Unprecedented Formation of Dinuclear Platinum(II) Complexes with μ-Alkenylidene Bridging Ligands from Reactions of $Pt(dppm)_2Cl_2$ with Alkyl Acetylenes

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Summary: A new series of dinuclear platinum(II) complexes, [Pt_2(μ-dppm)(dppm-P,P′)(μ-C═CRPPh_2CH_2PPh_2-P)(C≡CR)]$^{2+}$ (R = alkyl), has been synthesized, and the structure of one of the complexes was confirmed by X-ray crystallography. A proposed mechanism to account for their formation from the corresponding alkynyl precursors is suggested. Their luminescence properties are also reported.

Introduction

Recently, extensive spectroscopic work has been performed on the homonuclear d^8−d^8 metal complexes. Spectroscopic behavior unique to the d^8−d^8 system with metal−metal interaction has been reported, and some of the complexes have been shown to exhibit interesting and rich photophysical and photochemical properties.[1] A common structure for dinuclear d^8−d^8 metal complexes, other than that of a face-to-face configuration, is the A-frame structure in which the metals are bridged by two neutral diphosphines or related groups occupying a *trans* orientation at each metal center, with a bridging group or atom at the apex of the A-frame.[2,3] Recently, we reported a generalized synthetic route for the preparation of dinuclear A-frame platinum(II) aryl alkynyl complexes.[4] In an attempt to synthesize an extended series of dinuclear platinum(II) alkynyl complexes with an A-frame motif using alkyl acetylides, a novel series of dinuclear platinum(II) complexes with bridging alkenylidene ligands was obtained instead through the unexpected reaction of alkyl acetylene with $Pt(dppm)_2Cl_2$ in the presence of mercury(II) acetate. Such a reaction represents the first of its kind and is quite different from the synthetic routes commonly employed for the preparation of bridging alkenylidene complexes.[5−7]

Reaction of $Pt(dppm)_2Cl_2$ with 2 equiv of mercury(II) acetate and alkyl acetylene in ethanol gave [Pt_2(μ-dppm)(dppm-P,P′)(μ-C═CRPPh_2CH_2PPh_2-P)(C≡CR)]-Cl_2, which could be isolated as the hexafluorophosphate salt via metathesis reaction to give [Pt_2(μ-dppm)(dppm-P,P′)(μ-C═CRPPh_2CH_2PPh_2-P)(C≡CR)][PF_6]$_2$ [R = $^nC_6H_{13}$ (**1**), $^nC_8H_{17}$ (**2**), $^nC_{10}H_{21}$ (**3**)]; after recrystallization from acetonitrile/diethyl ether, complexes **1**−**3** were obtained as yellow crystals. The newly synthesized complexes were characterized by ^{1}H NMR, FAB mass spectrometry, and FT-Raman and gave satisfactory elemental analyses.[8−10] The structure of **1** was confirmed by X-ray crystallography.[11]

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(8) **1** Anal. Calcd for $C_{91}H_{92}F_{12}P_8Pt_2\cdot CH_2Cl_2$: C, 51.71; H, 4.40. Found: C, 51.53; H, 4.22. ^{1}H NMR (acetone-d_6): δ 0.15−1.15 (m, 22H, −$CH_2(CH_2)_4CH_3$), 3.40 (m, 4H, −$CH_2(CH_2)_4CH_3$), 4.10−4.80 (m, 6H, PCH_2P), 6.40−8.90 (m, 60H, phenyl protons). Positive FAB-MS at *m/z*: 1905 {M − PF_6}$^+$.

(9) **2** Anal. Calcd for $C_{95}H_{100}F_{12}P_8Pt_2\cdot CH_2Cl_2$: C, 52.58; H, 4.66. Found: C, 52.88; H, 4.54. ^{1}H NMR (acetone-d_6): δ 0.25−1.15 (m, 30H, −$CH_2(CH_2)_6CH_3$), 3.40 (m, 4H, −$CH_2(CH_2)_6CH_3$), 4.15−5.10 (m, 6H, PCH_2P), 6.40−8.90 (m, 60H, phenyl protons). Positive FAB-MS at *m/z*: 1860 {M − 2PF_6}$^+$·MeCN.

(10) **3** Anal. Calcd for $C_{99}H_{108}F_{12}P_8Pt_2\cdot 1.75CH_2Cl_2$: C, 52.33; H, 4.82. Found: C, 52.36; H, 4.50. ^{1}H NMR (acetone-d_6): δ 0.80−1.30 (m, 38H, −$CH_2(CH_2)_8CH_3$), 3.50 (m, 4H, −$CH_2(CH_2)_8CH_3$), 4.10−4.80 (m, 6H, PCH_2P), 6.40−8.80 (m, 60H, phenyl protons). Positive FAB-MS at *m/z*: 1872 {M − 2PF_6}$^+$.

(11) X-ray data: **1**, $C_{91}H_{92}P_6Pt_2\cdot 2PF_6\cdot 2CH_3CN$, M_r = 2133.78, monoclinic, space group $P2_1/c$, a = 15.046(3), b = 25.272(3), c = 25.812(2) Å, β = 104.06(2)°, V = 9620(2) Å^3, Z = 4, F(000) = 4264, D_c = 1.4891 g cm^{-3}, T = 301 K, μ(Mo Kα) = 31.26 cm^{-1}; convergence for 902 variable parameters by least-squares refinement on F with $w = 4F_o^2/[\sigma^2(F_o^2) + (0.024F_o^2)^2]$ for 7973 reflections with $F_o > 3\sigma(F_o)$ was reached at R = 0.053 and R_w = 0.068 with a goodness-of-fit of 2.25.

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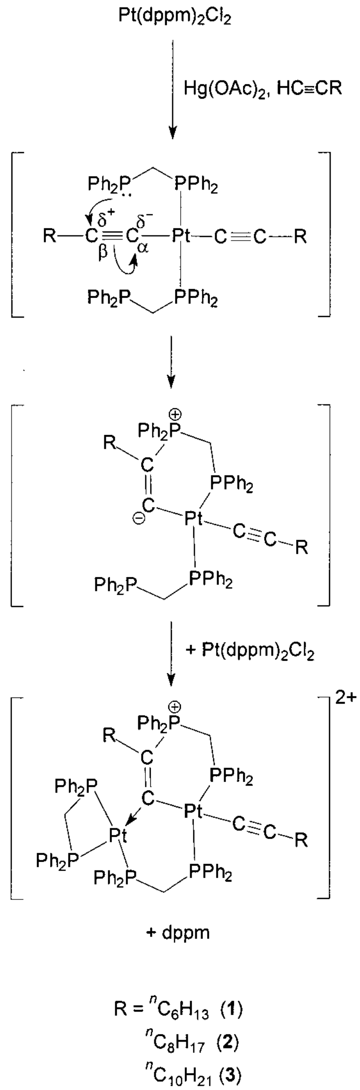
Scheme 1



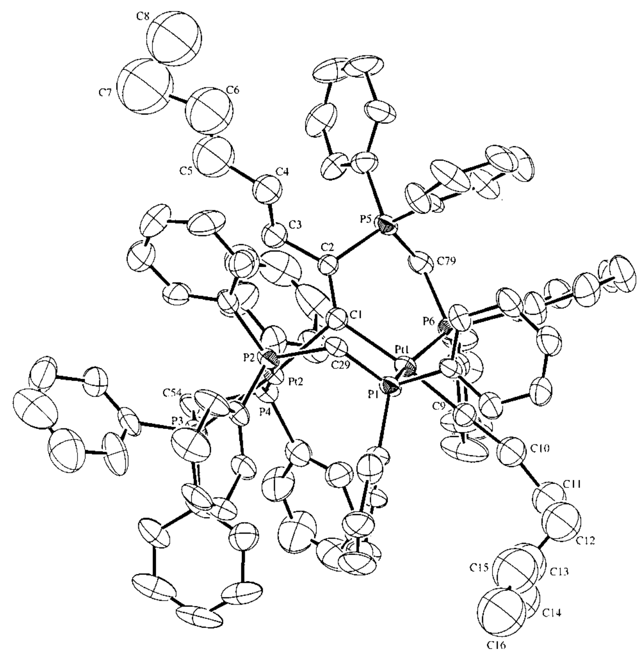


Figure 1. Perspective drawing of the complex cation **1** with atomic numbering scheme. Thermal ellipsoids were shown at the 40% probability level. Selected bond lengths (Å) and angles (deg): Pt(1)−P(1) 2.310(4), Pt(1)−C(1) 2.05(1), Pt(1)−P(6) 2.273(4), Pt(2)−C(1) 2.05(1), Pt(2)−P(2) 2.296(4), Pt(1)−C(9) 2.15(2), Pt(2)−P(3) 2.382(4), C(1)−C(2) 1.34(2), Pt(2)−P(4) 2.326(4), C(9)−C(10) 1.12(2), P(5)−C(2) 1.81(1), Pt(1)−C(1)−Pt(2) 104.5(6), C(1)−Pt(1)−C(9) 167.1(5), P(1)−Pt(1)−P(6), 156.2(1), Pt(1)−C(1)−C(2) 133(1), P(2)−Pt(2)−P(3) 102.9(1), Pt(2)−C(1)−C(2) 121(1), P(2)−Pt(2)−P(4) 172.5(1), Pt(1)−C(9)−C(10) 164(3), P(3)−Pt(2)−P(4) 70.8(1), P(1)−C(29)−P(2) 115.7(7), P(1)−Pt(1)−C(1) 93.6(4), P(3)−C(54)−P(4) 95.8(7), P(1)−Pt(1)−C(9) 88.4(4), P(5)−C(79)−P(6) 116.8(8), P(6)−Pt(1)−C(9) 86.6(4), C(1)−C(2)−C(3) 127(1), P(6)−Pt(1)−C(1) 96.5(4), C(9)−C(10)−C(11) 164(4), P(2)−Pt(2)−C(1) 90.9(4), P(5)−C(2)−C(1) 117(1), P(3)−Pt(2)−C(1) 164.8(4), Pt(1)−P(6)−C(79) 111.6(5), P(4)−Pt(2)−C(1) 94.9(4).

A plausible mechanism to account for the formation of this unusual class of platinum(II) μ-alkenylidene complexes has been proposed as shown in Scheme 1. It is likely that the mononuclear species [Pt(dppm-P)$_2$-(C≡CR)$_2$] was formed initially. Coordination of an alkyl acetylide to the metal center could transfer the nucleophilicity from C_β to C_α, as has been reported recently.[6b] Such polarization could also be made possible via the strong σ-donation of the terminally bound 1-alkynyl group *trans* to C_α on Pt_1. Electrophilic attack on the alkynyl C_β atom is charge controlled, while nucleophilic attack on C_α is frontier orbital controlled. Thus the C_β atom of the terminal 1-alkynyl group would readily be attacked by the uncoordinated phosphorus atom of a dppm ligand to form a stable six-membered ring with the Pt center. Further attack by the nucleophilic C_α atom onto a second molecule of $[Pt(P,P'\text{-dppm})_2]^{2+}$ followed by the loss of a dppm ligand gave **1**. The isolation of the dinuclear A-frame platinum(II) alkynyl complexes, $[Pt_2(\mu\text{-dppm})_2(\mu\text{-C≡CAr})(C≡CAr)_2]^+$ (Ar = aryl),[4] instead of the dinuclear platinum(II) μ-alkylidene complexes as in the present study when aryl acetylenes were used in place of alkyl acetylenes, may be a result of the differences in both the electronic and steric effects of aryl and alkyl acetylenes. A close scrutiny of the X-ray crystal structure of **1** would indicate that the formation of $[Pt_2(\mu\text{-dppm})(\text{dppm-}P,P')(\mu\text{-C=CArPPh}_2\text{CH}_2\text{PPh}_2\text{-P})(C≡CAr)]^{2+}$ is unlikely on steric grounds since the fitting of an aryl group between the chelating dppm ligand and the μ-C=CArPPh$_2$CH$_2$PPh$_2$-P moiety would be extremely sterically demanding.

Figure 1 shows the perspective view of the complex cation of **1** with atomic numbering. The structure of **1** consists of two platinum atoms bridged by one dppm ligand and a μ-C=C(^{n}C$_6$H$_{13}$)(PPh$_2$CH$_2$PPh$_2$−P) group. The bridging dppm ligand [P(1)−C(29)−P(2)] together with C(1) linked the two Pt atoms to form a six-membered $Pt_2P_2C_2$ ring in the twist boat conformation. The other dppm ligand [P(5)−C(79)−P(6)] bridges Pt-(1) and the −C=C^{n}C$_6$H$_{13}$ group, forming another six-membered PtP_2C_3 ring, with P(5) bonded to C(2) as a phosphonium ion. The remaining chelating dppm ligand [P(3)−C(54)−P(4)] is bonded to Pt(2), with a P(3)−Pt(2)−P(4) angle of 70.8(1)°, which is far from the square planar geometry expected at the Pt(2) center and is probably a result of the steric requirement of the dppm ligand. Although the Pt···Pt distance (3.2427(8) Å) is significantly longer than that found in $[Pt_2(P_2H_2O_5)_4]^{4-}$ (2.925(1) Å),[12] there is still indication of weak Pt···Pt interactions, as the bond separation is still within the

Table 1. Electronic Absorption, Emission, and FT-Raman Data for Complexes 1−3

Complex	Medium (T/K)	Absorption λ_{abs}/nm (ϵ/dm^3 mol^{-1} cm^{-1})	Emission λ_{em}/nm	ν(C≡C) /cm^{-1}	ν(C=C) /cm^{-1}
1	CH_3CN (298)	274 (21170), 336 (10250), 396 (6010)	*a*	2138	1588
	solid (77)		709		
	glass[b] (77)		661		
2	CH_3CN (298)	278 (18750), 336 (10900), 396 (6510)	*a*	2131	1587
	solid (77)		649		
	glass[b] (77)		670		
3	CH_3CN (298)	278 (21950), 336 (9400), 392 (5800)	*a*	2128	1588
	solid (77)		652		
	glass[b] (77)		660		

[a] Not emissive. [b] EtOH−MeOH (4:1, v/v).

range of the sum of van der Waals radii for Pt.[13] The Pt(1)−C(1) and Pt(2)−C(1) distances are identical (2.05(1) Å) and are within the range 1.99−2.15 Å generally observed for platinum−carbon σ bonds,[14] such that the two metal centers are symmetrically bridged by the $-C{=}C(^nC_6H_{13})\{PPh_2CH_2PPh_2\}$ group in a μ_2-arrangement. The C(1)−C(2) distance of 1.34(2) Å is close to the bond length for a normal C=C bond,[15] as is expected of an alkylidene group formed by the nucleophilic attack of the Pt−C≡C bond by the phosphorus atom of the dppm ligand, as proposed in Scheme 1. The Pt−P distances, in the range of 2.273(4)−2.382(4) Å, are normal and are similar to other reported Pt−P distances.[16] The terminal acetylide ligand is found to slightly deviate from linearity, with a Pt(1)−C(9)−C(10) angle of 164(3)° and a C(9)−C(10) distance of 1.12 Å.

The FT-Raman data of complexes **1**−**3** are shown in Table 1. The terminal acetylide group shows a ν(C≡C) stretching frequency at ca. 2130−2140 cm^{-1}, while the μ-alkenylidene group shows an intense ν(C=C) stretch at ca. 1590 cm^{-1}, which is at a lower frequency than that of free alkenylenic ν(C=C) stretch (ca. 1700 cm^{-1}). Indeed, the low ν(C=C) stretching frequency is not unusual, since similar stretching frequencies have been observed in the related $[Pt_2(CCl{=}CHCF_3)_2(PEt_3)_2]$, in which two bands were observed at 1598 and 1586 cm^{-1} in the IR spectrum.[17]

The electronic absorption spectra of complexes **1**−**3** show intense bands at ca. 278, 336, and 396 nm in acetonitrile. The photophysical data of complexes **1**−**3** are summarized in Table 1. In view of the close resemblance of the high-energy absorption band at 274−278 nm to that of the free dppm ligand, an assignment of the high-energy absorption as a dppm ligand-centered absorption is suggested. The band at 336 nm, which is at an energy similar to that of $[Pt(dppm\text{-}P)_2(C{\equiv}C^tBu)_2]$[18] and $[Pt(PEt_3)_2(C{\equiv}CH)_2]$[19] and at slightly higher energy than that of $[Pt(dppm\text{-}P)_2(C{\equiv}CPh)_2]$[18] and $[Pt(PEt_3)_2(C{\equiv}CPh)_2]$,[19] is assigned as a Pt-to-acetylide metal-to-ligand charge transfer (MLCT) transition, similar to that observed in the mononuclear alkynylplatinum(II) phosphine system. The low-energy absorption at 392−396 nm, which is absent in the mononuclear $[Pt(dppm\text{-}P)_2(C{\equiv}CR)_2]$ and $[Pt(PEt_3)_2(C{\equiv}CR)_2]$ complexes, is unique to the dinuclear Pt(II) μ-alkylidene system. With reference to previous spectroscopic studies on a related $[Pt_2(\mu\text{-}C{=}CHPh)(C{\equiv}CPh)(PEt_3)_4]^+$,[20] the low-energy absorption is tentatively assigned to a platinum-to-μ-alkenylidene MLCT transition, modified by weak metal−metal interaction, or a Pt_2-to-μ-alkylidene metal−metal bond-to-ligand charge transfer (MMLCT) transition. The lower absorption energy of the metal-to-μ-alkylidene than metal-to-acetylide MLCT transition is in line with the better π-accepting ability of the phosphonium-substituted bridging alkylidene ligand than the terminal acetylide group.

Excitation of complexes **1**−**3** at $\lambda > 350$ nm at 77 K in ethanol/methanol (4:1 v/v) glass produces bright red-orange emission centered at ca. 660−670 nm. With reference to previous spectroscopic work on the related $[Pt_2(\mu\text{-}C{=}CHPh)(C{\equiv}CPh)(PEt_3)_3Cl]$[20] and the close resemblance of their emission energies, the emission was assigned as derived from a spin-forbidden Pt_2-to-alkenylidene charge transfer (MMLCT) triplet origin. The excitation spectra exhibit excitation maxima at ca. 330 and 390 nm, which match closely with the absorption maxima of the corresponding complexes, supporting an assignment of the emission origin as derived from states of a Pt_2-to-alkenylidene charge transfer (MMLCT) character.

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Supporting Information Available: Tables of atomic coordinates, thermal parameters, bond lengths and angles, and structure factors of **1** are deposited. This material is available free of charge via the Internet at http://pubs.acs.org.

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