Synthesis and Crystal Structure of an Unusual Triplatinum Alkynyl-Bridged Complex

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The title complex [Pt₃(C≡C^tBu)₄COD)₂] (**3**) is obtained along with [Pt(C≡C^tBu)₂(COD)] (**2**) by the reaction of [PtCl₂(COD)] (**1**) with HC≡C^tBu in the presence of NaOEt. Complex **3** (X-ray) contains two square planar [Pt(C≡C^tBu)₂(COD)] units linked by a "naked" Pt atom, which is bonded to only one of the alkynyl ligands of each Pt(II) unit. Alternative routes to the synthesis of **3** are also presented.

Introduction

π-Alkyne complexes of platinum(0) have been extensively investigated,[1] and many types are presently known, including mononuclear derivatives with one[2] (type **A**, Scheme 1) or two [2e][3] (type **B**, Scheme 1) alkyne ligands and di- and triplatinum species in which the alkyne transversely bridges two metal atoms.[4] Zerovalent platinum complexes are, in general, the most useful precursors for this type of compound, but preparations starting from platinum(II) derivatives have also been reported.[1] Thus, η²-bis(hydroxy)(acetylene)platinum(0) complexes are prepared by treating K₂[PtCl₄] with the alkyne in aqueous ethanol[3a] and [Pt(alkyne)(PR₃)₂] derivatives can be prepared by reducing [*cis*-PtCl₂(PR₃)₂] with reducing agents in the presence of the alkyne.[5] However this latter process is not always clean since in some cases (for instance with terminal or halogen alkynes and depending on the PR₃ ligand, the R substituents of the alkynes, and the reducing agent used)

Scheme 1

mono- or bis(alkynyl)platinum(II) complexes or mixtures of products including the corresponding Pt(0) η²-alkyne compound[2j,6] are obtained. Since it is well-known that alkynes and σ-alkynyl complexes (MC≡CR) display similar ligand properties,[7,8] it is rather surprising that complexes with a PtC≡CR fragment coordinated to a

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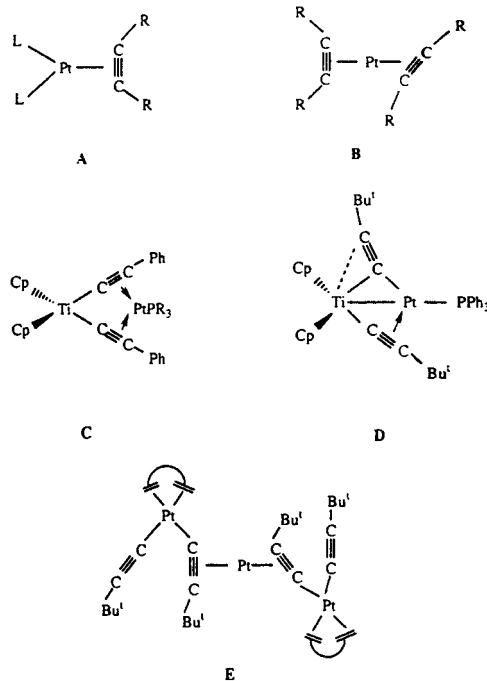[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1997.

(1) (a) Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 6, Chapter 39.8. (b) Nelson, J. H.; Jonassen, H. B. *Coord. Chem. Rev.* **1971,** *6*, 27.

(2) (a) Glanville, J. O.; Stewart, J. M.; Grim, S. O. *J. Organomet. Chem.* **1967,** *7*, 9. (b) Davies, B. W.; Payne, N. C. *Inorg. Chem.* **1974,** *13*, 1848. (c) Cook, C. D.; Wan, K. Y. *J. Am. Chem. Soc.* **1970,** *92*, 2595. (d) Davies, B. W.; Payne, N. C. *J. Organomet. Chem.* **1975,** *99*, 315. (e) Boag, N. M.; Green, M.; Grove, D. M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980,** 2170. (f) Ittel, S. D.; Ibers, J. A. *Adv. Organometallic Chem.* **1976,** *14*, 33. (g) Bernardus, J.; Heyns, B.; Stone, F. G. A. *J. Organomet. Chem.* **1978,** *160*, 337. (h) Koie, Y.; Shinoda, S.; Saito, Y. *J. Chem. Soc., Dalton Trans.* **1981,** 1082. (i) Baker, M. J.; Harrison, K. N.; Orpen, A. G.; Pringle, P. G.; Shaw, G. *J. Chem. Soc., Dalton Trans.* **1992,** 2607. (j) Sünkel, K.; Birk, U.; Robl, C. *Organometallics* **1994,** *13*, 1679.

(3) (a) Rochon, F. D.; Theophanides, T. *Can. J. Chem.* **1972,** *50*, 1325. (b) Green, M.; Grove, D. M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1976,** 759. (c) Walther, D.; Klettke, T.; Schimidt, A.; Gorls, H.; Imhof, W. *Organometallics* **1996,** *15*, 2314.

(4) (a) Boag, N. M.; Green, M.; Howard, J. A. K.; Spencer, J. L.; Stansfield, R. F. D.; Stone, F. G. A.; Thomas, M. D. O.; Vicente, J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1977,** 930. (b) Boag, N. M.; Green, M.; Howard, J. A. K.; Spencer, J. L.; Stansfield, R. F. D.; Thomas, M. D. O.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980,** 2182.

(5) (a) Chatt, J.; Rowe, G. A.; Williams, A. A. *Proc. Chem. Soc.* **1957,** 208. (b) Greaves, E. D.; Lock, C. J. L.; Maitlis, P. M. *Can. J. Chem.* **1968,** *46*, 3879. (c) Furlani, A.; Russo, M. V.; Villa, A. C.; Manfredotti, A. G.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1977,** 2154. (d) Furlani, A.; Carusi, P.; Russo, M. V. *J. Organomet. Chem.* **1974,** *67*, 315. (e) Tripathy, P. B.; Roundhill, D. M. *J. Organomet. Chem.* **1970,** *20*, 247. (f) Tripathy, P. B.; Renoe, B. W.; Adzamli, K.; Roundhill, D. M. *J. Am. Chem. Soc.* **1971,** *93*, 4406.
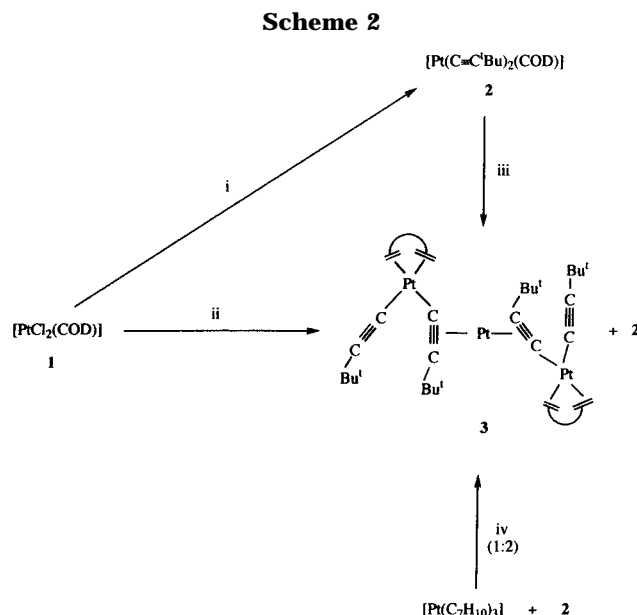
(6) (a) Empsall, H. D.; Shaw, B. L.; Stringer, A. J. *J. Organomet. Chem.* **1975,** *94*, 131. (b) Burgess, J.; Howden, M. E.; Kemmitt, R. D. W.; Sridhara, N. S. *J. Chem. Soc., Dalton Trans.* **1978,** 1577. (c) Furlani, A.; Licoccia, S.; Russo, M. V.; Chiesi Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1984,** 2197 and references therein. (d) Russo, M. V.; Furlani, A.; Licoccia, S.; Paolesse, R.; Chiesi Villa, A.; Guastini, C. *J. Organomet. Chem.* **1994,** *469*, 245.

Pt(0) center have never been isolated from the above reactions. Metalloalkynyl complexes of Pt(0) are also very rare: only the titanium−platinum derivatives [TiPt(μ-C≡CPh)$_2$(PR$_3$)Cp$_2$] (**C**, Scheme 1), obtained by treatment of [Ti(C≡CPh)$_2$Cp$_2$] with [Pt(C$_2$H$_4$)$_2$(PR$_3$)], have been isolated; no X-ray structure has been obtained.[9] Although these derivatives are considered as models for the as yet unobserved simple [Pt(alkyne)$_2$-(PR$_3$)] complexes, we have shown recently that [Ti-(C≡C^{t}Bu)$_2$Cp$_2$] reacts with [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] to yield [Cp$_2$Ti(μ-η^1:η^2-C≡C^{t}Bu)Pt(μ-η^1:η^2-C≡C^{t}Bu)PPh$_3$] (**D**, Scheme 1), which can be formally considered as the result of the oxidative addition of a Ti(IV)−C bond to a Pt(0) substrate to give the binuclear Ti(III)−Pt(I) complex **D**.[10]

In this paper, we report on the synthesis of a triplatinum complex [Pt$_3$(C≡C^{t}Bu)$_4$(COD)$_2$] (**3**) in which two different [Pt(C≡C^{t}Bu)$_2$(COD)] fragments act only as η^2-alkyne ligands to a Pt(0) center (**E**, Scheme 1), thus modeling complexes of type **B** with metalloalkynes. In this context, it should be noted that Stone and co-workers have previously reported both type **A** and **B** complexes containing one or two metallocarbyne Ln-M≡CR fragments coordinated to a Pt(0) center.[11]

Results and Discussion

It has been previously reported that the bis(alkylalkynido)(1,5-cyclooctadiene)platinum derivatives are considerably more difficult to prepare than the analogous bis(arylalkynido) complexes.[12] Thus, [Pt(C≡CR)$_2$-(COD)] (R = C$_6$H$_5$[12] or C$_6$H$_4$Me-p[13]) are prepared by

(7) (a) Forniés, J.; Gómez-Saso, M.-A.; Lalinde, E.; Martínez, F.; Moreno, M. T. *Organometallics* **1992**, *11*, 2873. (b) Berenguer, J. R.; Falvello, L.; Forniés, J.; Lalinde, E.; Tomás, M. *Organometallics* **1993**, *12*, 6. (c) Forniés, J.; Lalinde, E.; Martín, A.; Moreno, M. T. *J. Chem. Soc., Dalton Trans.* **1994**, 135. (d) Berenguer, J. R.; Forniés, J.; Lalinde, E.; Martín, A.; Moreno, M. T. *J. Chem. Soc., Dalton Trans.* **1994**, 3343. (e) Berenguer, J. R.; Forniés, J.; Martínez, F.; Cubero, J. C.; Lalinde, E.; Moreno, M. T.; Welch, A. J. *Polyhedron* **1993**, *12*, 1797. (f) Berenguer, J. R.; Forniés, E.; Lalinde, E.; Martínez, F. *J. Chem. Soc., Chem. Commun.* **1995**, 1237.

(8) (a) Erker, G.; Frömberg, W.; Benn, R.; Mynott, R.; Angermund, K.; Krüger, C. *Organometallics* **1989**, *8*, 911. (b) Yasufuku, K.; Yamazaki, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2664. (c) Lang, H.; Herres, M.; Zsolnai, L. *Organometallics* **1993**, *12*, 5008. (d) Janssen, M. D.; Herres, M.; Zsolnai, L.; Grove, D. M.; Spek, A. L.; Lang, H.; Van Koten, G. *Organometallics* **1995**, *14*, 1098. (e) Janssen, M. D.; Herres, M.; Spek, A. L.; Grove, D. M.; Lang, H.; Van Koten, G. *J. Chem. Soc., Chem. Commun.* **1995**, 925. (f) Lang, H.; Herres, M.; Imhof, W. *J. Organomet. Chem.* **1994**, *465*, 283. (g) Lang, H.; Blau, S.; Nuber, B.; Zsolnai, L. *Organometallics* **1995**, *14*, 3216 and references given therein. (h) Lang, H.; Köhler, K.; Büchner, M. *Chem. Ber.* **1995**, *128*, 525. (i) Lotz, S.; Van Rooyen, P. H.; Meyer, R. *Adv. Organomet. Chem.* **1995**, *37*, 219 and references therein.

(9) Ciriano, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A.; Wadepohl, H. *J. Chem. Soc., Dalton Trans.* **1979**, 1749.

(10) Berenguer, J. R.; Forniés, J. Lalinde, E.; Martín, A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2083.

(11) (a) Ashworth, T. V.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1979**, 42; *J. Chem. Soc., Dalton Trans.* **1980**, 1609. (b) Ashworth, T. V.; Chercuti, M. J.; Howard, J. A. K.; Stone, F. G. A.; Wisbey, S. J. *J. Chem. Soc., Dalton Trans.* **1981**, 763. (c) Green, M.; Howard, J. A. K.; James, A. P.; Nunn, C. M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1986**, 187. (d) Davies, S. J.; Hill, A. F.; Pilotti, M. U.; Stone, F. G. A. *Polyhedron* **1989**, *8*, 2265. (e) Elliot, G. P.; Howard, J. A. K.; Mise, T.; Moore, I.; Nunn, C. M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1986**, 2091. (f) Byers, P. K.; Carr, N.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1990**, 3701 and references therein. (g) Byers, P. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1991**, 93 and references therein. (h) Stone, F. G. A. *Pure Appl. Chem.* **1986**, *58*, 529. See also: Chi, Y.; Hwang, D.-K. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 10, Chapter 3.6.

(12) Cross, R. J.; Davidson, M. F. *J. Chem. Soc., Dalton Trans.* **1986**, 1987.

Scheme 2

i) ^{t}BuC≡CH / NaOEt [(2:4), low temperature (-10° to 0°C)], ethanol;

ii) ^{t}BuC≡CH / NaOEt [(2:4), (6° to r.t.)], ethanol;

iii) 0.5 equiv of (1) / NaOEt (3 equiv), ca. 6°C, ethanol;

iv) hexane, r.t.

reacting [PtCl$_2$(COD)] (**1**) and HC≡CR with NaOEt, while Cross *et al.*[12] have reported that all attempts to prepare the propynyl analogue (R = Me) were unsuccessful. Whitesides *et al.* reported that attempts to prepare [Pt(C≡C^{t}Bu)$_2$(COD)] (**2**) by treatment of **1** with LiC≡C^{t}Bu, Me$_3$SnC≡C^{t}Bu, or Hg(C≡C^{t}Bu)$_2$ led to failure.[14] However, we have recently obtained this complex, **2**, as a white microcrystalline solid by reaction of **1** and *tert*-butylacetylene with sodium ethoxide (**1**/^{t}BuC≡CH/NaOEt, 1:2:4) in ethanol at low temperature (−10 to 0 °C) (Scheme 2, i).[7a]

We have now found that, at slightly increased temperature, the **1**/^{t}BuC≡CH/NaOEt reaction system (1:2:4 molar ratio) leads to a mixture of an unexpected trinuclear complex [Pt$_3$(C≡C^{t}Bu)$_4$(COD)$_2$] (**3**) and the previously reported mononuclear derivative **2** (Scheme 2, path ii). Thus, treatment of [PtCl$_2$(COD)] (**1**) with a mixture (2:4) of ^{t}BuC≡CH and NaOEt in ethanol at ca. 6 °C results in the formation of a white suspension, the color of which changes to yellow upon warming the mixture to room temperature. Removal of the solvent followed by treatment of the resulting residue with deoxygenated water gives a cream yellow solid, the ^{1}H NMR of which shows it to be a mixture of **2** and **3** in a ratio of ca. 5.9:1. Treatment of this mixture with cold acetone followed by recrystallization of the resulting solid from CHCl$_3$/EtOH gives **3** as an air-stable microcrystalline yellow solid in 9% yield (based on **1**). Complex **3** analyzes as [Pt$_3$(C≡C^{t}Bu)$_4$(COD)$_2$] and exhibits a molecular peak in its FAB$^+$ mass spectrum (*m/z* 1127, 10%) with the expected isotopomer distribution, although the fragment [M$^+$ − COD] has the highest signal intensity (100%).

At room temperature, the ^{1}H NMR spectrum of **3** shows two singlet resonances at δ 1.19 and 1.27 ppm in 1:1 ratio, indicating the presence of inequivalent *tert*-

(13) Perera, S. D.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1993**, 3653.

(14) Hackett, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1449.

butylalkynyl ligands. In addition, the proton spectrum displays four resonances due to the cyclooctadiene ligand, one of them as a broad multiplet centered at 2.48 ppm due to the methylene protons and three of them [5.82 (1H), 5.73 (1H), and 5.49 (2H)] in the olefin region. Upon cooling of the sample, only the most intense olefinic resonance (δ 5.49) is split into two different resonances (1:1; δ 5.46 and 5.50) at −50 °C. The most remarkable feature in the IR spectrum of complex **3** is the presence of two medium-intensity ν(C≡C) absorptions at 1858 and 1825 cm^{-1}, suggesting the presence of bridging alkynyl groups.[7,8] Since these spectroscopic data do not define the structure, an X-ray diffraction study has been undertaken showing **3** to be formed by two Pt(C≡C^{t}Bu)$_2$(COD) units linked by a naked Pt(0) atom.

The presence of a Pt(0) center in **3** is unexpected, and in order to clarify its formation, we have explored different reaction conditions. We have observed, that in the absence of an excess of sodium ethoxide, neither the 1:2:2 nor the 1:3:3 (**1**/^{t}BuC≡CH/NaOEt) reaction system in EtOH gives any trace of **3**, suggesting that the reducing agent is probably the excess of NaOEt which is in competition with the ^{t}BuC≡C$^-$ for reaction with **1**.[15] In fact, complex **3** has also been synthesized in better yield (44%) by the reaction between **1** and 2 equiv of [Pt(C≡C^{t}Bu)$_2$(COD)] in the presence of an excess of NaOEt (6 equiv) under similar reactions conditions (Scheme 2, iii). Finally, and as expected, treatment of a hexane solution of the prereduced tris-(norbornene)platinum(0) compound [Pt(C$_7$H$_{10}$)$_3$] with [Pt(C≡C^{t}Bu)$_2$(COD)] (**2**) (molar ratio 1:2), at room temperature, cleanly affords complex **3** in good yield (77%) (Scheme 2, iv).

Having established the structure of **3**, and as a preliminary to measuring its ^{13}C NMR spectrum, we recorded the spectrum of complex **2** so as to compare the chemical shifts of the alkyne carbon atoms.[16] The C_α and C_β alkynyl carbons of **2** appear at δ 80.5 and 117.1 and are easily assigned since they show different coupling constants to the ^{195}Pt nuclei (1410 and 359 Hz, respectively). Both the chemical shifts and the coupling constants are similar to those observed in mono(alkynyl) complexes *trans*-[PtCl(C≡CR)L$_2$],[2j,17] in accord with the relatively low *trans* influence of the π-bonded COD ligand. The ^{13}C NMR spectrum of complex **3** at low temperature (−50 °C) exhibits, as expected, four alkyne carbon resonances (δ 146.0, 117.2, 115.5, and 83.6) although the ^{195}Pt satellites are not observed. The downfield resonance (δ 146.0) and the signal at δ 115.5 are tentatively assigned to the C_β and C_α carbon atoms of the coordinated alkynyl fragment, respectively. This assignment is based on the assumption that the downfield shift of the alkyne carbon atoms on metal coordination would be of similar magnitude (30−40 ppm) to those previously observed in complexes [Pt(η^2-alkyne)$_2$].[2e] Assignment of the resonances at δ 83.6 and 117.2 to the C_α and C_β carbon atoms of the terminal alkynyl groups, respectively, is in concordance with those observed in **2**.

(15) Similar alcoxy-promoted reductions have been previously observed: Sacco, A.; Mastrorilli, P. *J. Chem. Soc., Dalton Trans.* **1994**, 2761.

(16) Recently the ^{13}C solid-state NMR spectrum of complex **2** has been reported: Gay, I. D.; Yount, G. B. *Organometallics* **1996**, *15*, 2264.

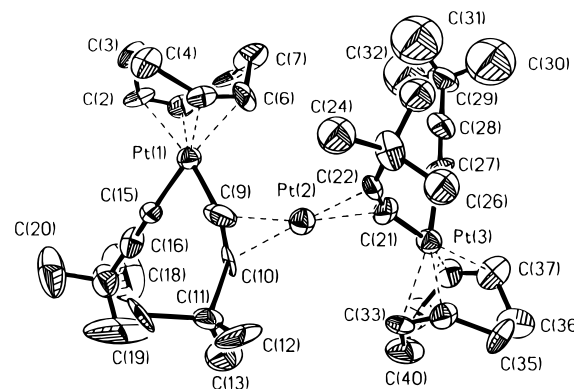(17) Sebald, A.; Stader, C.; Wrackmeyer, B.; Bensch, W. *J. Organomet. Chem.* **1986**, *311*, 233.

Figure 1. Molecular structure of complex **3**, showing the atom-numbering scheme.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3

Pt(1)−C(9)	1.97(3)	Pt(1)−C(15)	2.00(2)
Pt(1)−C(1)	2.18(2)	Pt(1)−C(2)	2.24(2)
Pt(1)−C(6)	2.24(2)	Pt(1)−C(5)	2.29(2)
Pt(2)−C(22)	1.99(2)	Pt(2)−C(10)	2.01(2)
Pt(2)−C(21)	2.07(2)	Pt(2)−C(9)	2.09(3)
Pt(3)−C(21)	1.97(2)	Pt(3)−C(27)	1.99(3)
Pt(3)−C(34)	2.19(2)	Pt(3)−C(37)	2.23(2)
Pt(3)−C(38)	2.24(2)	Pt(3)−C(33)	2.27(2)
C(9)−C(10)	1.27(3)	C(15)−C(16)	1.17(3)
C(21)−C(22)	1.27(3)	C(27)−C(28)	1.21(3)
C(9)−Pt(1)−C(15)	88.5(9)	C(22)−Pt(2)−C(10)	155.2(9)
C(22)−Pt(2)−C(21)	36.3(7)	C(10)−Pt(2)−C(21)	157.8(9)
C(22)−Pt(2)−C(9)	151.0(9)	C(10)−Pt(2)−C(9)	36.2(8)
C(21)−Pt(2)−C(9)	153.9(9)	C(21)−Pt(3)−C(27)	88.0(10)
C(10)−C(9)−Pt(1)	165(2)	C(9)−C(10)−C(11)	150(2)
C(16)−C(15)−Pt(1)	176(2)	C(15)−C(16)−C(17)	175(3)
C(22)−C(21)−Pt(3)	160(2)	C(21)−C(22)−C(23)	149(2)
C(28)−C(27)−Pt(3)	174(2)	C(27)−C(28)−C(29)	179(3)

Structure of [Pt$_3$(C≡C^{t}Bu)$_4$(COD)$_2$] (3). The molecular structure of [Pt$_3$(C≡C^{t}Bu)$_4$(COD)$_2$], **3**, is shown in Figure 1. Selected bond distances and angles are given in Table 1. It is at first sight apparent that **3** is built up from two similar [Pt(C≡C^{t}Bu)$_2$(COD)] units which are connected via a reduced platinum atom, Pt-(2). The most remarkable feature is that Pt(2) is only bonded to two acetylenic fragments, one associated with each [Pt(C≡C^{t}Bu)$_2$(COD)] unit. This structural feature contrasts with the structures previously found for the trinuclear cations [Pt$_2$Cu(C≡CPh)$_4$(dppe)]$^+$ [18] and [Pt$_2$Ag(C≡CPh)$_4$(PPh$_3$)$_4$]$^+$,[19] in which each of the two orthogonal Pt(C≡CPh)$_2$L$_2$ fragments acts as a didentate diyne ligand to copper or silver, respectively. The pseudo-tetrahedral geometry observed around the central Pt(2) atom closely resembles that previously found in bis(alkyne)platinum(0) complexes (**B**);[2e,3a] it is also similar to the closely related complex Pt{Cp(CO)$_2$W≡C-Tol}$_2$ (**F**)[11b] in which two metal alkylidyne moieties are linked by a Pt atom; but the latter compound also contains semibridging carbonyl ligands which interact with the Pt center. As would be expected from the geometry of a formally Pt(0) compound, the dihedral angle between Pt(2)−C(9)−C(10) and Pt(2)−C(21)−C(22) is 90.92(2)° and compares well with those found in [Pt(RC≡CR)$_2$] [R = Ph,[2e] 82°; R = C(OH)Et$_2$,[3a] 86°] and in **F** (97°).[11b] The bond distances between Pt(2) and

(18) Yamazaki, S.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1993**, 3051.

(19) Ara, I.; Berenguer, J. R.; Forniés, J.; Lalinde, E.; Moreno, M. T. *J. Organomet. Chem.* **1996**, *510*, 63.

the alkynyl carbon atoms [range 1.99(2) Å for Pt(2)−C(22) to 2.09(3) Å for Pt(2)−C(9)] compares well with the corresponding values found in [Pt(RC≡CR)$_2$] (R = Ph, 2.022(5) Å; R = C(OH)Et$_2$, 2.054(11) Å] and in **F** [average 2.015(10) Å] and are in the range generally measured for carbon−platinum σ bonds.[11] In fact these distances are identical to the remaining Pt(1,3)−C σ bonds [range 1.97(2) Å for Pt(3)−C(21) to 2.00(2) Å for Pt(1)−C(15)]. As expected the Pt(1,3)−C olefin (COD) bond distances [range 2.18(2) Å for Pt(1)−C(1) to 2.29-(2) Å for Pt(1)−C(5)] are longer and are consistent with the values reported in the literature for related bonds.[20,21] The mean value of the alkynyl C−C bond distance of the Pt(2)-π complexed C−C triple bonds (1.27(3) Å) are as expected longer than those of the uncomplexed fragments [C(15)−C(16) 1.17(3) Å; C(27)−C(28) 1.21(3) Å], but due to the large standard deviations involved no rigorous comparisons can be made. The alkynyl bend-back angles provide, however, a more useful criterion for evaluating the perturbation of the alkynyl skeleton upon coordination.[2b] In complex **3** the bend-back angles at C$_\alpha$ [15° for C(9) and 20° for C(21)] and at C$_\beta$ [30° for C(10) and 31° for C(22)] of the Pt(2)-π-complexed fragments are similar to those found in [Pt-(RC≡CR)$_2$] (R = Ph, 27°; R = C(OH)Et$_2$, 25°). As expected, the terminal alkynyl ligands do not deviate significantly from linearity (Table 1).

The trimetallic Pt(1)···Pt(2)···Pt(3) sequence is not linear [Pt(1)−Pt(2)−Pt(3) 123.3°], and the very long Pt-(2)···Pt(1,3) distances [3.619(1) and 3.678(1) Å] exclude the possibility of metal−metal bonding.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of nitrogen. Acetone and hexane were purified by distillation with appropriate drying agents, and absolute ethanol was deoxygenated prior to use. Microanalyses (C, H) and IR spectra were obtained as described elsewhere.[7] ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX 300 instrument, and chemical shifts are reported in δ units (parts per million) relative to external tetramethylsilane. The mass spectrum (FAB$^+$) was obtained in a VG Autospec spectrometer.

Preparation of [Pt$_3$(C≡C^{t}Bu)$_4$(COD)$_2$] (3). (A) Reaction of 1 and ^{t}BuC≡CH/NaOEt in EtOH. A mixture of ^{t}BuC≡CH (0.483 g, 5.879 mmol) and sodium ethoxide (10.869 mmol) prepared from 0.25 g of sodium and 10 mL of dry EtOH was added, dropwise, to a cooled (6 °C) suspension of [PtCl$_2$-(COD)] (1 g, 2.672 mmol) in EtOH (5 mL) from a pressure-equalizing dropping funnel. The mixture was stirred for 1 h at this temperature before being warmed to room temperature, with continued stirring for a further 90 min. The resulting yellow-orange suspension was evaporated to dryness and the residue treated with deoxygenated water yielding a cream yellow solid (1.05 g), which was filtered out and repeatedly washed with water (3 × 10 mL). The ^{1}H NMR spectrum of this solid in CDCl$_3$ showed it to be a mixture of complexes **2** and **3** in a ratio of ca. 5.9:1. This solid was treated with cold acetone (15 mL), giving 0.16 g of a yellow solid [mixture of **2** and **3** (1.5:1)], which was crystallized from CHCl$_3$ and EtOH affording complex **3** as a lemon-yellow microcrystalline solid (0.09 g, yield 9% based on **1**). Concentration of the mother liquors (ca. 5 mL) gave an additional pale-yellow fraction of the mixture of **2** and **3** (0.15 g, ratio 3.8:1). Finally, removal

of the solvent (acetone) and addition of *n*-hexane afforded a cream-white solid identified by NMR as the mononuclear complex **2** (0.60 g) contaminated by a small amount of **3**.

If the reaction of **1** and ^{t}BuC≡CH/NaOEt is carried out using a stoichiometric mixture of ^{t}BuC≡CH and NaOEt (1/^{t}BuC≡CH/NaOEt, 1/2.2/2.2 or 1/3/3), only the mononuclear complex **2** is obtained.

3. Anal. Found: C, 42.67; H, 4.84. Calcd for C$_{40}$H$_{60}$Pt$_3$: C, 42.66; H, 5.37. IR (cm^{-1}) ν(C≡C): 1858 (w), 1825 (m). ^{1}H NMR (CDCl$_3$): at 20 °C δ 1.19 (s, 18H, ^{t}Bu), 1.27 (s, 18H, ^{t}Bu), 2.51 (m, 16H, CH$_2$, COD), 5.49 (s, br, 4H), 5.73, 5.82 (s, 4H) [CH, COD]; at −50 °C δ 1.21 (s, 18H, ^{t}Bu), 1.30 (s, 18H, ^{t}Bu), 2.43 (m, 16H, CH$_2$, COD), 5.46 (s), 5.50 (s) (4H), 5.74 (s), 5.79 (s) (4H). ^{13}C NMR (CDCl$_3$, −50 °C): δ 146.0 [C$_\beta$, C$_2$^{t}Bu(b)], 117.2 [C$_\beta$, C$_2$^{t}Bu(t)], 115.5 [C$_\alpha$, C$_2$^{t}Bu(b)], 108.0, 107.6, 103.7, 103.6 (=CH, COD), 83.6 [C$_\alpha$, C$_2$^{t}Bu(t)], 32.3, 32.00, 30.8, 29.9, 29.6, 29.2, 28.9, 28.1 [CH$_2$, COD, ^{t}Bu(t), ^{t}Bu(b)]. MS (FAB$^+$): *m/z* 1127 [M + 2H]$^+$ (10%), *m/z* 1043 [M − C≡C^{t}Bu]$^+$ (15%), *m/z* 1017 [M − COD]$^+$ (100%), *m/z* 963 [Pt$_3$(COD)$_2$(C≡C^{t}Bu)$_2$] (32%).

2.[7a] [13]C (CDCl$_3$, −50 °C): δ 117.1 (C$_\beta$, [2]$J_{Pt−C}$ = 359 Hz, C$_2$^{t}Bu), 102.3 (=CH, COD, J^{195}Pt$−$[13]C = 80 Hz), 80.5 (C$_\alpha$, [1]$J_{Pt−C}$ = 1410 Hz), 31.9 (CH$_2$, COD, $J_{Pt−C}$ = 8Hz), 30.0 [C(CH$_3$)$_3$], 28.7 (CMe$_3$, [3]$J_{Pt−C}$ = 24 Hz).

(B) Reaction of 1 with NaOEt and 2. To 0.161 g (0.43 mmol) of [PtCl$_2$(COD)], **1**, in 10 mL of EtOH at 5 °C was added slowly an excess (6 equiv) of NaOEt in ethanol (from 0.06 g of Na and 5 mL of EtOH). After the reaction mixture was stirred for 10 min at low temperature, one 0.4 g portion (0.86 mmol) of [Pt(C≡C^{t}Bu)$_2$(COD)] (**2**) was added. The suspension was stirred at room temperature for 2 h and 30 min and afterward evaporated to dryness. The resulting residue was treated with H$_2$O, filtered out, and air dried. Stirring this solid with cold acetone (8 mL) separates complex **3** (0.15 g). Removal of the solvent, addition of hexane (3 mL), and subsequent cooling to −30 °C provides an additional fraction (60 mg) of complex **3**. Total yield: 44%.

(C) Reaction of 2 with [Pt(C$_7$H$_{10}$)$_3$]. To a colorless solution of tris(bicyclo[2.2.1]heptane)platinum(0)[22] (0.08 g, 0.168 mmol) in hexane (15 mL) was added [Pt(C≡C^{t}Bu)$_2$-(COD)] (**2**) (0.156 g, 0.336 mmol). The solution immediately turned deep yellow, and after stirring of the mixture for a few (ca. 3) minutes, a yellow solid precipitated. The mixture was stirred for 20 min, and then the yellow solid formed (**3**) was filtered off. On concentration of the filtrate with subsequent cooling to −30 °C, a second fraction of **3** was obtained (total yield 145 mg, 77%).

X-ray Diffraction Study. Crystals of complex **3** were obtained by slow diffusion of ethanol into a concentrated solution of the complex in chloroform. In a preliminary examination of a crystalline sample of compound **3** at room temperature, it was observed that the compound suffers a rapid decomposition. For the structure determination, then, a crystal was removed from the tube in which it was grown and rapidly placed in a nitrogen cold stream on a Stoe AED-2 four-circle diffractometer. Although somewhat large, the crystal was not cut or otherwise processed before being placed on the diffractometer. Normal procedures were used for determination of the unit cell and lattice parameters, which were verified by independent examination of two other crystals. For the crystal from which the data were collected, the Laue group ($m\bar{3}$) and lattice parameters were checked by axial photography of the axes [100], [010], [001], [1,−1,0], and [1,−1,−1]. The ω−θ scan technique was used for collection of intensity data. During data collection, crystal and instrument stability were monitored through the intensities of three reflections, remeasured every 45 min. These showed no significant change through the course of data collection. A unique set of data, consisting of 6534 measurements, was

(20) In ref 1 see chapter 39.
(21) (a) [PtCl$_2$(COD)]: Syed, A.; Stevens, E. D.; Cruz, S. G. *Inorg. Chem.* **1984**, *23*, 3673. (b) [Pt(COD)$_2$]: Howard, J. A. K. *Acta Crystallogr., Sect. B.* **1982**, *38*, 2896. (c) Grassi, M.; Meille, S. V.; Musco, A.; Pontellini, R.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1990**, 251.

(22) Crascall, L. E.; Spencer, J. L. *Inorg. Synth.* **1990**, *28*. 127.

gathered. Absorption corrections were based on azimuthal scans (ψ-scans) of 5 reciprocal lattice vectors.

The structure was solved by direct methods[23] and refined by full-matrix least squares. Although the structure solution presented no difficulty, it was clear that the crystal had suffered some adverse effect, probably before the beginning of data collection. For example, although anisotropic refinement of all of the non-hydrogen atoms proceeded without difficulty, no hydrogen atoms were located in difference Fourier maps and none was included in the structural model. At the end of refinement, a difference Fourier had a number of large positive and negative peaks, between $+2.29$ and -1.03 e/Å³; nine positive peaks had $\rho > 1.0$ e/Å³. Most of the larger peaks were near the metal atoms and could have been results of residual uncorrected absorption ($\mu = 101.7$ cm⁻¹) and/or series termination errors.

The largest peak, however, was located in an interstitial region, at 1.4 Å from methyl carbon atom C(26) and 2.7 Å from methyl carbon atom C(14) of the molecule at $1 - z$, $-0.5 + x$, $0.5 - y$. It was not possible to treat this site as a carbon atom in the structural model as its isotropic displacement parameter diverged to large values. The presence of this peak could, on the basis of crystallographic considerations alone, raise a question of whether there were some other entities present in

small proportions. (The distance of 2.7 Å from a methyl carbon atom excludes the possibility that this peak represents another, unexpected atom on the butyl chain that includes C(26).) Since chemical spectroscopy in this case establishes the identity of the compound unambiguously, we conclude that this peak is spurious, as are the other large peaks in the difference map. Nevertheless, one should be conscious of the relatively poor quality of these structural results in using them alongside the other results presented in this paper. This structure determination leaves no doubt about the connectivity of compound **3**; but although we do present geometric comparisons with analogous systems in the Discussion, for reference purposes, we do not wish to imply that this is an exceedingly precise determination.

Supporting Information Available: Tables of refined cell constants with the most relevant data, anisotropic thermal parameters, atom positional parameters and U values, and complete bond lengths and angles for **3** (5 pages). Ordering information is given on any current masthead page.

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(23) SHELXL-93: FORTRAN-77 program for the refinement of crystal structures from diffraction data. Sheldrick, G. M. *J. Appl. Crystallogr.*, in preparation. Other crystallographic calculations were done with the commercial package SHELXTL-PLUS, Release 4.11/V, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1990.