Preliminary Communication

Unusual stabilization of cationic "M(η^3-allyl)$^{+n}$ (M = Pt, Pd) units by a dianionic *cis*-{$Pt(C_6F_5)_2(C{\equiv}CSiMe_3)_2\}^{2-}$ fragment

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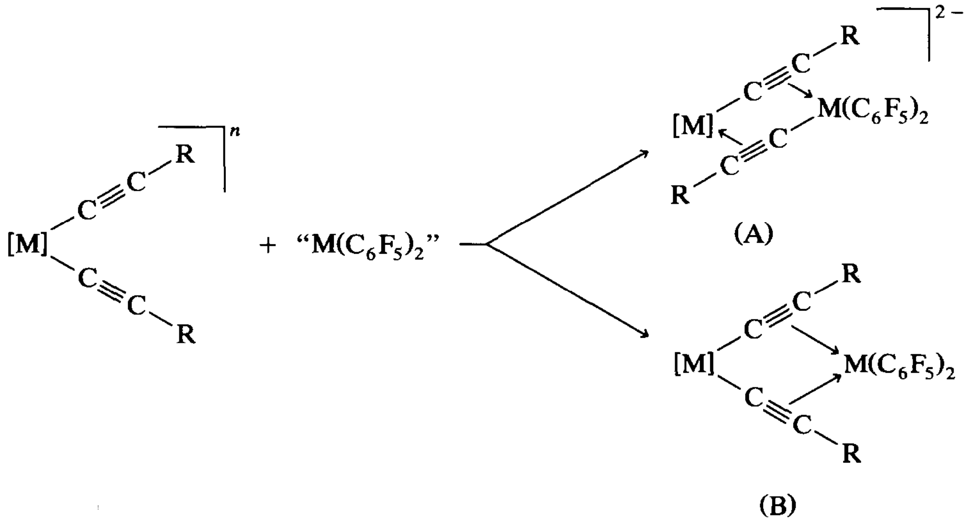
Abstract

Chloride abstraction from $[\{M(\eta^3-C_3H_5)Cl\}_n]$ (M = Pt, n = 4 or M = Pd, n = 2) by $(NBu_4)_2$[*cis*-$Pt(C_6F_5)_2(C{\equiv}CSiMe_3)_2$] (**1**) gives rise to novel homo- and hetero-dinuclear zwitterionic derivatives (NBu_4)[{*cis*-$Pt(C_6F_5)_2(C{\equiv}CSiMe_3)_2\}M(\eta^3$-$C_3H_5)$] (M = Pt **2**; M = Pd **3**) which are formed by a M(η^3-allyl)$^+$ unit attached to both alkynyl ligands of the {*cis*-$Pt(C_6F_5)_2(C{\equiv}CSiMe_3)_2\}^{2-}$ fragment. The structure of **3** has been established by X-ray diffraction.

Key words: Platinum; Palladium; X-ray structure; Alkynyl; Pentafluorophenyl; Dinuclear

Organometallic complexes with hydrocarbon bridges are of interest since they provide useful models for species thought to be present in heterogeneous catalytic reactions and on metal surfaces [1]. We [2] and others [3] have successfully used bis(σ-alkynyl) compounds to prepare homo- and hetero-dinuclear doubly alkynyl bridging complexes, and different reaction pathways have been observed depending on the bis(σ-alkynyl) derivative used [2,3]. Recently we have described the reaction between [*cis*-$Pt(C_6F_5)_2(THF)_2$] (M = Pt, or Pd; THF = tetrahydrofuran) and [*cis*-$Pt(C_6F_5)_2(C{\equiv}CR)_2]^{2-}$ which results in anionic complexes $[(C_6F_5)_2Pt(\mu$-$C{\equiv}CR)_2M(C_6F_5)_2]^{2-}$ (Scheme 1, A) through alkynyl transfer, and these complexes were suggested to be formed via intermediate polar species $[\{(C_6F_5)_2Pt(C{\equiv}CR)_2\}M(C_6F_5)_2]^{2-}$ (Scheme 1, B) that subsequently transfer one alkynyl group from one metal to the other, forming the less polar final complexes (Scheme 1, type A) [2a].

In this communication we report on the reactions of $(NBu_4)_2$[*cis*-$Pt(C_6F_5)_2(C{\equiv}CSiMe_3)_2$] **1** [4*] with $[M(C_3H_5)Cl]_n$ (M = Pt, n = 4; M = Pd, n = 2) which form novel homo- or hetero-dinuclear anionic derivatives (NBu_4)[{*cis*-$Pt(C_6F_5)_2(C{\equiv}CSiMe_3)_2\}M(\eta^3$-$C_3H_5)$]



[M] = PtL_2 (L_2 = 2 PPh_3; dppe, COD), n = 0; $Pt(C_6F_5)_2$, n = −2 [2a]
M = Pt, Pd

Scheme 1.

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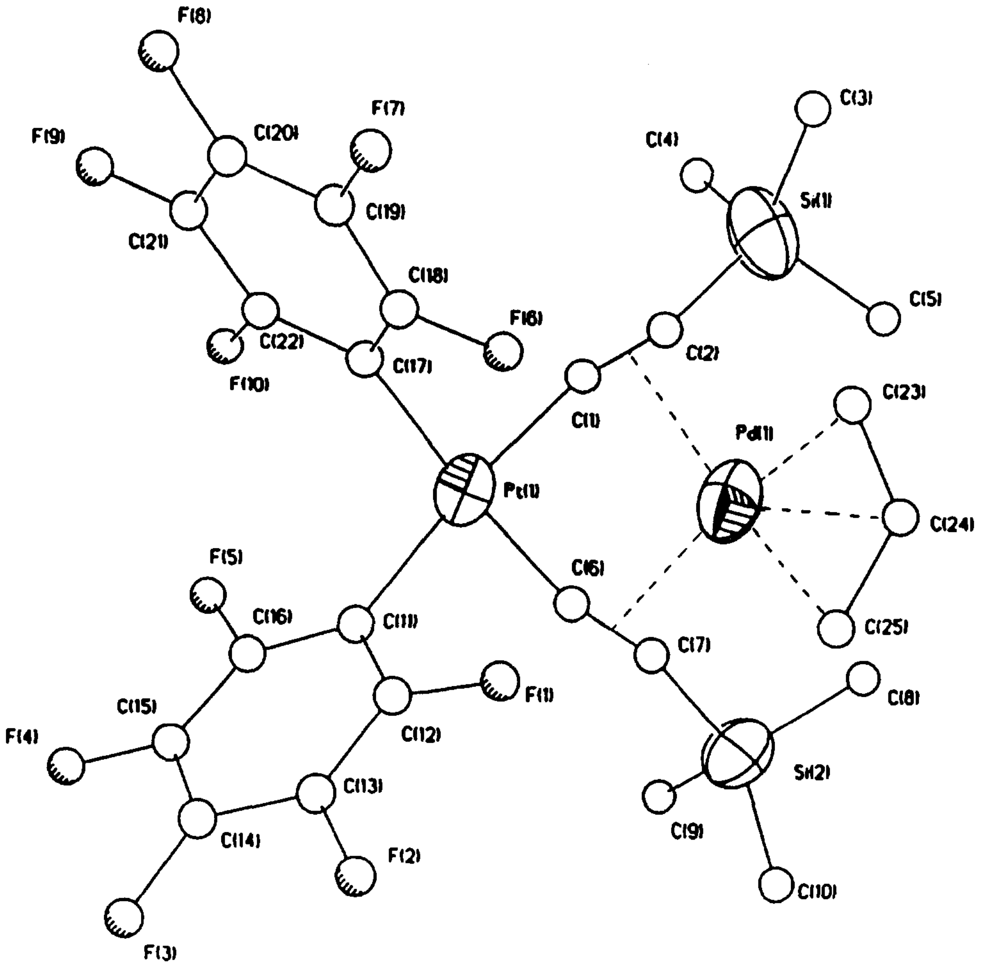

Fig. 1. View of the structure of the anion $[\{Pt(C_6F_5)_2(C{\equiv}CSiMe_3)_2\}Pd(\eta^3\text{-}C_3H_5)]^-$ in complex 3 with the atomic numbering scheme. Selected bond lengths (Å) and angles (°). Pt(1)–C(1) 2.031(17), Pt(1)–C(6) 1.986(18), Pt(1)–C(11) 2.070(16), Pt(1)–C(17) 2.078(16), C(1)–C(2) 1.201(25), C(6)–C(7) 1.238(27), Pd(1)–C(1) 2.279(17), Pd(1)–C(2) 2.357(19), Pd(1)–C(6) 2.289(18), Pd(1)–C(7) 2.349(20), Pd(1)–C(23) 2.119(27), Pd(1)–C(24) 2.100(26), Pd(1)–C(25) 2.149(26), Pt(1)–Pd(1) 3.049(2), C(1)–Pt(1)–C(6) 81.8(7), Pt(1)–C(1)–C(2) 167.7(16), C(1)–C(2)–Si(1) 167.4(17), Pt(1)–C(6)–C(7) 167.6(16), C(6)–C(7)–Si(2) 165.5(18).

(M = Pt **2**; M = Pd **3**). The formation of complexes **2** and **3** is very unusual since they are highly polar anionic species (formally zwitterionic) in which the dianionic $\{cis\text{-}Pt(C_6F_5)_2(C{\equiv}CSiMe_3)_2\}^{2-}$ chelates a cationic $[M(\eta^3\text{-allyl})]^+$ fragment. In spite of this no alkynylation processes have been observed in these reactions and no complexes of type A (with one acetylide σ-bonded to each metal) have been formed. Furthermore, the formation of dinuclear organometallic complexes with such different ligands is also very rare [7].

The reaction of $(NBu_4)_2[cis\text{-}Pt(C_6F_5)_2(C{\equiv}CSiMe_3)_2]$ (**1**) with $[\{Pt(C_3H_5)Cl\}_4]$ in a 4:1 molar ratio in acetone affords **2** [8a*] as a white crystalline solid. Similarly, the reaction of $(NBu_4)_2[cis\text{-}Pt(C_6F_5)_2(C{\equiv}CSiMe_3)_2]$ with $[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]$ in a 2:1 molar ratio affords complex **3** as a yellow microcrystalline solid [8b]. Both processes are summarized in eqn. (1).

$$n(NBu_4)_2[Pt(C_6F_5)_2(C{\equiv}CSiMe_3)_2]+[\{M(C_3H_5)Cl\}_n] \xrightarrow[M = Pt,\ n = 4;\ M = Pd,\ n = 2]{} n(NBu_4)[\{Pt(C_6F_5)_2(C{\equiv}CSiMe_3)_2\}M(\eta^3-C_3H_5)]+n(NBu_4)Cl \qquad (1)$$

Satisfactory analytical and conductivity data [8*] are obtained for **2** and **3**. The ^1H and ^{19}F NMR spectra of each complex at room temperature shows that in solution both the C_6F_5, and the trimethylsilyl groups are equivalent [8*]. Their IR spectra [8*] exhibit two strong $\nu(C{\equiv}C)$ absorptions (1909, 1875 cm^{-1} **2**; 1955, 1938 cm^{-1} **3**) at lower frequencies than those observed for

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* Reference number with an asterisk indicates a note in the list of references.

the mononuclear precursor **1** (2028, 2009 cm^{-1}) and in the range expected for carbon–carbon triple bonds side-on-coordinated to a transition metal [2,3].

The stable and unusual combination of an allyl and two alkynyl groups in these complexes prompted us to explore the structure of one and a single-crystal diffraction study was therefore carried out on **3** [9*]. This study supports the spectroscopic data and shows (Fig. 1) that the dinuclear compound consists of a $\{Pd(\eta^3\text{-}C_3H_5)\}^+$ unit stabilized by symmetric side-on coordination of the palladium atom to the $C\equiv C$ bonds of both alkynyls of the *cis*-$\{Pt(C_6F_5)_2(C\equiv CSiMe_3)_2\}^{2-}$ fragment. The palladium atom is further symmetrically coordinated to an allyl group. The dihedral angle between the η^3-allyl group and the plane formed by the Pd atom and the midpoints of the $C\equiv C$ triple bonds (120.6(1.9)°) and the angle at C(24) [118.4(24)°] are similar to those found in other (η^3-allyl) palladium complexes [7]. The platinum atom is in a slightly distorted square planar environment and the bond lengths and angles of the acetylene skeletons are very similar to those found in $[\{Pt(dppe)(C\equiv CPh)_2\}Pt(C_6F_5)_2]$ [2a]. The central PtC(1)C(2)C(16)C(17)Pd core is not planar and the Pt(1) ··· Pd(1) vector forms an angle of 123.4(2)° with the perpendicular to the coordination plane of Pt(1) and of 68.0(19)° with the perpendicular to the η^3-allyl group. A similar nonplanar structure has also been found in $[\{Pt(dppe)(C\equiv CPh)_2\}Pt(C_6F_5)_2]$ [2a] but $[\{L_2Ti(C\equiv CPh)_2\}Co(CO)]$ [3c] and $[\{L_2Ti(C\equiv CSiMe_3)_2\}FeCl_2]$ [3d] display planar Ti(acetylide)M (M = Co or Fe) cores. Finally, the Pt(1) ··· Pd(1) distance (3.049(2) Å) is greater than the sum of covalent radii, excluding any metal–metal bonding.

Acknowledgments

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References and notes

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4 $(NBu_4)_2[Pt(C_6F_5)_2(C\equiv CSiMe_3)_2]$ (**1**) was prepared by treating *cis*-$[Pt(C_6F_5)_2(THF)_2]$ [5] with $LiC\equiv CSiMe_3$ and $(NBu_4)Br$ in a similar way to that previously described for $(NBu_4)_2[Pt(C_6F_5)_2(C\equiv C^tBu)_2]$ [6] (yield 80%). Anal. Calc.: C, 53.67; H, 7.51; N, 2.32. Found: C, 53.67; H, 8.2; N, 2.20% Λ_M (in CH_3CN solution): 244.62 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): $\nu(C\equiv C)$ 2028s, 2009s; $\nu(C_6F_5)_{\text{x-sens}}$ 782s, 774s. ^1H NMR ($CDCl_3$, ppm, TMS): δ −0.09 (s, $SiMe_3$); 0.93 [t, $-CH_3$, (^{n}Bu)], 1.40 [m, $-CH_2$, (^{n}Bu)], 1.7 [m, CH_2, [^{n}Bu)], 3.5 [m, $N-CH_2-$, (^{n}Bu)]; ^{19}F NMR ($CDCl_3$, ppm, $CFCl_3$): δ −114.6 [d, $F_{oo'}$, $^3J_{(Pt-F)} = 376$ Hz]; −169.0 (m, F_p and $F_{mm'}$).

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8 (a) $(NBu_4)[\{Pt(C_6F_5)_2(C\equiv CSiMe_3)_2\}Pt(\eta^3\text{-}C_3H_5)]$ **2**. To a stirred yellow suspension of $[Pt(\eta^3\text{-}C_3H_5)Cl]_4$ (0.045 g, 0.0408 mmol) in dry acetone (30 ml), and under N_2, was added 0.2 g (0.163 mmol) of **1**. After 0.5 h of stirring at room temperature, the resulting pale yellow solution was filtered and evaporated to dryness. Addition of EtOH yields **2** as a white solid. (45% yield). Anal. Calc.: C, 40.95; H, 4.94; N, 1.16. Found: C, 41.13; H, 5.01; N, 1.44% Λ_M (in acetone solution): 96 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): $\nu(C\equiv C)$ 1909s, 1875s; $\nu(C_6F_5)_{\text{x-sens}}$ 798s, 784s. ^1H NMR ($CDCl_3$, ppm, TMS): −0.04 (s, $SiMe_3$), 0.94 [t, $-CH_3$, (^{n}Bu)], 1.35 [m, CH_2, (^{n}Bu)], 1.54 [m, $-CH_2$, (^{n}Bu)], 3.18 [m, $N-CH_2-$, (^{n}Bu)], 4.24 [m, C–H, (allyl)], 3.89 [d, 2 H_{syn}, $J_{syn} = 7.1$ Hz, $J(Pt-H_{syn}) \sim 15.2$ Hz, (allyl)], 2.19 [d, 2 H_{anti}, $J_{anti} = 11.5$ Hz, $J(Pt-H_{anti}) = 59.1$ Hz, (allyl)]; ^{19}F NMR ($CDCl_3$, ppm, $CFCl_3$): δ −115.8 [d, $F_{oo'}$, $^3J_{(Pt-F)} = 442$ Hz]; −166.2 (t, F_p), −166.9 (m, $F_{mm'}$). (b) $(NBu_4)[\{Pt(C_6F_5)_2(C\equiv CSiMe_3)_2\}Pd(\eta^3\text{-}C_3H_5)]$ **3**. To a pale-yellow solution of $[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]$ (0.045 g, 0.124 mmol) in dry acetone (10 ml) and under N_2, was added **1** (0.3 g, 0.248 mmol) and the mixture was stirred for 10 min. The resulting deep yellow solution was evaporated to dryness and the slow addition of EtOH rendered **3** as a yellow microcrystalline product. Evaporation of the filtrate to dryness and treatment of the residue with water afforded a second fraction of **3** (total yield 77%). Anal. Calc.: C, 44.22; H, 5.34; N, 1.26. Found: C, 44.43; H, 5.28; N, 1.44% Λ_M (in acetone solution): 103.6 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): $\nu(C\equiv C)$ 1955s, 1938s; $\nu(C_6F_5)_{\text{x-sens}}$ 787s, 778s. ^1H NMR ($CDCl_3$, ppm, TMS): 0.08 (s, $SiMe_3$), 0.92 [t, $-CH_3$, (^{n}Bu)], 1.34 [m, CH_2, (^{n}Bu)], 1.58 [m, $-CH_2$, (^{n}Bu)], 3.16 [m, overlap $N-CH_2-$, (^{n}Bu) and 2H_{anti} (allyl)], 4.47 [d, 2 H_{syn}, $J_{syn} = 6.34$ Hz, (allyl)], 5.3 [m, C–H, (allyl)]; ^{19}F NMR ($CDCl_3$, ppm, $CFCl_3$): −115.53 [d, $F_{oo'}$, $^3J_{(Pt-F)} = 399$ Hz]; −167.3 (m, F_p and $F_{mm'}$).

9 Crystals of **3** suitable for X-ray analysis were grown by slow diffusion of n-hexane into an acetone solution of **3** at low temperature (−30°C). Crystal data for **3** NBu_4 $[PtPd(C_6F_5)_2(C_2SiMe)_2(C_3H_5)]$ $C_{41}H_{59}NF_{10}Si_2PdPt$, M = 1113.57. Monoclinic, space group $C2/c$, $a = 40.989(8)$, $b = 11.438(2)$, $c = 21.910(4)$ Å, $\beta = 97.03(3)°$. $V = 10195.08$, $Z = 8$, $D_c = 1.45$ g cm^{-3}. Data were collected on a STOE AED2-Siemens diffractometer from the range scanned ($4 \le 2\theta \le 47$), 7975 data were recorded to give 4084 observed $[F^2 \ge 4\sigma(F^2)]$ reflections. The structure was solved by direct methods (Pt atom) and refined by least-squares analysis. Absorption correction was based on psi-scan measurements. The final R and R_w were 0.0597 and 0.0614 for 505 parameters.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. At the end of the refinement, we observed in a difference Fourier map, *ca.* 5 weak peaks lying in an interstitial region. Two of these peaks were largest 0.9 eA^{-3}, however it was not possible to refine any reasonable combination of these sites (modelled as disordered acetone), either with or without distance restraints or thermal parameter constraints. A packing diagram (available as supplementary material) shows an interstitial cavity capable of accommodating a molecule of acetone.