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Synthesis of Bis(η^2-alkyne) Trinuclear Zwitterionic Platinum Hydride Complexes by Reaction of [*trans*-Pt(C_6F_5)$_2$(C≡CR)$_2$]$^{2-}$ with the Solvento Species [*trans*-PtHL$_2$(acetone)]$^+$

Irene Ara,[†] Jesús R. Berenguer,[‡] Juan Forniés,*[,†] Elena Lalinde,*[,‡] and
M. Teresa Moreno[‡]

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón,
Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas,
50009 Zaragoza, Spain, and Departamento de Química, Universidad de La Rioja,
26001 Logroño, Spain

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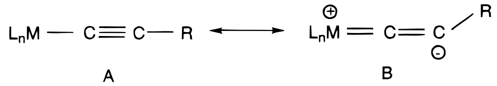
The alkynylation of *trans*-[Pt(C_6F_5)$_2$(tht)$_2$] (tht = tetrahydrothiophene) with LiC≡CR in diethyl ether (R = Ph, SiMe$_3$) or THF (R = ^{t}Bu) leads to novel dianionic species [*trans*-Pt(C_6F_5)$_2$(C≡CR)$_2$]$^{2-}$ (R = Ph (**1**), SiMe$_3$ (**2**), ^{t}Bu (**3**)) which have been isolated as tetrabutylammonium salts. Treatment of (NBu$_4$)$_2$[*trans*-Pt(C_6F_5)$_2$(C≡CR)$_2$] (R = Ph, SiMe$_3$, ^{t}Bu) with 2 equiv of cationic hydride reagents of the type [*trans*-PtHL$_2$(acetone)]$^+$ (L = PPh$_3$, PEt$_3$) in acetone form, *via* a ligand replacement, simple bis(η^2-alkyne) trinuclear zwitterionic complexes *trans,trans,trans*-{[Pt(C_6F_5)$_2$(μ-η^1:η^2-C≡CR)$_2$](PtHL$_2$)$_2$} (R = Ph, L = PPh$_3$ (**4a**), PEt$_3$ (**4b**); R = SiMe$_3$, L = PPh$_3$ (**5a**), PEt$_3$ (**5b**); R = ^{t}Bu, L = PEt$_3$ (**6b**)). The structure of complex **4b** has been determined by X-ray diffraction methods.

Introduction

A large number of transition σ-alkynyl complexes have been described, and it is well-known that the reactivity of the alkynyl ligand is a sensitive function of the nature of the alkynyl substituent, the attached metal and its ligands, and the overall charge of the complex.[1] It is well documented that alkynyl complexes containing electron-donating transition metal fragments generally undergo α-attack by nucleophiles and β-attack by electrophiles.[1bd,2] This reactivity has been rationalized on the basis of resonance forms A and B (Chart 1), with form B becoming more important as the electron density on the complex increases and as the ligands and the alkynyl substituents become more electron releasing.

The insertion of acetylenes into a M−H bond, which is a fundamental step of many catalytic cycles, is a well-known process;[3] however, in spite of the similarity between σ-alkynyl complexes and acetylenes, the reactions of transition-metal hydrides with metal−alkynyl compounds have been scarcely explored. The few cases that have been published show quite a normal behavior on the basis of the established trends in reactivity of metal−alkynyl complexes and metal hydrides (Scheme 1). For example, Bullock *et al.* have shown that relatively acidic transition-metal hydrides, such as Cp(CO)$_3$MH (M = Cr, Mo, W), protonate the β-carbon of metal−alkynyl complex [Cp(PMe$_3$)$_2$RuC≡CMe] rendering the cationic ruthenium vinylidene with a metal anion as counterion (Scheme 1a).[4] Opposite regiochemistry has been observed in the reaction of the same alkynyl complex with the hydridic metal hydride [Cp$_2$ZrHCl]$_n$ which provides the corresponding 1,2-dimetalloalkene (Scheme 1b).[5] Lukehart and co-workers have also nicely demonstrated that the Pt−H bond of [*trans*-PtH(PEt$_3$)$_2$(acetone)]$^+$ adds regioselectively across the C≡C triple bond of terminal alkynyl ligands to give homo- or heterodinuclear complexes containing bridging alkenylidene ligands (Scheme 1c).[6] The mechanism for these Pt−H addition reactions has not been fully proved, although it has been pointed out that the regiochemistry observed is that expected for having initial coordination of the C≡C multiple bond to the coordinatively unsaturated complex [HPt(PEt$_3$)$_2$]$^+$, followed by 1,2-addition of the polarized bond Pt$^{\delta-}$−H$^{\delta+}$ across the unsaturated

Chart 1



[†] Universidad de Zaragoza.

[‡] Universidad de La Rioja.

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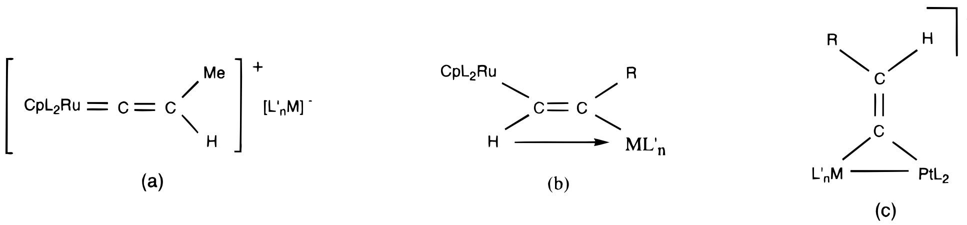
Scheme 1



a) $L'_nM = Cp(CO)_3M$ (M = Cr, Mo, W); L = PMe_3
b) $ML'_n = Cp_2ZrCl$; L = PMe_3; R = Me, H
c) $ML'_n = ML_2C{\equiv}CR$ (M = Pt, R = Ph, Me, H or M = Pd, Ni; R = Ph), $AuPPh_3$, AuL, $Cp(CO)_2Fe$ or $Cp(CO)_3W$; L = PEt_3

bond, with the H ligand adding to the β-carbon atom.

In the course of the last few years we have been investigating the ability of the very reactive anionic alkynyl substrates $[Pt(C{\equiv}CR)_4]^{2-}$ and $[cis\text{-}Pt(C_6F_5)_2(C{\equiv}CR)_2]^{2-}$ to stabilize polynuclear platinum complexes bearing alkynyl groups as unique bridging ligands.[7] Continuing our work in this field, here we describe the syntheses and characterization of the corresponding dianionic $[trans\text{-}Pt(C_6F_5)_2(C{\equiv}CR)_2]^{2-}$ species stabilized with NBu_4^+ cations as counterions and also report their reactions with $[trans\text{-}PtHL_2(acetone)]^+$ (L = PPh_3, PEt_3) in a 1:2 molar ratio. Surprisingly and in contrast with Lukehart's results, these reactions afford simple trinuclear zwitterionic complexes *trans,trans,trans*-$\{[Pt(C_6F_5)_2(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CR)_2](PtHL_2)_2\}$, in which the starting precursor $[RC{\equiv}CPtL_2C{\equiv}CR]^{2-}$ (L = C_6F_5) is only acting as a bridging diyne ligand between two different cationic $[trans\text{-}PtHL_2]^+$ fragments. The crystal structure of *trans,trans,trans*-$\{[Pt(C_6F_5)_2(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CPh)_2][PtH(PEt_3)_2]_2\}$ (**4b**) is reported.

Results and Discussion

While heteroleptic neutral alkynyl mononuclear complexes of platinum are relatively common,[1a,8] similar mixed organo−alkynyl anionic compounds are quite rare.[9] Recently, we have described the synthesis of anionic $(NBu_4)_2[cis\text{-}Pt(C_6F_5)_2(C{\equiv}CR)_2]$ (R = Ph, ${}^tBu$,[7b] $SiMe_3$[7e]) and have shown that they are suitable precursors for the synthesis of homo- and heterobinuclear complexes stabilized through a doubly alkynyl bridging system.[7c,e,f] In view of these results, we considered the preparation of the isomeric *trans* anionic species $[trans\text{-}Pt(C_6F_5)_2(C{\equiv}CR)_2]^{2-}$ of interest since the presence of π donor ligands in *trans* positions make them suitable precursors to di- or trinuclear mono μ-C≡CR complexes.

So, complexes $(NBu_4)_2[trans\text{-}Pt(C_6F_5)_2(C{\equiv}CR)_2]$ can be synthesized by prolongated treatment (24 h) of $trans\text{-}[Pt(C_6F_5)_2(tht)_2]$ (tht =tetrahydrothiophene) with an excess of LiC≡CR in diethyl ether (R = Ph, $SiMe_3$) or tetrahydrofuran (R = ${}^tBu$) (eq 1). This causes the displacement of both tht ligands and leads to the formation of the anionic species $[trans\text{-}Pt(C_6F_5)_2(C{\equiv}R)_2]^{2-}$, which, by addition of NBu_4Br, can be crystallized as NBu_4^+ salts in excellent yields (eq 1; see Experimental Section).

$$[trans\text{-}Pt(C_6F_5)_2(tht)_2] + LiC{\equiv}CR + NBu_4Br\ (excess) \rightarrow (NBu_4)_2[trans\text{-}Pt(C_6F_5)_2(C{\equiv}R)_2] + 2LiBr + 2tht \quad (1)$$

$$R = Ph\ (\mathbf{1}),\ SiMe_3\ (\mathbf{2}),\ {}^tBu\ (\mathbf{3})$$

Their analytical and spectroscopic data are given in the Experimental Section. In agreement with the *trans* geometry (D_{2h}) assigned to complexes **1**−**3**, their IR spectra show a single band (2077 cm^{-1} (**1**), 2014 cm^{-1} (**2**), 2091 cm^{-1} (**3**)) due to $\nu(C{\equiv}C)$ (B_{2u}) along with one band due to the X-sensitive mode of the C_6F_5 group.[10] As expected, the ${}^{19}F$ NMR spectra exhibit signals due to only one type of C_6F_5 ligand and the ${}^1H$ NMR spectra of **2** and **3** show only singlet resonances for the methyl groups of the trimethylsilyl or *tert*-butylalkynyl ligands, respectively. The ${}^{13}C$ NMR spectra of **1** show, in addition to the expected resonances due to phenyl and NBu_4 groups, two singlet signals at 103.9 and 121.5 ppm, which can be tentatively assigned to the acetylenic carbon resonances C_α and C_β, respectively. However, complexes **2** (R = $SiMe_3$) and **3** (R = ${}^tBu$) show only a singlet signal in the acetylenic region due to C_α or C_β atoms (δ 102.1, **2**; δ 107.5, **3**).

The *trans*-bis(alkynyl)bis(pentafluorophenyl)platinate(II) derivatives **1**−**3** can be regarded as simple metallo-1,4-diynes and should be expected to be highly nucleophilic and reactive due to the negative charges on the complexes. Since the Pt−H bond of the cationic hydride reagents $[trans\text{-}PtH(PEt_3)_2]^+$ is known to add, without exception, across the alkynyl C≡C triple bonds of metallo[6] or elementa (main group) substituted alkynyl compounds,[11] we decided initially to explore their reactivity toward these anionic substrata (**1**−**3**) in order to ascertain the nature of the resulting products, as well as the mechanism involved in this type of process.

Treatment of the *in situ* generated cationic hydride reagents $[trans\text{-}PtHL_2(acetone)](ClO_4)$ (L = PPh_3, PEt_3) (see Experimental Section) with $(NBu_4)_2[trans\text{-}Pt(C_6F_5)_2(C{\equiv}CR)_2]$ (R = Ph, $SiMe_3$, ${}^tBu$) in acetone solution at room temperature for R = Ph, or at low temperature

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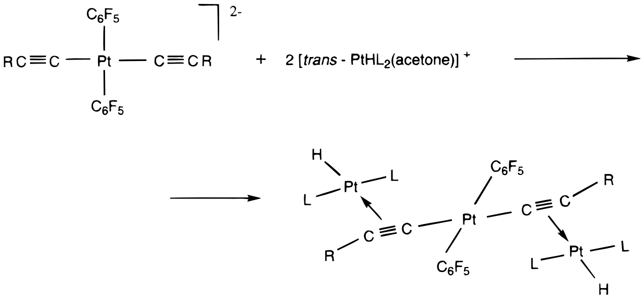
(−10 °C) for R = $SiMe_3$ or ${}^tBu$, in a 2:1 molar ratio, afforded, unexpectedly, the simple bis(μ-alkyne) trinuclear zwitterionic neutral complexes *trans*,*trans*,-*trans*-{[$Pt(C_6F_5)_2(\mu$-η^1:η^2-C≡CR$)_2$]($PtHL_2)_2$} in moderate (R = Ph, L = PPh_3 (**4a**), PEt_3 (**4b**)) or low yield (R = $SiMe_3$, L = PPh_3 (**5a**), PEt_3 (**5b**); R = ${}^tBu$, L = PEt_3 (**6b**)), according to eq 2. However, all attempts to synthesize the analogue derivative **6a** by treating $(NBu_4)_2$[*trans*-$Pt(C_6F_5)_2(C{\equiv}C^tBu)_2$] with 2 equiv of [*trans*-$PtH(PPh_3)_2$(acetone)$]^+$ were unsuccessful, since the reactions gave mixtures of products which have not been further investigated.



R = Ph; L = PPh_3 **4a**, PEt_3 **4b**
R = $SiMe_3$; L = PPh_3 **5a**, PEt_3 **5b**
R = ^{t}Bu; L = PEt_3 **6b** (2)

Compounds **4a**,**b**,**5a**,**b**, and **6b** were characterized by elemental analyses and spectroscopic methods (see Experimental Section). The IR spectra showed a similar pattern in the ν(Pt−H) and ν(C≡C) regions for all compounds. They exhibit one strong absorption in the 2145−2160 cm^{-1} range, which can be assigned to the ν(Pt−H) vibrations and which is typical for terminal hydride ligands.[12] The values observed in our complexes are lower than those reported for the chloride precursor *trans*-[$PtHClL_2$] (2220 cm^{-1} for L = PPh_3[13] and 2210 cm^{-1} for L = PEt_3[14]) but higher than those reported for complexes of the type *trans*-[PtH(C≡CR)-L_2][15] (2015−2050 cm^{-1}), suggesting that the alkynyl ligands bound in a π fashion exert a lower *trans* influence than when they are σ-bonded but higher than the Cl atom.

On the other hand, there is a very strong ν(C≡C) absorption (two for **4b** and **5a**) in the expected region (1836−1963 cm^{-1}) for side-on μ-η^1:η^2-C≡CR groups.[7] The ${}^{19}F$ and ${}^{31}P$ NMR spectra give evidence of highly symmetric systems. Thus, the ${}^{19}F$ NMR spectra exhibit the typical pattern of three signals in a 2:1:2 ratio (2 F_o:F_p:2 F_m; **4b**, **5b**, and **6b**) or two signals in a 2:3 ratio (2 F_o:F_p and 2 F_m; **4a** and **5a**) due to two equivalent C_6F_5 groups, for which the plane of coordination is a mirror plane. Moreover, the ${}^{31}P$ NMR spectra exhibit a singlet with platinum satellites, consistent with the *trans* arrangement of the phosphine ligands in the [$PtHL_2$] moieties. Finally, the presence of the hydride ligand is evidenced by a triplet (−9.08 to −11.39 ppm) due to coupling to two equivalent phosphine ligands (${}^2J_{H-P_{cis}}$ ≅ 13.5 Hz), accompanied by the expected platinum satellites. The relatively high values of ${}^1J_{Pt-H}$ (1080−1255 Hz) is indicative of the terminal nature of the hydride ligand[12] and the relatively low *trans* influence of the π-bonded alkynyl ligands. The low stability in solution of **4b**, **5**, and **6b** and low solubility of **4a** prevented their characterization by ${}^{13}C$ NMR spectroscopy.

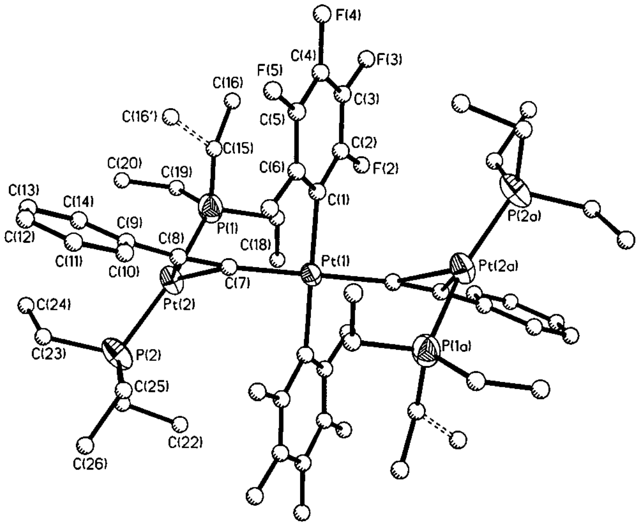


Figure 1. Molecular structure of complex **4b**, showing the atom-numbering scheme.

The definitive characterization of **4**−**6** as bis(η^2-alkyne) trinuclear complexes came from a single-crystal X-ray diffraction study on complex **4b**. A view of the molecular geometry of this complex is shown in Figure 1. A summary of the fundamental crystallographic data and stuctural parameters is given in Table 1. Final positional parameters appear in Table 2, and selected interatomic distances and angles are listed in Table 3. This study supports the spectroscopic data and confirms that the starting dianionic fragment [*trans*-$Pt(C_6F_5)_2$-$(C{\equiv}CPh)_2]^{2-}$ is acting only as a bridging diyne ligand between two identical cationic [*trans*-$PtH(PEt_3)_2]^+$ units [related by an inversion center located on Pt(1)], which indicates that the *trans* geometries around the platinum centers have been preserved throughout the reaction.

The central Pt(1) atom is located in an approximately square-planar environment formed by the two C_{ipso} atoms of C_6F_5 groups (mutually *trans*) and one C_α carbon atom of each C≡CPh ligand, the Pt(1)-C distances being similar to those found in the anions {*cis*-[$Pt(C_6F_5)_2(\mu$-η^1:μ^2-C≡CPh$)_2$]Ag(PPh_3)$\}^-$ [16] or [*cis*-Pt-$(C_6F_5)_2(\mu$-η^1:η^2-C≡CSiMe$_3)_2ML_n]^-$ [ML_n = Pd(η^3-C_3H_5),[7e] $HgBr_2$[7f]]. The coordination of the terminal platinum atoms Pt(2) and Pt(2a) can be described as distorted

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Table 1. Crystallographic Data and Structure Refinement Parameters for *trans,trans,trans*-$\{[Pt(C_6F_5)_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{\equiv}CPh)_2][PtH(PEt_3)_2]_2\}$ (4b)

empirical formula	$C_{52}H_{72}F_{10}P_4Pt_3$
fw	1596.30
cryst system	triclinic
space group	$P\bar{1}$
unit cell dimens	$a = 10.438(3)$ Å, $\alpha = 89.98(2)°$ $b = 11.863(4)$ Å, $\beta = 73.88(2)°$ $c = 13.071(4)$ Å, $\gamma = 69.68(2)°$
V	1449.81 Å^3
Z	2
D(calc)	1.10 Mg/m^3
abs coeff	7.39 mm^{-1}
F(000)	768.0
cryst size	0.23 × 0.34 × 0.11 mm
temp	200(1) K
wavelength	0.710 73 Å
2θ range for data collcn	4−47°
index ranges	$-12 \leq h \leq 12, -13 \leq k \leq 13, 0 \leq l \leq 15$
reflcns collcd	4329
indepdt reflcns	3863 ($R_{\text{int}} = 0.0347$)
data/restraints/params	2999/0/324
goodness-of-fit indicator^a	1.131
R indices [2999 reflcns with $I > 2\sigma(I)$]^a	$R = 0.0325$, w$R = 0.0437$
R indices (all 3863 data)^a	$R = 0.0462$, w$R = 0.0473$
mean, max |shift/esd|, final cycle	0.000, 0.000
largest diff peak and hole	1.15 and −0.91 e/Å^3

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

square-planar. The Pt(2) atom is linked to two phosphine ligands (mutually *trans*) and π bonded to the carbon−carbon triple bond of the C(7)−C(8)−Ph alkynyl group with the fourth position occupied by the hydrido ligand. This latter atom has not been directly located by this analysis, but its position (*trans* to the η^2-alkyne interaction) can be inferred from the NMR data and from the arrangement of the heavy atoms. The Pt(2)−P distances, 2.274(3) and 2.289(3) Å, fall in the range of distances usually observed in Pt(II) phosphine complexes.[12b-f,15] The coordination of the alkynyl fragment to Pt(2) causes, as expected, the reduction of the P(1)−Pt(2)−P(2) angle to the value of 165.5(1)° due to the lesser steric demand of the hydride ligand.

The $\mu\text{-}\eta^1\text{:}\eta^2$-C(7)−C(8)−Ph ligand is unsymmetrically bonded to Pt(2) with the C_β atom closer to Pt(2) [Pt(2)−C(8) = 2.265(10) Å] than the C_α atom [Pt(1)−C(7) = 2.443(10) Å]. This contrasts with the symmetrical π linkage found in the dinuclear derivative *cis,trans*-$[(CO)(C_6F_5)_2Pt(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{\equiv}CPh)Pt(C{\equiv}CPh)(PPh_3)_2]$ (**7**)[17] and suggests some degree of participation of the metal-substituted vinylidene resonance structure B (Chart 2B), in addition to the dominant contribution of the π-complex A (Chart 2A).[2d,18]

In accord with this consideration, (i) the Pt(1)···Pt(2) distance of 3.904(2) Å is longer than that observed in the related monoalkynyl bridged complex **7**[17] and (ii) the acetylenic skeleton Pt(1)−C(7)−C(8)−C(9) acquires a *cis*-bent arrangement in such a way that the deviation from linearity is more pronounced at C_β [C(7)−C(8)−C(9) = 156.6(11)°] than at the C_α [Pt−C(7)−C(8) = 169.1(8)°]. As expected, the C(7)−C(8) vector is oriented essentially perpendicular to the local coordination plane of Pt(2) [the angle formed by the vector defined by Pt(2) and the midpoint of the C≡C bond and the C(7)−C(8) vector is 81.4(5)°] and is inclined by 1.01(8)° to this

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for *trans,trans,trans*-$\{[Pt(C_6F_5)_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{\equiv}CPh)_2][PtH(PEt_3)_2]_2\}$ (4b)

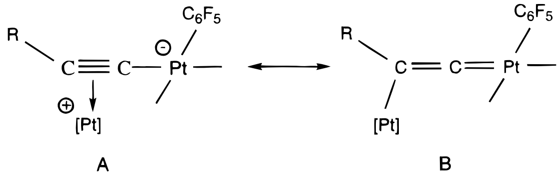
	x	*y*	*z*	U(eq)^a
Pt(1)	0	5000	5000	32(1)
Pt(2)	552(1)	3116(1)	2360(1)	44(1)
P(1)	−1620(3)	3117(2)	3344(2)	52(1)
P(2)	2583(3)	2948(3)	1022(2)	56(1)
F(2)	−3038(5)	4902(5)	6458(4)	56(2)
F(3)	−3690(7)	3495(7)	7914(6)	89(4)
F(4)	−1573(8)	1694(8)	8452(7)	126(5)
F(5)	1205(7)	1431(7)	7537(7)	105(4)
F(6)	1897(5)	2854(5)	6081(5)	61(3)
C(1)	−507(9)	3943(7)	6191(7)	40(4)
C(2)	−1927(11)	4056(9)	6691(8)	55(5)
C(3)	−2296(11)	3320(11)	7436(9)	64(5)
C(4)	−1244(14)	2421(11)	7722(10)	80(6)
C(5)	166(11)	2298(9)	7263(9)	65(5)
C(6)	484(10)	3067(8)	6517(8)	47(4)
C(7)	1069(9)	3488(7)	4013(7)	36(3)
C(8)	1797(9)	2466(8)	3551(7)	44(4)
C(9)	2906(11)	1261(9)	3359(8)	60(5)
C(10)	4077(13)	1082(11)	3787(9)	86(6)
C(11)	5182(16)	15(15)	3605(12)	118(8)
C(12)	5159(19)	−911(14)	3033(13)	116(9)
C(13)	4041(18)	−794(12)	2604(12)	104(8)
C(14)	2881(14)	319(8)	2756(9)	78(6)
C(15)	−1521(12)	2196(10)	4467(11)	74(6)
C(16)	−2935(25)	2069(24)	5015(20)	78(12)
C(16′)	−804(31)	938(27)	4453(26)	105(15)
C(17)	−2961(10)	4612(9)	3950(10)	67(5)
C(18)	−3296(14)	5451(11)	3080(13)	95(7)
C(19)	−2508(15)	2537(14)	2559(13)	98(8)
C(20)	−1704(24)	1400(16)	1912(17)	146(13)
C(21)	2234(15)	3948(17)	−20(11)	109(10)
C(22)	1532(18)	5304(14)	444(14)	105(9)
C(23)	3447(16)	1428(14)	240(12)	105(8)
C(24)	2550(18)	941(15)	−143(14)	125(10)
C(25)	4024(11)	3132(13)	1394(9)	77(6)
C(26)	5384(14)	3052(18)	458(11)	115(10)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for *trans,trans,trans*-$\{[Pt(C_6F_5)_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{\equiv}CPh)_2][PtH(PEt_3)_2]_2\}$(4b)

Pt(1)−C(1)	2.068(9)	Pt(1)−C(7)	1.984(8)
Pt(2)−P(1)	2.274(3)	Pt(2)−P(2)	2.289(3)
Pt(2)−C(7)	2.443(10)	Pt(2)−C(8)	2.265(10)
C(7)−C(8)	1.232(11)	C(8)−C(9)	1.462(12)
C(1)−Pt(1)−C(7)	87.7(3)	P(1)−Pt(2)−P(2)	165.5(1)
P(1)−Pt(2)−C(7)	89.6(2)	P(2)−Pt(2)−C(7)	104.8(2)
P(1)−Pt(2)−C(8)	99.5(2)	P(2)−Pt(2)−C(8)	92.1(2)
C(7)−Pt(2)−C(8)	30.0(3)	Pt(1)−C(7)−Pt(2)	123.4(4)
Pt(1)−C(7)−C(8)	169.1(8)	Pt(2)−C(7)−C(8)	66.9(6)
Pt(2)−C(8)−C(7)	83.0(7)	Pt(2)−C(8)−C(9)	120.3(7)
C(7)−C(8)−C(9)	156.6(11)		

Chart 2



[Pt] = *trans*-$PtH(PEt_3)_2$

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plane [least-squares plane defined by Pt(2), P(1), P(2), and the midpoint of C(7)−C(8)].

Concluding Remarks

As noted in the Introduction, metallo or elementa (main group) substituted alkynyl substrates insert easily into the Pt−H bond of [*trans*-PtH(PEt$_3$)$_2$(solvento)]$^+$ to give *cis* addition complexes as the kinetic products. It has been suggested that the first step in these reactions, as well as in the insertion of alkynes into a Pt−H bond of related complexes,[19] is the formation of a complex in which the C≡C triple bond of the alkyne (or alkynyl fragment) is η^2-coordinated to the metal center. In this context, the synthesis of the trinuclear complexes **4**−**6** is unexpected and the structure of **4b** provides a strong indication that such species exist. The dianionic nature of the starting precursors [*trans*-Pt(C$_6$F$_5$)$_2$(C≡CR)$_2$]$^{2-}$, and perhaps the presence of C$_6$F$_5$ groups, seems to be influential on the behavior of **1**−**3** as simple 3-platinapenta-1,4-diyne ligands toward the very reactive species [*trans*-PtHL$_2$(acetone)]$^+$. However, it should be noted that the influence of the electronic factor is not clear. We have recently found[20] that the reaction between *cis*-[Pt(C$_6$F$_5$)$_2$(CO)(THF)] (THF = tetrahydrofuran) and *trans*-[PtH(C≡CPh(PPh$_3$)$_2$] affords the binuclear μ-phenylethenylidene complex [(OC)(C$_6$F$_5$)$_2$Pt(μ-C≡C(Ph)H)Pt(PPh$_3$)$_2$] (**8**). The formation of this complex **8** could be the result of an initial alkynylation of the *cis*-[Pt(C$_6$F$_5$)$_2$(CO)] fragment and simultaneous formation of a binuclear zwitterionic species *cis,trans*-[(OC)(C$_6$F$_5$)$_2$Pt$^-$(μ-C≡CPh)Pt$^+$H(PPh$_3$)$_2$], which probably evolves *via cis,cis* isomerization and *cis* 1,2 addition to yield the final μ-phenylethenylidene complex **8**.

Experimental Section

All manipulations were performed under N$_2$ atmosphere using standard Schlenk techniques. All solvents were distilled from appropriate drying agents. Elemental analyses of C, H, and N and IR spectra were obtained as described elsewhere.[7] ^{1}H, ^{19}F, ^{13}C, and ^{31}P NMR spectra were recorded on either a Varian XL-200 or a Bruker ARX 300 instrument. Chemical shifts are reported in ppm relative to external standards (SiMe$_4$, CFCl$_3$, and 85% H$_3$PO$_4$). Conductivities were measured in *ca.* 5×10^{-4} M acetone solutions using a Phillips 9501/01 conductimeter, and mass spectra were obtained in a VG Autospec spectrometer. Starting materials *trans*-[Pt(C$_6$F$_5$)$_2$(tht)$_2$][21] and *trans*-[PtHClL$_2$] (L = PPh$_3$,[13b] PEt$_3$[13c]) were prepared according to literature procedures. AgClO$_4$ was prepared by following a method previously described[22] but using Ag$_2$CO$_3$ as precursor.

Preparation of (NBu$_4$)$_2$[*trans*-Pt(C$_6$F$_5$)$_2$(C≡CR)$_2$] (R = Ph (1), SiMe$_3$ (2), ^{t}Bu (3)). A typical preparation for complex **1** was as follows: A solution of Li^{n}Bu in hexane (2.36 M, 1.47 mL, 3.47 mmol) was added dropwise during 5 min to a diethyl ether solution (30 mL) of PhC≡CH (0.36 g, 3.48 mmol) at −10 °C. After 20 min of stirring, *trans*-[Pt(C$_6$F$_5$)$_2$(tht)$_2$] (0.491 g, 0.696 mmol) was added and the mixture stirred for 24 h at room temperature. The resulting white suspension was evaporated to dryness, and the residue was treated with deoxygenated water (50 mL). The aqueous solution was filtered and added dropwise to a solution of NBu$_4$Br (0.570 g, 1.532 mmol) in water (10 mL), causing the precipitation of **1** as a white solid, which was filtered off, washed repeatedly with deoxygenated water, and, finally, air dried (0.443 g, 87% yield). Anal. Calcd for C$_{60}$H$_{82}$F$_{10}$N$_2$Pt: N, 2.30; C, 59.25; H, 6.79. Found: N, 2.06; C, 58.96; H, 6.68. IR (cm^{-1}): ν(C≡C) 2077 (vs); ν(C$_6$F$_5$)$_{\text{X-sensitive}}$ 765 (s). ^{19}F NMR (CD$_3$COCD$_3$): δ −111.5 (d, F$_o$, $^3J_{\text{Pt-Fo}}$ = 415 Hz); −170.5 (t, F$_p$, $^3J_{\text{F-F}}$ = 20.5 Hz); −168.5 (m, F$_m$). ^{13}C NMR (CD$_3$COCD$_3$): δ 150−135 (br, C$_6$F$_5$); 132.0 (C$_{\text{ipso}}$, Ph); 130.4, 126.8, 121.5 (s, Ph); 120.1 (s, C$_\beta$, platinum satellites not observed); 103.9 (s, C$_\alpha$, platinum satellites not observed); 58.0 (s, N−CH$_2$, ^{n}Bu); 23.2 (s, −CH$_2$−, ^{n}Bu); 19.0 (s, −*C*H$_2$−CH$_3$, ^{n}Bu); 12.6 (s, CH$_3$, ^{n}Bu). Λ_M (in acetone) = 182 Ω^{-1} cm^2 mol^{-1}.

Complexes **2** and **3** were obtained similarly but using a larger excess of LiC≡CR (LiC≡CR/Pt = 8/1), and in the case of **3**, THF was used as solvent.

2: Li^{n}Bu (2.36 M, 2.40 mL, 5.67 mmol), SiMe$_3$C≡CH (0.56 g, 5.67 mmol), *trans*-[Pt(C$_6$F$_5$)$_2$(tht)$_2$] (0.5 g, 0.7 mmol); 0.400g, 78% yield. Anal. Calcd for C$_{54}$H$_{90}$F$_{10}$N$_2$PtSi$_2$: N, 2.32; C, 53.67; H, 7.51. Found: N, 2.27; C, 53.61; H, 8.07. IR (cm^{-1}): ν(C≡C) 2014 (s, sh); ν(C$_6$F$_5$)$_{\text{X-sensitive}}$ 759 (s). ^{1}H NMR (CDCl$_3$): δ −0.16 (s, SiMe$_3$); 0.89 [t, −CH$_3$, ^{n}Bu]; 1.29 [m, −CH$_2$, ^{n}Bu]; 1.59 [m, −CH$_2$−, ^{n}Bu]; 3.35 [m, NCH$_2$, ^{n}Bu]. ^{19}F NMR (CDCl$_3$): δ −112.1 (d, F$_o$, $^3J_{\text{Pt-Fo}}$ = 339 Hz); −169.8 (t, F$_p$, $^3J_{\text{F-F}}$ = 19.3 Hz); −169.2 (m, F$_m$). ^{13}C NMR (CD$_3$COCD$_3$, −50 °C): δ 102.1 (s, C$_\alpha$ or C$_\beta$); 57.3 (s, N-CH$_2$, ^{n}Bu); 22.7 (s, −CH$_2$−, ^{n}Bu); 18.7 (s, −*C*H$_2$−CH$_3$, ^{n}Bu); 12.5 (s, CH$_3$, ^{n}Bu); 0.81 (s, SiMe$_3$). Λ_M (in acetone) = 142 Ω^{-1} cm^2 mol^{-1}.

3: Li^{n}Bu (2.36 M, 1.83 mL, 4.31 mmol), ^{t}BuC≡CH (0.35 g, 4.31 mmol), *trans*-[Pt(C$_6$F$_5$)$_2$(tht)$_2$] (0.38 g, 0.54 mmol); 0.335 g, 90% yield. Anal. Calcd for C$_{56}$H$_{90}$F$_{10}$N$_2$Pt: N, 2.38; C, 57.18; H, 7.71. Found: N, 2.20; C, 56.91; H, 8.01. IR (cm^{-1}): ν(C≡C) 2091 (vs); ν(C$_6$F$_5$)$_{\text{X-sensitive}}$ 756 (s). ^{1}H NMR (CD$_3$COCD$_3$): δ 0.97 (s, ^{t}Bu); 0.89 [t, −CH$_3$, ^{n}Bu]; 1.35 [m, −CH$_2$, ^{n}Bu]; 1.78 [m, −CH$_2$−, ^{n}Bu]; 3.54 [m, NCH$_2$, ^{n}Bu]. ^{19}F NMR (CD$_3$COCD$_3$): δ −110.0 (d, F$_o$, $^3J_{\text{Pt-Fo}}$ = 398 Hz); −171.8 (t, F$_p$, $^3J_{\text{F-F}}$ = 19.5 Hz); −169.8 (m, F$_m$). ^{13}C NMR (CD$_3$COCD$_3$): δ 107.5 (s, C$_\alpha$ or C$_\beta$); 59.2 (s, N−CH$_2$, ^{n}Bu); 33.4 (s, ^{t}Bu); 24.3 (s, −CH$_2$−, ^{n}Bu); 19.8 (s, −*C*H$_2$−Me, ^{n}Bu); 13.4 (s, CH$_3$, ^{n}Bu). Λ_M (in acetone) = 169 Ω^{-1} cm^2 mol^{-1}.

Preparation of *trans,trans,trans*-{[Pt(C$_6$F$_5$)$_2$(μ-η^1:η^2-C≡CPh)$_2$](PtHL$_2$)$_2$} (L = PPh$_3$ (4a), PEt$_3$ (4b)). To a filtered solution of 0.198 mmol of [*trans*-PtH(PPh$_3$)$_2$(acetone)]-(ClO$_4$) (prepared from 0.15 g (0.198 mmol) of *trans*-[PtHCl-(PPh$_3$)$_2$] and AgClO$_4$ (0.041 g, 0.198 mmol) in 30 mL of acetone) was added 0.115 g (0.095 mmol) (0.95 molar equiv) of **1**, giving a deep yellow solution. After 10 min of stirring at room temperature, a yellow solid precipitated. The mixture was stirred for 30 min and then concentrated to *ca.* 10 mL. The solid was filtered off, washed with acetone (1 mL), and air dried (0.119 g, 58% yield). Anal. Calcd for C$_{100}$H$_{72}$F$_{10}$P$_4$Pt$_3$: C, 55.28; H, 3.34. Found: C, 54.96; H, 3.69. IR (cm^{-1}): ν(Pt−H) 2145 (s); ν(C≡C) 1932 (vs); ν(C$_6$F$_5$)$_{\text{X-sensitive}}$, this absorption can not be assigned unambiguously. FAB mass spectrum: molecular peak not observed, *m/z* 719, [Pt(PPh$_3$)$_2$]$^+$, 100%. ^{1}H NMR (CDCl$_3$): δ 7.27 (m, 60 H, PPh$_3$); 6.70 (t, 2 H$_p$, Ph), 6.44 (t, 4 H$_m$, Ph); 5.70 (d, 4 H$_o$, Ph); −9.08 (t, 2 H, Pt−H, $^1J_{\text{Pt-H}}$ = 1088 Hz, $^2J_{\text{P-H}}$ = 13.4 Hz). ^{19}F NMR (CDCl$_3$): δ −109.2 (d, F$_o$, $^3J_{\text{Pt-Fo}}$ = 351 Hz); −165.7 (m, F$_p$ and F$_m$). ^{31}P NMR (CDCl$_3$): δ 24.11 (s, $^1J_{\text{Pt-P}}$ = 2986 Hz).

Using a similar procedure, the reaction between *trans*-[PtHCl(PEt$_3$)$_2$] (0.120 g, 0.256 mmol), AgClO$_4$ (0.053 g, 0.256 mmol), and (NBu$_4$)$_2$[*trans*-Pt(C$_6$F$_5$)$_2$(C≡CPh)$_2$] (0.148 g, 0.122 mmol) gave **4b** as a yellow solid (0.101 g, 52% yield). Anal. Calcd for C$_{52}$H$_{72}$F$_{10}$P$_4$Pt$_3$: C, 39.13; H, 4.55. Found: C, 39.46; H, 4.60. IR (cm^{-1}): ν(Pt−H) 2151 (s); ν(C≡C) 1989 (m), 1949 (vs). FAB mass spectrum: molecular peak not observed, *m/z* 431, [Pt(PEt$_3$)$_2$]$^+$, 100%. ^{1}H NMR (CDCl$_3$): δ 7.29, 7.10 (m, 10 H, Ph); 1.64 (m, 24 H, CH$_2$, PEt$_3$), 0.95 (m, 36 H, CH$_3$, PEt$_3$); −9.6 (t, 2 H, Pt−H, $^1J_{\text{Pt-H}}$ = 1255 Hz, $^2J_{\text{P-H}}$ = 13.5 Hz). ^{19}F

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NMR ($CDCl_3$): δ -113.0 (d, F_o, $^3J_{Pt-Fo} = 346$ Hz; -166.8 (t, F_p, $^3J_{F-F} = 20$ Hz); -166.1 (m, F_m). ^{31}P NMR ($CDCl_3$): δ 20.44 (s, $^1J_{Pt-P} = 2640$ Hz).

Preparation of *trans,trans,trans*-$\{[Pt(C_6F_5)_2(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CSiMe_3)_2](PtHL_2)_2\}$ (L = PPh_3 (5a), PEt_3 (5b)). To an acetone solution (40 mL) of *trans*-$[PtHCl(PPh_3)_2]$ (0.222 g, 0.29 mmol) was added 0.060 g (0.290 mmol) of $AgClO_4$, and the mixture was stirred at room temperature for 1 h. The resulting AgCl was removed by filtration through Celite, and the filtrate was concentrated to *ca.* 15 mL and cooled to -10 °C. Then, 0.178 g (0.140 mmol) of **2** was added, resulting in the formation of a yellow solution. The mixture was stirred for 20 min, and the white solid formed was filtered off and recrystallized from CH_2Cl_2/hexane. Under these conditions **5a** crystallizes with one molecule of CH_2Cl_2 (observed by ^1H NMR) (0.038 g, 12% yield). Anal. Calcd for $C_{95}H_{82}F_{10}P_4Pt_3Si_2Cl_2$: C, 50.71; H, 3.67. Found: C, 50.75; H, 3.19. IR (cm^{-1}): ν(Pt−H) 2160 (m); ν(C≡C) 1872 (sh), 1836 (s, br). FAB mass spectrum: molecular peak not observed, *m/z* 719, $[Pt(PPh_3)_2]^+$, 100%. ^1H NMR ($CDCl_3$): δ 7.52 (m, 24 H, Ph, PPh_3); 7.38 (m, 36 H, Ph, PPh_3); -1.09 (s, 18 H, $SiMe_3$); -10.39 (t, 2 H, Pt−H, $^1J_{Pt-H} = 1088.6$ Hz, $^2J_{P-H} = 13.5$ Hz). ^{19}F NMR ($CDCl_3$): δ -111.5 (dm, F_o, $^3J_{Pt-Fo} = 360$ Hz); -165.2 (m, F_p and F_m). ^{31}P NMR ($CDCl_3$): δ 22.90 (s, $^1J_{Pt-P} = 3006$ Hz).

Complex **5b** was prepared by following a similar procedure using *trans*-$[PtHCl(PEt_3)_2]$ (0.161 g, 0.344 mmol), $AgClO_4$ (0.07 g, 0.344 mmol), and **2** (0.200 g, 0.165 mmol) as starting materials. The white solid was not recrystallized (0.052 g, 20% yield). Anal. Calcd for $C_{46}H_{80}F_{10}P_4Pt_3Si_2$: C, 34.78; H, 5.07. Found: C, 35.05; H, 5.22. IR (cm^{-1}): ν(Pt−H) 2148 (s); ν(C≡C) 1886 (vs). FAB mass spectrum: *m/z* 1587 ($[M]^+$, 20%), 1420 ($[M - C_6F_5]^+$, 15%), 1009 ($[Pt_2(C_6F_5)(PEt_3)_3(C{\equiv}CSiMe_3)]^+$, 51%), 890 ($[Pt_2(C_6F_5)(PEt_3)_2(C{\equiv}CSiMe_3)]^+$, 47%), 695 ($[Pt(C_6F_5)(PEt_3)_2(C{\equiv}CSiMe_3)]^+$, 54%), 597 ($[Pt(C_6F_5)(PEt_3)_2]^+$, 90%), 431 ($[Pt(PEt_3)_2]^+$, 100%). ^1H NMR ($CDCl_3$): δ 1.67 (m, 24 H, CH_2, PEt_3), 0.94 (m, 36 H, CH_3, PEt_3); -0.13 (s, 18 H, $SiMe_3$), -11.12 (t, 2 H, Pt−H, $^1J_{Pt-H} = 1249$ Hz, $^2J_{P-H} = 13.6$ Hz). ^{19}F NMR ($CDCl_3$): δ -113.2 (dm, F_o, $^3J_{Pt-Fo} = 371$ Hz; -167.4 (t, F_p, $^3J_{F-F}$ 19.9 Hz); -166.7 (m, F_m). ^{31}P NMR ($CDCl_3$): δ 19.80 (s, $^1J_{Pt-P} = 2683$ Hz).

Preparation of *trans,trans,trans*-$\{[Pt(C_6F_5)_2(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}C^tBu)_2][PtH(PEt_3)_2]_2\}$ (6b). To a cooled (-10 °C) solution (4 mL) of [*trans*-$PtH(PEt_3)_2$(acetone)](ClO_4), prepared from 0.200 g (0.428 mmol) of *trans*-$[PtHCl(PEt_3)_2]$ and $AgClO_4$ (0.089 g, 0.428 mmol) in acetone (40 mL), was added an acetone solution (5 mL) of **3** (0.201 g, 0.171 mmol). The mixture was stirred for 15 min, and then the resulting yellow solid was filtered off, washed with cold acetone (1 mL, -20 °C), and air dried (0.101 g, 38% yield). Anal. Calcd for $C_{48}H_{80}F_{10}P_4Pt_3$: C, 37.04; H, 5.18. Found: C, 36.70; H, 5.15. IR (cm^{-1}): ν(Pt−H) 2147 (s); ν(C≡C) 1955 (s, br). FAB mass spectrum: molecular peak not observed, *m/z* 593 ($[Pt(C{\equiv}C^tBu)_2(PEt_3)_2]^+$, 38%), 511 ($[Pt(C{\equiv}C^tBu)(PEt_3)_2]^+$, 35%), 431 ($[Pt(PEt_3)_2]^+$, 100%). ^1H NMR ($CDCl_3$): δ 1.70 (m, 24 H, CH_2, PEt_3); 0.98 (m, 36 H, CH_3, PEt_3); 0.84 (s, 18 H, ^tBu); -9.90 (t, 2 H, Pt−H, $J_{Pt-H} = 1147$ Hz, $^2J_{P-H} = 13.5$ Hz). ^{19}F NMR ($CDCl_3$): δ 112.5 (d, F_o, $^3J_{Pt-Fo} = 378$ Hz); -168.2 (t, F_p, $^3J_{F-F} = 20.3$ Hz; -167.1 (m, F_m). ^{31}P NMR ($CDCl_3$): δ 19.48 (s, $J_{Pt-P} = 2708$ Hz).

X-ray Crystal Structure Determination of *trans,trans,trans*-$\{[Pt(C_6F_5)_2(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CPh)_2][PtH(PEt_3)_2]_2\}$ (4b). Single crystals of **4b** in the form of pale yellow plates were obtained by slow diffusion of *n*-hexane into a $CHCl_3$ solution of the bulk solid at room temperature. A representative crystal was fixed with epoxy on top of a glass fiber and transferred to the cold gas stream (200 K) of a Siemens STOE/AED2 four-circle diffractometer (graphite-monochromated Mo Kα radiation). Cell constants were obtained from setting angles of 25 carefully measured reflections in the range $20 < 2\theta < 28°$. Data were collected by the $\omega/2\theta$ method in the range $4 < 2\theta < 47°$. Three check reflections, measured after every 360 min of beam exposure, showed no systematic variations in decay. Data were corrected for Lorentz and polarization effects. An absorption correction based on ψ-scans (9 reflections) was applied, with transmission factors of 1.000 and 0.498. The structure was solved by the heavy-atom method, which revealed the positions of the Pt atoms. The remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses and subjected to anisotropic full-matrix least-squares refinement. One of the C atoms, C(16), was found to be disordered at half-occupacy over two sites. Hydrogen atoms were included at calculated positions (C−H = 0.96 Å). A total of 2999 reflections with $I > 2\sigma I_o$ were used to refine 324 parameters. Final residuals were $R = 0.0325$ and $wR = 0.0437$. The highest peaks in the final difference map (≤ 1.15 e Å^{-3}) are close to one of the Pt atoms and have no chemical significance.

All calculations were performed on a local area VAX cluster (VAX/VMS V5.5) with the Siemens SHELXTL PLUS software package.[23]

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Supporting Information Available: Tables of anisotropic thermal parameters, hydrogen atom positional parameters and *U* values, and complete bond lengths and angles for **4b** (4 pages). Ordering information is given on any current masthead page.

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[23] SHELXTL-PLUS, *Software Package for the Determination of Crystal Structures*, Release 4.0; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990.