at room temperature, the solution was evaporated to dryness and the residue was treated with OEt_2 (20 mL) to render a white solid (**6**), which was filtered off. Yield: 76%. Anal. Found (Calcd for $C_{89}H_{73}F_{25}N_1P_3Pt_2$): C, 50.25 (50.55); H, 3.63 (3.48); N, 0.64 (0.66).

FAB$^-$ MS: *m/z* 1877 $[Pt_2(C_6F_5)_5(dppm)(PPh_3)]^-$. IR ($cm^{-1}$): C_6F_5 X-sensitive mode,[10] 848 m, 794 m; others, 1633 w, 1606 w, 1498 s, 1465 vs, 1098 s, 957 s; dppm, 697 m, 538 m, 509 m, 484 m; PPh_3, 743 m. ^1H NMR ($CDCl_3$): δ 7.0 (br, 35H, aromatic), 3.4 (br, 2H, CH_2). ^{19}F NMR ($CDCl_3$): δ −116.2 (br, 6F, *o*-F), −117.1 (br, 2F, *o*-F), −118.6 [br, $^3J(^{195}Pt,F)$ = 310.6 Hz, 2F, *o*-F], −162.0 (br, 1F, *p*-F), −163.0 (m_c, 2F, *m*-F), −164.0 (br, 1F, *p*-F), −164.7 (br, 2F, *m*-F), −166.4 (br, 9F, 3 *p*-F + 6 *m*-F). ^{31}P NMR ($CDCl_3$): δ 14.3 [$^1J(^{195}Pt,P)$ = 2430 Hz], 13.6 [$^1J(^{195}Pt,P)$ = 2642 Hz], 4.0 [$^1J(^{195}Pt,P)$ = 2317 Hz].

$[NBu_4][(C_6F_5)_3Pt(\mu\text{-}dppm)Pd(C_6F_5)_2(p\text{-}toluidine)]$ (7). To a solution of $[NBu_4][PtPd\ (C_6F_5)_5(dppm)]$ (**4**, 0.266 g, 0.151 mmol) in CH_2Cl_2 (30 mL) was added *p*-toluidine (0.016 g, 0.151 mmol) (molar ratio 1:1). After 1 h of stirring at room temperature, the solution was evaporated to dryness and the residue was treated with ^{i}PrOH (20 mL) to render a white solid (**7**), which was filtered off and washed with *n*-hexane. Yield: 71%. Anal. Found (Calcd for $C_{78}H_{67}F_{25}N_2P_2PdPt$): C, 50.18 (50.09); H, 4.03 (3.61); N, 1.64 (1.50).

IR (cm^{-1}): C_6F_5 X-sensitive mode,[10] 818 m, 785 m; others, 1636 w, 1608 w, 1499 s, 1463 vs, 1097 s, 957 s; dppm, 534 m, 498 m; *p*-tol, 3348 w. ^1H NMR ($CDCl_3$): δ 7.1 (m_c, 24H, aromatic), 3.4 (br, 2H, CH_2), 2.2 (br, 2H, NH_2), 1.6 (s, 3H, CH_3). ^{19}F NMR ($CDCl_3$): δ −116.0 (m_c, 10F, *o*-F), −166.0 (br, 15F, 5 *p*-F + 10 *m*-F). ^{31}P NMR ($CDCl_3$): δ 20.1, 7.3 [$^1J(^{195}Pt,P)$ = 2595 Hz].

Crystallographic Analysis of 1. Colorless crystals were grown by slow diffusion of *n*-hexane into a solution of **1** in chloroform at −30 °C. A representative crystal was selected and mounted on a Siemens/

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Table 1. Crystallographic Data for $[NBu_4][(C_6F_5)_3Pt\{\mu\text{-}Ph_2PCH_2PPh(\eta^2\text{-}Ph)\}Pt(C_6F_5)_2]$ (**1**) and $[NBu_4][(C_6F_5)_3Pt(\mu\text{-dppm})(C_6F_5)_2(CO)]\cdot 0.65CHCl_3$ (**5**)

	1	**5**
chem formula	$C_{71}H_{58}F_{25}N_1P_2Pt_2$	$C_{72.65}H_{58.65}Cl_{1.95}F_{25}N_1O_1P_2Pt_2$
fw	1852.3	1958.0
temp (°C)	25(1)	0(1)
wavelength (Å)	0.71073	0.71073
space group	*Fdd*2	*Pn*
unit cell dimens		
a (Å)	26.520(7)	12.259(2)
b (Å)	83.69(3)	16.375(3)
c (Å)	13.835(5)	18.851(4)
α (deg)	90	90
β (deg)	90	100.99(3)
γ (deg)	90	90
volume (Å^3)	30705(17)	3714.8(12)
Z	16	2
density (calcd) (Mg/m^3)	1.603	1.788
abs coeff (μ) (mm^{-1})	3.816	4.020
R indices [$I > 2\sigma(I)$][a]	$R = 0.0876$, $wR = 0.2074$	$R = 0.0338$, $wR = 0.0906$
final *R* indices (all data)	$R = 0.1726$, $wR = 0.2952$	$R = 0.0544$, $wR = 0.1042$

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. Goodness-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$; $w = 1/\sigma^2(F) + 0.001051F^2$.

STOE AED2 4-circle diffractometer. The basic crystallographic parameters for this complex are listed in Table 1. Data were collected at 298 K by the ω scan technique. Three standard reflections were measured after every 45 min of beam exposure during data collection, showing slow crystal decomposition. For this reason, a ψ scan correction was not applied. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares. All non-hydrogen atoms of the anion were assigned anisotropic displacement parameters The hydrogen atoms of the dppm ligand were omitted from the model. The NBu_4 cation is disordered over two positions with partial occupancies of 0.5. During refinement it was necessary to apply geometrical constraints to the C−C and C−N distances. All non-hydrogen atoms of the cation were assigned a common isotropic displacement parameter, and the hydrogen atoms were omitted from the model.

A difference map following the final refinement shows only three peaks with electronic density higher than 1 e Å^{-3}, which are located near the platinum atoms. The value of *R* (0.0876) is probably due not only to the partial decomposition of the crystal during data collection but also to problems arising from having a very long crystallographic axis [$b = 83.69(3)$ Å].

The data-to-parameter ratio in the final refinement was 4.5:1. The structure was refined on F_o^2, and all reflections were used in the least-squares calculations.

Crystallographic Analysis of $5\cdot 0.65CHCl_3$. A batch of colorless crystals of $5\cdot 0.65CHCl_3$ was grown by slow diffusion of *n*-hexane into a solution of **5** in chloroform at low temperature (−30 °C). A representative crystal was selected and mounted on an Enraf-Nonius CAD4 diffractometer fitted with a ULT1 low-temperature device (N_2 stream). The basic crystallographic parameters for this complex are listed in Table 1. Data were collected at 273 K. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares. After isotropic convergence an empirical absorption correction[11] was applied. All non-hydrogen atoms were assigned anisotropic displacement parameters. Aromatic hydrogen atoms were constrained to idealized geometries, and the isotropic displacement parameter of each of the hydrogen atoms was set to a value of 1.2 times the equivalent isotropic displacement parameter of its parent carbon atom. Seven atomic sites in an interstitial zone were modeled as two partially occupied disordered $CHCl_3$ molecules, sharing a common carbon atom. Each chlorine atom was disordered over two positions with partial occupancies of 0.50 and 0.15. Minor restraints were applied to the C−Cl distance and Cl−C−Cl angles. The hydrogen atoms of the NBu_4 cation and solvent molecule were omitted from the model.

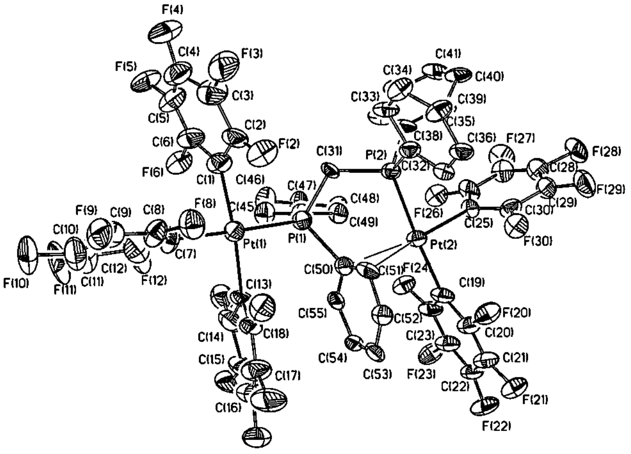

Figure 1. Perspective drawing of the $[(C_6F_5)_3Pt_2(\mu\text{-dppm})Pt(C_6F_5)_2]^-$ anion.

The data-to-parameter ratio in the final refinement was 5.5:1. The structure was refined on F_o^2, and all reflections were used in the least-squares calculations.

Programs and computers used and sources of scattering factors are given in refs 12 and 13.

Results and Discussion

As anticipated, the mononuclear complex $[NBu_4][Pt(C_6F_5)_3(dppm\text{-}\kappa^1P)]$ reacts with *cis*-$[M(C_6X_5)_2(thf)_2]$ [M = Pd, Pt and X = Cl, F] in CH_2Cl_2, yielding the corresponding dinuclear compounds of general formula $[NBu_4][(C_6F_5)_3Pt(\mu\text{-}Ph_2PCH_2PPh_2)M(C_6X_5)_2]$. Thus the reactions result in the displacement of the two thf molecules and formation of 1:1 adducts (eq 1).

$$[NBu_4][Pt(C_6F_5)_3(dppm\text{-}\kappa^1P)] + cis\text{-}[M(C_6X_5)_2(thf)_2] \rightarrow [NBu_4][(C_6F_5)_3Pt(\mu\text{-}Ph_2PCH_2PPh_2)M(C_6X_5)_2] + 2thf \quad (1)$$

$$M = Pd, Pt \text{ and } X = Cl, F$$

These reactions take place in good yields under mild conditions. To establish unequivocally the structure of these binuclear compounds, a crystallographic study of complex **1** was undertaken.

Molecular Structure of $[NBu_4][(C_6F_5)_3Pt\{\mu\text{-}Ph_2PCH_2PPh(\eta^2\text{-}Ph)\}Pt(C_6F_5)_2]$ (1). The structure of the complex anion is shown in Figure 1. Selected geometrical parameters are given in Table 2. The core of the anion contains two platinum centers which are 5.599 Å apart and bridged by the dppm ligand acting as a 6e$^-$ donor (2e$^-$ to Pt1, 4e$^-$ to Pt2) with one of the phenyl rings on P1 acting as a η^2-donor ligand. The platinum centers complete their coordination environments with three and two C_6F_5 groups, respectively. The Pt−C bond distances for the C_6F_5 groups range from 2.03(4) to 2.10(4) Å, while the Pt−C bond distances for the η^2-phenyl interaction are longer [Pt(2)−C(50) = 2.42(3) and Pt(2)−C(51) = 2.39(3) Å] and similar to the

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[11] DIFABS: Walker, N. G.; Stuart, D. *Acta Cystallogr., Sect. A* **1983**, *39*, 158.

[12] The X-ray diffraction data were processed on a Local Area VAX cluster (VMS V5.5-2) with the commercial package SHELXTL-PLUS Release 4.21/V, Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990.

[13] Sheldrick, G. M. *SHELXL-93*: FORTRAN-77 Program for the Refinement of Crystal Structures from Diffraction Data; University of Göttingen, 1993.

Table 2. Selected Bond Distances (Å) and Angles for the Complex $[NBu_4][Pt_2(C_6F_5)_5(\mu\text{-dppm})]$ (**1**)

Pt(1)−C(1)	2.10(4)	Pt(1)−C(13)	2.07(4)
Pt(1)−C(7)	2.06(4)	Pt(1)−P(1)	2.269(9)
Pt(2)−C(19)	2.03(4)	Pt(2)−C(25)	2.05(3)
Pt(2)−C(50)	2.42(3)	Pt(2)−C(51)	2.39(3)
Pt(2)−P(2)	2.273(9)	P(1)−C(31)	1.87(3)
P(2)−C(31)	1.83(3)	C(50)−C(51)	1.47(5)
C(50)−C(55)	1.39(5)	C(51)−C(52)	1.38(5)
C(52)−C(53)	1.39(5)	C(53)−C(54)	1.41(6)
C(54)−C(55)	1.44(5)		

C(7)−Pt(1)−C(1)	83(2)	C(7)−Pt(1)−C(13)	90(2)
C(1)−Pt(1)−P(1)	94.9(12)	C(13)−Pt(1)−P(1)	91.7(11)
C(19)−Pt(2)−C(25)	86.6(14)	C(25)−Pt(2)−P(2)	89.8(10)
C(50)−Pt(2)−P(2)	86.9(8)	C(51)−Pt(2)−P(2)	87.2(8)
C(55)−C(50)−C(51)	120(3)	C(50)−C(51)−C(52)	119(3)
C(51)−C(52)−C(53)	123(4)	C(52)−C(53)−C(54)	117(4)
C(53)−C(54)−C(55)	123(4)	C(54)−C(55)−C(50)	117(4)
P(1)−C(31)−P(2)	116(2)	C(19)−Pt(2)−C(51)	97.0(13)
C(19)−Pt(2)−C(50)	96.1(14)		

shortest distances found in other η^2-aryl−platinum interactions.[14] The Pt−P bond distances [Pt(1)−P(1) = 2.269(9) and Pt(2)−P(2) = 2.273(9) Å] are equal within experimental error.

The bond angles around each platinum center range from 83(2)° to 94.9(12)° for cis ligands and from 173(2)° to 178(1)° for trans ligands. The coordination planes of the platinum atoms form an angle of 7.0°. The P(1)−C(31)−P(2) angle is 116(2)°, and the phosphorus atoms are in slightly distorted tetrahedral environments. The C(50)−C(51) distance [1.47(5) Å] is similar to distances found in other platinum complexes containing η^2-aryl interactions.[14] The C−C distances of the phenyl ring involved in the η^2-phenyl interaction are equal within experimental error; that is, the aromaticity of the ring is maintained and this fact indicates that the η^2-phenyl interaction is very weak, as its subsequent reactivity confirms.

NMR spectroscopic data are in agreement with the solid-state structure. The ^{31}P NMR spectra (see Experimental Section) of the products show two signals for the two phosphorus atoms of the dppm ligand. One of these displays platinum satellites with a value of $^1J_{Pt-P}$ similar to that found in $[NBu_4][Pt(C_6F_5)_3(\text{dppm-}\kappa^1P)]$ ($^1J_{Pt-P}$: 2617 Hz), and hence we assigne it to the P atom bound to the $Pt(C_6F_5)_3$ fragment. The other signal, assigned to the other P atom, appears at different chemical shifts than in the starting material and, as expected, displays platinum satellites only in the Pt/Pt complexes (see Experimental Section), indicating the bridging behavior of the dppm. The room-temperature ^{1}H NMR spectra of **1**−**4** in $CDCl_3$ show a broad signal for the 20 aromatic protons and one multiplet for the two methylene protons, indicating a fluxional behavior of the phenyl rings at room temperature. Low-temperature measurements on complex **1** in CD_2Cl_2 on a 300 MHz spectrometer between −100 and −20 °C show two multiplets for the two methylene protons at 3.31 and 3.50 ppm and several signals in the range between 6 and 10 ppm, some of which were severely overlapped. To obtain a better separation between signals and allow their assignment, the ^{1}H NMR spectrum and the ^{1}H−^{1}H COSY at −40 °C were registered on a 500 MHz spectrometer. From these experiments five signals, each one corresponding to one proton, are identified as belonging to the phenyl group bonded to platinum (labeled −Ph-**a** in the Experimental Section), in agreement with a static η^2-phenyl-platinum interaction which makes the hydrogen atoms of this phenyl group nonequivalents at that temperature. Moreover three sets of three related signals with integrating ratios 2H:2H:1H are also observed, each set being due to one of the noninteracting phenyl rings (see Experimental Section Ph-b, Ph-c, Ph-d).The signals assigned to the ortho-hydrogens appear either as doublets of doublets or as pseudotriplets because in all cases the $^3J_{P-o-H}$ values are similar to the corresponding $^3J_{m-H-o-H}$. This latter point has been confirmed by ^{1}H{^{31}P} NMR experiments at −40 °C. The 2-H atom shows neither ^{195}Pt-satellites nor a significant upfield shift, as would be expected[15] for an η^2 coordination; however the presence of five resonances in the ^{1}H NMR spectrum of **1** at −40 °C due to the hydrogen atoms of the phenyl group η^2-coordinated to platinum confirms that this type of interaction is mantained in solution at that temperature.

Complexes containing η^2-arene−metal interactions are of current interest, because they have been proposed as intermediate species in the transition-metal-catalyzed hydrogenation of arenes[16] and in inter-[17,18] as well as in intramolecular[18,19] oxidative-addition processes of C(sp^2)−E bonds (E = H or F) to metal centers. The strength of the η^2-arene−metal interaction depends on the nature of both the arene and the complex fragment. However, this kind of interaction is usually weak and can easily be broken by reaction with other ligands.[20] A notable exception to this general trend concerns the $Os(NH_3)_5^{2+}$ fragment, which binds arenes so strongly that it behaves as a protecting group for the C=C double bond attached to it.[21]

The presence of η^2-arene−metal coordination has been

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Table 3. Selected Bond Distances (Å) and Angles for the Complex $[NBu_4][Pt_2(C_6F_5)_5(\mu\text{-dppm})(CO)]\cdot0.65CHCl_3$ (**5**)

Pt(1)−C(2)	2.06(2)	Pt(1)−C(14)	2.06(2)
Pt(1)−C(8)	2.07(2)	Pt(1)−P(1)	2.279(4)
Pt(2)−C(1)	1.90(2)	Pt(2)−C(20)	2.05(2)
Pt(2)−C(26)	2.09(2)	Pt(2)−P(2)	2.326(4)
P(1)−C(56)	1.82(2)	P(2)−C(56)	1.83(2)
O(1)−C(1)	1.14(2)		
C(2)−Pt(1)-C(14)	89.5(7)	C(2)−Pt(1)-C(8)	85.5(7)
C(14)−Pt(1)-P(1)	91.2(5)	C(8)−Pt(1)-P(1)	93.8(5)
C(1)−Pt(2)-C(26)	90.5(8)	C(20)−Pt(2)-C(26)	85.7(6)
C(1)−Pt(2)-P(2)	94.7(6)	C(20)−Pt(2)-P(2)	89.2(5)
P(1)−C(56)-P(2)	130.3(10)		

proposed prior to intramolecular C−H activation in the synthesis of cyclometalated complexes by metalation of arene rings of coordinated ligands. Jones and Feher inferred the existence of a η^2-arene intermediate in the C−H activation of $[(C_5Me_5)Rh(PMe_2CH_2C_6H_5)]$, producing the aryl-hydride derivative $[(C_5Me_5)Rh(PMe_2CH_2C_6H_4)H]$,[17] but the η^2-aryl−Rh complex could not be observed. Complex **1** shows an intramolecular η^2-phenyl−Pt interaction which can be regarded as the intermediate derivative in a intramolecular C−H activation process. However, the anticipated subsequent step of oxidative addition to afford the phenyl-hydride−Pt complex does not take place, and complex **1** is recovered unaltered after heating to reflux in toluene for half an hour. The study of the thermal stability of **1** by TGA (to check the possibility of an intramolecular C−H activation at higher temperatures) shows the expected weight loss corresponding to HC_6F_5 (the logical product of the reductive elimination) at temperatures very close to the decomposition temperature.

The weak character of the η^2-phenyl−Pt interaction suggests that these compounds are suitable precursors into which other ligands could be introduced, affording products which are also dinuclear. Thus dichloromethane solutions of **1** and **2** react, respectively, with monodentate ligands such as CO, PPh_3, and *p*-toluidine displacing the η^2-phenyl−metal interaction and yielding dinuclear compounds of general formula $[NBu_4][(C_6F_5)_3Pt(\mu\text{-dppm})M(C_6F_5)_2L]$ [M = Pt, L = CO **5**, PPh_3 **6**; M = Pd, L = *p*-tol **7**] (eq 2).

$$[NBu_4][(C_6F_5)_3Pt\{\mu\text{-}Ph_2PCH_2PPh(\eta^2\text{-}Ph)\}M(C_6F_5)_2] + L \rightarrow [NBu_4][(C_6F_5)_3Pt(\mu\text{-dppm})M(C_6F_5)_2L] \quad (2)$$

$$M = Pt \text{ and } L = CO, PPh_3$$

$$M = Pd \text{ and } L = p\text{-tol}$$

The new compounds have been characterized by elemental analyses and spectroscopic means (IR and NMR). The IR spectra show the typical absorption for the CO [$\nu(CO) = 2109\ cm^{-1}$], PPh_3, and *p*-toluidine [$\nu(NH) = 3348\ cm^{-1}$] ligands. The ^{31}P NMR spectra show for complex **5** two signals for the two P atoms of the dppm ligand with platinum satellites [$^1J(^{195}Pt,P) = 2611$ and 2194 Hz]; for complex **6** three signals, two for the P atoms of the dppm and the other for the P atom of the PPh_3, all of them with platinum satellites [$^1J(^{195}Pt,P) = 2642$, 2430, and 2317 Hz]; for complex **7** two signal for the phosphorus atoms of the dppm ligand but as expected only one with platinum satellites [$^1J(^{195}Pt,P) = 2595$ Hz].

In addition, the solid-state structure of **5** has been established by X-ray diffraction.

Crystal Structure of $[NBu_4][(C_6F_5)_3Pt(\mu\text{-dppm})Pt(C_6F_5)_2(CO)]$ (5). Selected geometrical parameters are given in Table 3. A thermal ellipsoid drawing of the structure of the complex anion appears as Figure 2.

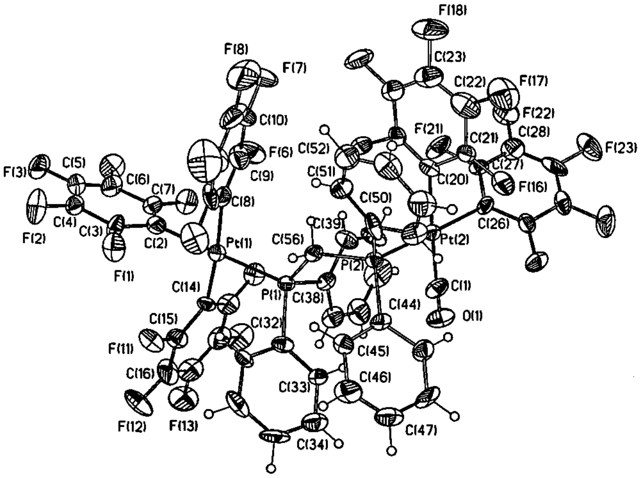
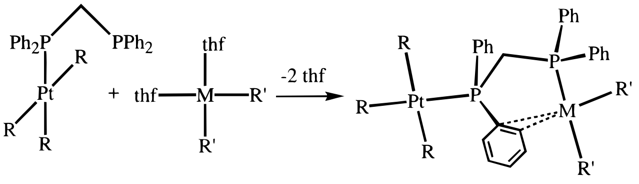


Figure 2. Perspective drawing of the $[(C_6F_5)_3Pt_2(\mu\text{-dppm})Pt(C_6F_5)_2(CO)]^-$ anion.

Scheme 1



M = Pd, Pt
R = C_6F_5
R' = C_6F_5, C_6Cl_5

1 M= Pt; R'= C_6F_5
2 M= Pd; R'= C_6F_5
3 M= Pt; R'= C_6Cl_5
4 M= Pd; R'= C_6Cl_5

Compound **5** is a homodinuclear species which contains two different platinum fragments ["$Pt(C_6F_5)_2(CO)$" and "$Pt(C_6F_5)_3$"] linked, through the platinum centers, by the P atoms of the bridging dppm ligand. Each platinum center is in a distorted square-planar environment, and the dihedral angle formed by the two coordination planes is 112.3°. The bond angles around each platinum center range from 85.5(7)° to 94.7(6)° for cis ligands and from 172.5(5)° to 179.0(5)° for trans ligands. The Pt−P bond distances [Pt(1)−P(1) = 2.279(4), Pt(2)−P(2) = 2.326(4) Å] are similar to distances found in other platinum complexes containing P-donor ligands.[14] The P(1)−C(56)−P(2) angle [130.3(10)°] is larger than that expected for sp^3 hybridization at the carbon atom, this value being the largest found for similar species containing the dppm ligand acting as a bridge between two metal centers.[22]

The C−O distance [1.14(2) Å] is similar to that found in other complexes containing CO terminal ligands.[23] The absence of the η^2-phenyl interaction in **5** makes the dppm ligand more flexible and allows a longer Pt(1)−Pt(2) distance (6.373 Å) than in **1**.

Conclusions

The reactions of $[NBu_4][Pt(C_6F_5)_3(\text{dppm-}\kappa^1P)]$ and *cis*-$[M(C_6X_5)_2(thf)_2]$ (M = Pt, Pd; X = F, Cl) proceed through the displacement of both thf groups and formation of the corresponding dinuclear complexes; see Scheme 1. The dppm ligand acts as a six-electron donor ligand with one of the phenyl groups

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[22] Data were retrieved from the Cambridge Structural Database. Allen, F. H.; Kennard, O. *Chem. Des. Automation News* **1993**, *8*, 1 and 31.

[23] Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

η^2-coordinated to one of the platinum centers. Obviously in such a situation the resulting compound is a 32-electron complex and no Pt→M bond is required. Since no steric hindrance seems to be the reason for the absence of a Pt→M bond in complex **1** (this would only require both platinum coordination planes to be perpendicular), the formation of the η^2-Pt−phenyl bond instead of the Pt→Pt bond has to be due to electronic preferences.

Acknowledgment. We thank Dr. Babil Menjón for helpful discussions, the Unitat de RMN D'Alt Camp (Universitat de Barcelona) for the measurement of NMR spectra at −40 °C in the Bruker DMX-500, and the Comisión Interministerial de Ciencia y Tecnología (Spain) for financial support (Project PB95-003-CO-1) and for a grant (to A.J.R.).

Supporting Information Available: Tables of crystallographic data and refinement parameters, atomic coordinates, full lists of bond distances and angles, anisotropic displacement parameters, and H atom coordinates for complexes $[NBu_4][(C_6F_5)_3Pt\{\mu\text{-}Ph_2PCH_2PPh(\eta^2\text{-}Ph)\}Pt(C_6F_5)_2]$ and $[NBu_4][(C_6F_5)_3Pt(\mu\text{-dppm})Pt(C_6F_5)_2(CO)]\cdot 0.65CHCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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