Unusual Bridging of the Metal Centers in a Heterometallic Titanium–Platinum Complex. X-ray Structure of $[Cp_2Ti(\mu_2\text{-}\eta^1\text{-}C{\equiv}C^tBu)_2Pt(C_6F_5)_2]{\cdot}CH_2Cl_2$

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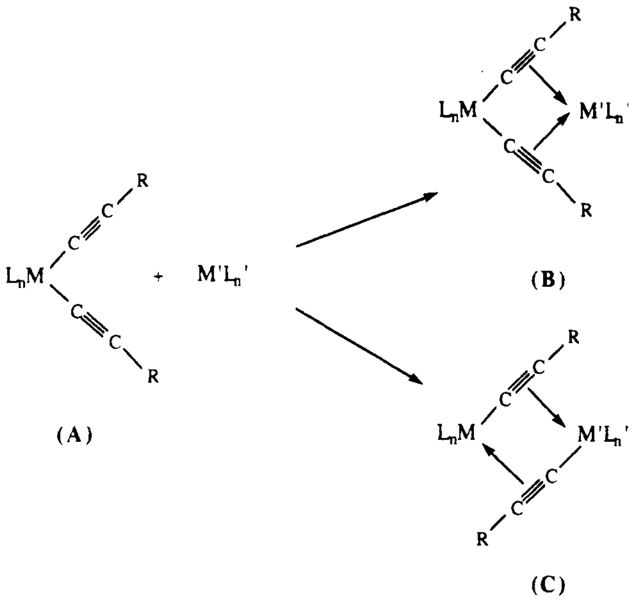
Summary: The reaction between $[Cp_2Ti(C{\equiv}C^tBu)_2]$ *(1) and* $[cis\text{-}Pt(C_6F_5)_2(THF)_2]$ *gives the mixed complex* $[Cp_2Ti(\mu_2\text{-}\eta^1\text{-}C{\equiv}C^tBu)_2Pt(C_6F_5)_2]$ *(2), which has been shown by X-ray crystallography to contain a system of two asymmetric* $\mu_2\text{-}\eta^1$*-alkynyl ligands bridging both metal centers. Complex 2 crystallizes as the dichloromethane solvate in the monoclinic crystal system, space group* $P2_1/n$*, with* $a = 133.725$ *(2) Å,* $b = 15.875$ *(2) Å,* $c = 16.424$ *(3) Å,* $\beta = 99.58$ *(2)°,* $V = 3529$ *(1) Å*^{3}*, and* $Z = 4$*. A model of 447 parameters was refined to 3586 diffraction data, giving residuals of* $R = 0.0390$*,* $R_w = 0.0558$*, and quality-of-fit = 1.367. The Pt–Ti distance is 2.831 (2) Å.*

Bis(σ-alkynyl) complexes (type A, Scheme I) can be used for the preparation of homo- and heterobinuclear complexes containing bridging σ-π-alkynyl groups between the metal centers. However, different reaction pathways have been observed depending on the metal and the type of bis(alkynyl) derivative. Thus, bis(alkynyl)metallocene titanium(IV) derivatives have been used as organometallic bidentate chelate ligands, producing systems of type B,[1-3] but the analogous zirconium and hafnium derivatives give metallocyclic systems of type C.[4,5] On the other hand, treatment of $[cis\text{-}M(C_6F_5)_2(THF)_2]$ (M = Pd, Pt; THF = tetrahydrofuran) with neutral bis(alkynyl)platinum complexes $[cis\text{-}PtL_2(C{\equiv}CR)_2]$ gives derivatives of type B, while similar reactions with anionic alkynylplatinate(II) complexes $Q_2[cis\text{-}Pt(C_6F_5)_2(C{\equiv}CR)_2]$ result in the formation of compounds of type C, probably via intermediate species of type B, which only rarely have been isolated.[6]

As part of our current research on polynuclear complexes with bridging acetylide groups,[6-8] we are studying the reactivity of different types of acetylide derivatives with $[cis\text{-}M(C_6F_5)_2(THF)_2]$ (M = Pd, Pt) in order to prepare heterometallic acetylide-bridged complexes and we report here the facile synthesis of an unusual titanium–platinum derivative $[Cp_2Ti(\mu_2\text{-}\eta^1\text{-}C{\equiv}C^tBu)_2Pt(C_6F_5)_2]$ obtained by the reaction of $[cis\text{-}Pt(C_6F_5)_2(THF)_2]$ with $[Cp_2Ti(C{\equiv}C^tBu)_2]$.

Scheme I



$[Cp_2Ti(C{\equiv}C^tBu)_2]$[9] (1) reacts in CH_2Cl_2 with $[cis\text{-}Pt(C_6F_5)_2(THF)_2]$ (molar ratio 1:1) to give a deep-red solution from which air-stable, red crystals of $[Cp_2Ti(\mu_2\text{-}\eta^1\text{-}C{\equiv}C^tBu)_2Pt(C_6F_5)_2]$ (2) (53% yield) are obtained[10] (eq 1). Analytical and mass spectral data are in accord with this formulation. The ^1H and ^{19}F NMR spectra of 2 at room temperature show that in solution the two cyclopentadienyl groups, the two C_6F_5 ligands, and the two *tert*-butyl groups, respectively, are mutually equivalent—i.e., that at least in solution complex 2 is symmetric. On the other hand, the IR spectrum shows the $\nu(C{\equiv}C)$ vibration at an unusually high frequency (2042 cm^{-1}), only 19 cm^{-1} lower than the corresponding vibration in complex 1, the starting material. Such a small decrease in frequency would

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(10) Synthesis and analytical data for **2**: To a yellow solution of $[Cp_2Ti(C{\equiv}C^tBu)_2]$ (0.253 g, 0.74 mmol) in CH_2Cl_2 (20 cm^3) was added 0.5 g (0.74 mmol) of $[cis\text{-}Pt(C_6F_5)_2(THF)_2]$.[11] After 10 min of stirring at room temperature, the resulting mixture was filtered off and the deep-red solution was concentrated and cooled at −30 °C yielding red crystals of **2** (0.3457 g, 53% yield). Under these conditions, **2** crystallizes with CH_2Cl_2 (observed by ^1H NMR); recrystallization from benzene gives the unsolvate product. Anal. Calc: C, 46.96; H, 3.24. Found: C, 46.62; H, 3.09. IR data: $\nu(C{\equiv}C)$ 2042 (s) cm^{-1}; ν x-sens (C_6F_5) 798 (s), 783 (s) cm^{-1}.[12] ^1H NMR ($CDCl_3$, 299.95 MHz, ppm, TMS): 6.4 (s, Cp), 5.33 (s, CH_2Cl_2), 1.04 (s, ^tBu). ^{19}F NMR ($CDCl_3$, 282.29 MHz, ppm, $CFCl_3$): −118.4 [d, F_o, $^3J_{Pt\text{-}F_o} = 395$ Hz], −163.8 (t, F_p), −165.8 (m, F_m). ^{13}C NMR ($CDCl_3$, 75.43 MHz, ppm, TMS), 29.6 ($-CH_3$), 31.0 ($C(CH_3)_3$), 113.6 (C_5H_5), 133.2 (only one signal without Pt satellites is observed; it can be due to either C_α or C_β). EI-MS: $m/z = 869$ [M$^+$] (20%), $m/z = 702$ [$M - C_6F_5^+$] (100%).

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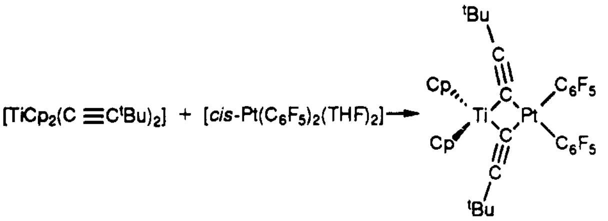

(1)

indicate that **2** does not show a binuclear structure of type B or C, for which a considerable π component (with a larger decrease in $\nu(C\equiv C)$) has been proposed. In order to establish the bonding features of the alkynyl ligands in this compound, a single-crystal X-ray study has been carried out.[13] The molecular structure, from a dichloromethane solvate of **2**, is shown in Figure 1. Selected bond distances and bond angles are given in the caption of Figure 1. The most remarkable feature of this structure is that the alkynyl bridging ligands are engaged in asymmetric σ bonding (μ_2-η^1) with both the titanium and platinum centers. The difference in the distances Ti(1)–C(13) and Ti(1)···C(14) (2.257 (10) and 3.049 (11) Å, respectively), as well as that between Ti(1)–C(19) and Ti(1)···C(20) (2.240 (10) and 2.954 (12) Å, respectively), clearly shows that σ-bonding dominates the interaction between titanium and the acetylide bridges. The M–C(acetylide) distances are rather different, with Pt–C shorter than Ti–C, suggesting that the σ Pt–C bond is stronger than the corresponding Ti–C bond. It is clear that the platinum atom—possibly as a result of its greater expanse of electron density available for σ-bonding, in comparison to that of Ti(IV)—forms stronger σ-bonds to the acetylide bridges. This is also suggested by the fact that the bridging ligands are tilted in such a way that their σ-bonding orbitals point more toward the platinum atom.

Finally, the platinum center is in a slightly distorted square planar environment and the titanium center is in a distorted tetrahedral environment formed by the C(13) and C(19) atoms and the centroids of the two cyclopentadienyl groups. The core of the dinuclear molecule (the two metals and the four σ-bonded carbon atoms) is essentially planar, with none of the atoms deviating from the mean plane by more than 0.11 Å.

The Pt–Ti distance, 2.831 (2) Å, lies between the distances found in two complexes for which dative Pt→Ti interactions have been suggested.[14] The Pt–μC–Ti angles in **2** are somewhat smaller than 90° (see the caption to Figure 1), lending support to the possibility of a direct bonding interaction between the metal centers.

This type of binuclear complex, with two alkynyl bridging ligands σ-bonded to both metal centers, is not common. In fact, the only examples of such complexes which have been crystallographically characterized involve main-group elements or f-orbital centers exclusively.[15-21]

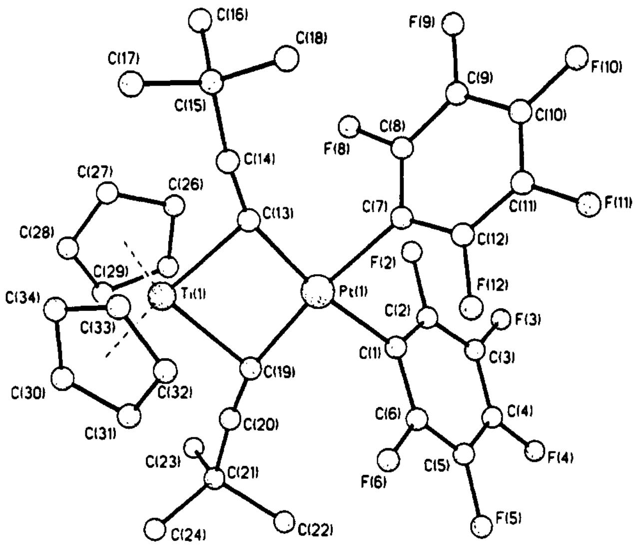

Figure 1. Molecular structure of $Cp_2Ti(\mu_2\text{-}\eta^1\text{-}C\equiv C^tBu)_2Pt(C_6F_5)_2\cdot CH_2Cl_2$. Selected bond distances (Å) and angles (deg): Ti(1)–C(13) = 2.257 (10), Ti(1)–C(19) = 2.240 (10), Pt(1)–C(13) = 2.014 (11), Pt(1)–C(19) = 2.019 (11), Pt(1)–C(1) = 2.043 (9), Pt(1)–C(7) = 2.059 (9), C(13)–C(14) = 1.234 (16), C(19)–C(20) = 1.197 (16), Ti(1)–Pt(1) = 2.831 (2); Ti(1)–C(13)–Pt(1) = 82.8 (4), Ti(1)–C(19)–Pt(1) = 83.2 (4), C(13)–Ti(1)–C(19) = 89.8 (4), C(13)–Pt(1)–C(19) = 103.8 (4), C(1)–Pt(1)–C(7) = 85.7 (4), Pt(1)–C(13)–C(14) = 158.1 (8), Ti(1)–C(13)–C(14) = 118.8 (7), Pt(1)–C(19)–C(20) = 161.5 (9), Ti(1)–C(19)–C(20) = 115.1 (8), C(13)–C(14)–C(15) = 172 (1), C(19)–C(20)–C(21) = 173 (1).

There do exist, however, examples of transition-metal compounds with a single bridging alkynyl ligand, and other bridging ligands, in which the alkynyl bridge shows the same mode of bonding that we observe here.[22-26]

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Supplementary Material Available: Tables of crystal data, atomic positional and equivalent isotropic displacement parameters, and bond distances and bond angles for **2** (8 pages). Ordering information is given on any current masthead page.

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[13] X-ray-quality crystals of **2** were obtained by cooling at –20 °C a saturated dichloromethane solution. Crystal data for **2**: $PtTiC_{34}H_{28}F_{10}\cdot CH_2Cl_2$, fw 954.47, monoclinic, space group $P2_1/n$, a = 13.725 (2) Å, b = 15.875 (2) Å, c = 16.424 (3) Å, β = 99.58 (2)°, V = 3529 (1) Å^3, Z = 4, d_{calc} = 1.797 g/cm^3, μ(Mo Kα) = 46.36 cm^{-1}. Data were collected by a Stoe AED-2 diffractometer at –40.0 (2) °C, in the 2θ range 4.0–45.0°. The structure was solved by direct methods. A model comprising 447 parameters was refined to 3586 data with $|F_o|^2 \geq 3\sigma|F_o|^2$, giving final residuals of R = 0.0390, R_w = 0.0558, and quality-of-fit = 1.367.

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