1014 *Organometallics* **1996,** *15,* 1014−1022

Unusual Formation and Reactivity of a Diplatinum μ-Phenylethenylidene Complex: Synthesis and Structures of *cis,cis*-$[(PPh_3)(C_6F_5)_2Pt(\mu\text{-}\eta^1\text{:}\eta^3\text{-CHPhCCO})Pt(PPh_3)_2]$ and *cis,cis*-$[(PPh_3)_2Pt\{\mu\text{-}\eta^2(C,S)\text{:}\eta^1(C)\text{-C(SPh)(CH}_2\text{Ph)}\}Pt(C_6F_5)_2(CO)]$ Dinuclear Compounds

Irene Ara,[†] Jesús R. Berenguer,[‡] Juan Forniés,*[,†] Elena Lalinde,*[,‡] and
Milagros Tomás[†]

*Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón,
Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain, and Departamento de Química,
Universidad de La Rioja, 26001 Logroño, Spain*

Received November 17, 1995[⊗]

The μ-phenylethenylidene-bridged diplatinum complex $[(OC)(C_6F_5)_2Pt(\mu\text{-C}{=}\text{CHPh})Pt(PPh_3)_2]$, **1**, synthesized from the reaction between the mononuclear alkynyl−hydride *trans*-$[Pt(C{\equiv}CPh)H(PPh_3)_2]$ and *cis*-$[Pt(C_6F_5)_2(CO)(THF)]$ (THF = tetrahydrofuran), displays a remarkable reactivity associated with the μ-vinylidene ligand under mild conditions. The reaction of **1** with PPh_3 (molar ratio 1:1) produces an unprecedented reductive coupling of the CO ligand and the vinylidene bridging group to give the compound *cis,cis*-$[(PPh_3)(C_6F_5)_2Pt(\mu\text{-}\eta^1\text{:}\eta^3\text{-CHPhCCO})Pt(PPh_3)_2]$, **2**, which contains an expanded, unsaturated benzylideneketene bridging ligand. On the other hand, treatment of **1** with PhSH generates the new diplatinum compound *cis,cis*-$[(PPh_3)_2Pt\{\mu\text{-}\eta^2(C,S)\text{:}\eta^1(C)\text{-C(SPh)(CH}_2\text{Ph)}\}Pt(C_6F_5)_2(CO)]$, **3**, formed by a formal addition of the PhSH to the carbon−carbon double bond of the vinylidene group in **1**. The structures of **2** and **3** have been fully elucidated by X-ray diffraction studies.

Introduction

Organometallic complexes in which two or more metals are linked by a hydrocarbon bridge have been extensively studied as models for species postulated to be present in several important metal-catalyzed reactions.[1] Investigation on the ways in which metal−carbon and carbon−carbon bonds are made and broken in these soluble complexes can provide useful information about similar processes that occur in homogeneous catalytic reactions and on metal surfaces. Vinylidene-bridged complexes are a type of C_2-bridged compounds which are attracting considerable interest.[2] Recent reports demonstrate interesting chemistry at μ-alkenylidene ligands,[2bc,3] and furthermore, surface-bound vinylidene ligands have been proposed to play a key role in hydrocarbon chain growth in the heterogeneously catalyzed Fischer−Tropsch process ("McCandlish mechanism").[3f−h,4]

Methods for preparing this type of compound are generally based on (a) addition of an electrophile to a bridging acetylide,[2de,5] (b) metal coordination of adequate metal−ligand fragments to a terminal vinylidene ligand,[6] or (c) generation of a vinylidene fragment from *gem*-dihalo olefins in the presence of a potential or actual binuclear system.[3bc,7] Another route to such species involves the isomerization of terminal alkynes.[2c,8] This last process (acetylene to vinylidene tautomerism), thoroughly investigated on mononuclear metal systems,[2ab,9] has been much less studied on binuclear species and is not well understood. Theoretical calcula-

---

[†] Universidad de Zaragoza.

[‡] Universidad de La Rioja.

[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1996.

(1) For reviews of organometallic hydrocarbon-bridged complexes, see: (a) Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. *Chem. Rev.* **1983**, *83*, 135. (b) Moss, J. R.; Scott, L. G. *Coord. Chem. Rev.* **1984**, *60*, 171. (c) Casey, C. P.; Audett, J. D. *Chem. Rev.* **1986**, *86*, 339. (d) Beck, W.; Niemer, B.; Wiesser, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 923 and references given therein.

(2) (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59. (b) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (c) García Alonso, F. J.; Riera, V.; Ruiz, M. A.; Tiripicchio, A.; Tiripicchio Camellini, M. *Organometallics* **1992**, *11*, 370. (d) Froom, S. F. T.; Green, M; Mercer, R. J.; Nagle, K. R.; Orpen, A. G.; Rodrigues, R. A. *J. Chem. Soc., Dalton Trans.* **1991**, 3171. (e) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Rodríguez, L. *Organometallics* **1993**, *12*, 4219. (f) Akita, M.; Terada, M.; Moro-Oka, Y. *Organometallics* **1991**, *10*, 2961. (g) Rubaylo, A. I.; Senotrusov, D. G.; Paulenko, N. I.; Kovalenko, S. V.; Antonova, A. B.; Johansson, A. A.; Avramov, P. V. *J. Mol. Struct.* **1993**, *293*, 81.

(3) (a) Conole, G. C.; Froom, S. F. T.; Green, M.; McPartlin, M. *J. Chem. Soc., Chem. Commun.* **1989**, 92. (b) Jacobsen, E. N.; Bergman, R. G. *Organometallics* **1984**, *3*, 329. (c) Jacobsen, E. N.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 2023. (d) Yamazaki, H.; Wakatsuki, Y. *J. Organomet. Chem.* **1984**, *272*, 251. (e) Casey, C. P.; Marder, S. R. *Organometallics* **1985**, *4*, 411. (f) Hoel, E. L.; Ansell, G. B.; Leta, S. *Organometallics* **1984**, *3*, 1633. (g) Hoel, E. L.; Ansell, G. B.; Leta, S. *Organometallics* **1986**, *5*, 585. (h) Hoel, E. L. *Organometallics* **1986**, *5*, 587. (i) Casey, C. P.; Austin, E. A. *Organometallics* **1986**, *5*, 584. (j) Casey, C. P.; Austin, E. A. *J. Am. Chem. Soc.* **1988**, *110*, 7106. (k) Lewandos, G. S.; Doherty, N. M.; Knox, S. A. R.; MacPherson, K. A.; Orpen, A. G. *Polyhedron* **1988**, *7*, 83. (l) Casey, C. P.; Miles, W. H.; Fagan, P. J.; Haller, K. J. *Organometallics* **1985**, *4*, 559. (m) Baralt, E.; Lukehart, C. M.; McPhail, A. T.; McPhail, D. R. *Organometallics* **1991**, *10*, 516. (n) Etienne, M.; Guerchais, J. E. *J. Chem. Soc., Dalton Trans* **1989**, 2187. (o) Etienne, M.; Talarmin, J.; Toupet, L. *Organometallics* **1992**, *11*, 2058.

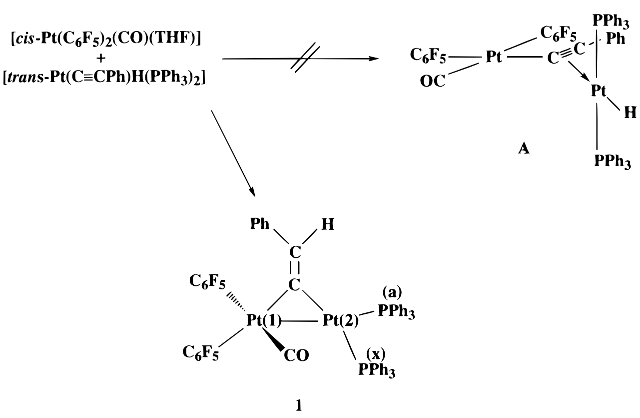
(4) (a) McCandlish, L. E. *J. Catal.* **1983**, *83*, 362. (b) Erley, W.; McBreen, P. H.; Ibach, H. *J. Catal.* **1983**, *84*, 229. (c) Gibson, V. C.; Parkin, G.; Bercaw, J. E. *Organometallics* **1991**, *10*, 220. (d) Hills, M. M.; Parmenter, J. E.; Weinberg, W. H. *J. Am. Chem. Soc.* **1987**, *109*, 597.

(5) (a) Mercer, R. J.; Green, M.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1986**, 567. (b) Froom, S. F. T.; Green, M.; Mercer, R. J.; Nagle, K. R.; Orpen, A. G.; Schwiegk, S. *J. Chem. Soc., Chem. Commun.* **1986**, 1666. (c) Mercer, R. J.; Green, M.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1986**, 567.

tions by Silvestre and Hoffman[10] showed that a concerted 1,2-hydrogen shift, accepted in related reactions mediated by a single metal center, was energetically unlikely on a binuclear system, although this transformation *via* an acetylide−hydride intermediate appeared to be plausible. Although strong support for such a mechanism comes from Lukehart's systematic synthesis of bridging vinylidene complexes by the addition of a Pt−H bond across the carbon−carbon triple bond of several metal alkynyl compounds,[11] experimental evidence for such acetylide−hydride intermediates has been sparse.[8h]

In this paper, we report the synthesis and characterization of a new vinylidene-bridged dinuclear platinum complex $[(OC)(C_6F_5)_2Pt(\mu\text{-}C{=}CHPh)Pt(PPh_3)_2]$, **1**, which has been obtained by direct reaction between the alkynyl−hydride mononuclear complex *trans*-$[Pt(C{\equiv}CPh)H(PPh_3)_2]$ and *cis*-$[Pt(C_6F_5)_2(CO)(THF)]$ (THF = tetrahydrofuran). Furthermore, some aspects of its remarkable reactivity are also included. Particularly interesting are the reactions of **1** with PPh_3 and thiophenol under mild conditions. The Lewis base triphenylphosphine induces an unprecedented reductive coupling of the CO ligand and the vinylidene bridging group yielding the first μ-η^1:η^3 benzylideneketene dinuclear platinum complex $[(PPh_3)(C_6F_5)_2Pt(\mu\text{-}CHPhCCO)Pt(PPh_3)_2]$, **2**. By contrast, PhSH adds to the carbon−carbon double bond of the :C=CHPh group of **1** to give the dinuclear platinum complex $[(PPh_3)_2Pt(PhSCCH_2Ph)Pt(C_6F_5)_2(CO)]$, **3**, which contains a μ-η^2(*C*,*S*):η^1(*C*) (benzylthiophenoxy)methylene bridging ligand. These reactions add to a growing body of evidence suggesting that μ-alkenylidenes in dinuclear and polynuclear complexes are versatile reactive ligands for which a rich chemistry can be anticipated.[2b]

Scheme 1



Results and Discussion

In previous studies[12] involving the monocarbonyl complex *cis*-$[Pt(C_6F_5)_2(CO)(THF)]$ (THF = tetrahydrofuran), we have discovered its unusual reactivity toward terminal alkynyl compounds $L_nMC{\equiv}CR$, which results in the formation of mono μ-η^2-acetylide-bridged dinuclear zwitterionic derivatives of the type $[(CO)(C_6F_5)_2Pt^-(\mu\text{-}\eta^2\text{-}C{\equiv}CR)M^+L_n]$[12] through an unexpected alkynylation of the monocarbonyl fragment "*cis*-$Pt(C_6F_5)_2(CO)$", probably brought about by the enhanced acidity of the platinum center, due to the electron-withdrawing nature of the C_6F_5 groups and the good π-acceptor properties of the CO ligand. As an extension on the study of the reactivity of this monocarbonyl complex *cis*-$[Pt(C_6F_5)_2(CO)(THF)]$, we have carried out its reaction with *trans*-$[PtH(C{\equiv}CPh)(PPh_3)_2]$, which does not produce the expected μ-η^2-acetylide hydride zwitterionic complex (**A**, Scheme 1) but the phenylethenylidene-bridged dinuclear $[(OC)(C_6F_5)_2Pt(\mu\text{-}C{=}CHPh)Pt(PPh_3)_2]$, **1**.

Thus, when the phenylacetylide−hydride complex, *trans*-$[Pt(C{\equiv}CPh)H(PPh_3)_2]$, is treated with 1 equiv of *cis*-$[Pt(C_6F_5)_2(CO)(THF)]$ in CH_2Cl_2, at room temperature for 15 h, the diplatinum complex $[(OC)(C_6F_5)_2Pt(\mu\text{-}C{=}CHPh)Pt(PPh_3)_2]$, **1**, is isolated in 55% yield as an air-stable microcrystalline orange product. Analytical and mass spectral data are in accord with this formulation. Spectroscopic data (NMR and IR) are consistent with a "T-frame" structure (C_1 symmetry, shown in Scheme 1), similar to those reported by Lukehart *et al.* for several neutral and cationic diplatinum complexes containing analogous phenylethenylidene bridging ligands,[11,13] with the main coordination planes of the two platinum atoms having an orthogonal relative orientation. The IR spectrum shows the ν(CO) band at 2083 cm^{-1}, thus confirming the presence of a terminal carbonyl ligand. Moreover, the presence of two absorptions at 807 and 795 cm^{-1}, due to the IR-active vibrations of the X-sensitive mode of the C_6F_5 groups,[12,14] and the presence of four absorptions at 542, 522, 513, and 508 cm^{-1}, due to the PPh_3 ligands,[15] suggests a mutually

---

(6) (a) Werner, H.; Wolf, J.; Müller, G.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 431. (b) Werner, H.; Wolf, J.; Müller, G.; Krüger, C. *J. Organomet. Chem.* **1988**, *342*, 381. (c) Kolobova, N. E.; Ivanov, L. L.; Zhvanko, O. S.; Batsanov, A. S.; Struchkov, Yu. T. *J. Organomet. Chem.* **1985**, *279*, 419. (d) Antonova, A. B.; Kovalenko, S. V.; Korniyets, E. D.; Petrovsky, P. V.; Gulbis, G. R.; Johansson, A. A. *Inorg. Chim. Acta* **1985**, *96*, 1. (e) Werner, H.; García Alonso, F. J.; Otto, H.; Peters, K.; von Schenering, H. G. *J. Organomet. Chem.* **1985**, *289*, C5. (f) Werner, H.; García Alonso, F. J.; Otto, H.; Peters, K.; von Schenering, H. G. *Chem. Ber.* **1988**, *121*, 1565. (g) Weinand, R.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1985**, 1145. (h) Schneider, D.; Werner, H. *Organometallics* **1993**, *12*, 4420.

(7) (a) Fontaine, X. L. R.; Higgins, S. J.; Shaw, B. L.; Thornton-Pett, M.; Yichang, W. *J. Chem. Soc., Dalton Trans.* **1987**, 1501. (b) Higgins, S. J.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1629. (c) Fontaine, X. L. R.; Higgins, S. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1988**, 1179. (d) Davies, J. A.; Pinkerton, A. A.; Syed, R.; Wilmer, M. *J. Chem. Soc., Chem. Commun.* **1988**, 47.

(8) (a) García Alonso, F. J.; García Sanz, M.; Riera, V.; Ruiz, M. A.; Tiripicchio, A.; Tiripicchio-Camellini, M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 116. (b) Antonova, A. B.; Kolobova, N. E.; Petrovsky, P. V.; Lokshin, B. V.; Obezyuk, N. S. *J. Organomet. Chem.* **1977**, *137*, 55. (c) Alt, A. G.; Engelhardt, H. E.; Steinlein, E.; Rogers, R. D. *J. Organomet. Chem.* **1988**, *344*, 321. (d) Berry, D. H.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 7181. (e) Berry, D. H.; Eisenberg, R. *Organometallics* **1987**, *6*, 1796. (f) Dickson, R. S.; Fallon, G. D.; McClure, F. I.; Nesbit, R. J. *Organometallics* **1987**, *6*, 215. (g) Doherty, N. M.; Elschenbroich, C.; Kneuper, H. J.; Knox, S. A. R. *J. Chem. Soc., Chem. Commun.* **1985**, 170. (h) Xiao, J.; Cowie, M. *Organometallics* **1994**, *12*, 463.

(9) (a) Bianchini, C.; Peruzzini, M.; Vacca, A.; Zanobini, F. *Organometallics* **1991**, *10*, 3697 and references therein. (b) Bly, R. S.; Zhong, Z.; Kane, C.; Bly, R. K. *Organometallics* **1994**, *13*, 899 and references therein.

(10) Silvestre, J.; Hoffmann, R. *Helv. Chim. Acta* **1985**, *68*, 1461.

(11) (a) Afzal, D.; Lenhert, P. G.; Lukehart, C. M. *J. Am. Chem. Soc.* **1984**, *106*, 305. (b) Afzal, D.; Lukehart, C. M. *Organometallics* **1987**, *6*, 546.

(12) Berenguer, J. R.; Forniés, J.; Lalinde, E.; Martínez, F.; Urriolabeitia, E.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1994**, 1291.

(13) Baralf, E.; Boudreaux, E. A.; Demas, J. N.; Lenhert, P. G.; Lukehart, C. M.; McPhail, A. T.; McPhail, D. R.; Myers, J. B., Jr.; Sacksteder, L.; True, W. R. *Organometallics* **1989**, *8*, 2417.

(14) (a) Maslowsky, E., Jr. *Vibrational Spectra of Organometallic Compounds*; Wiley: New York, 1977; p 437. (b) Usón, R.; Forniés, J.; Espinet, P.; Fortuño, C.; Tomás, M.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1988**, 3005.

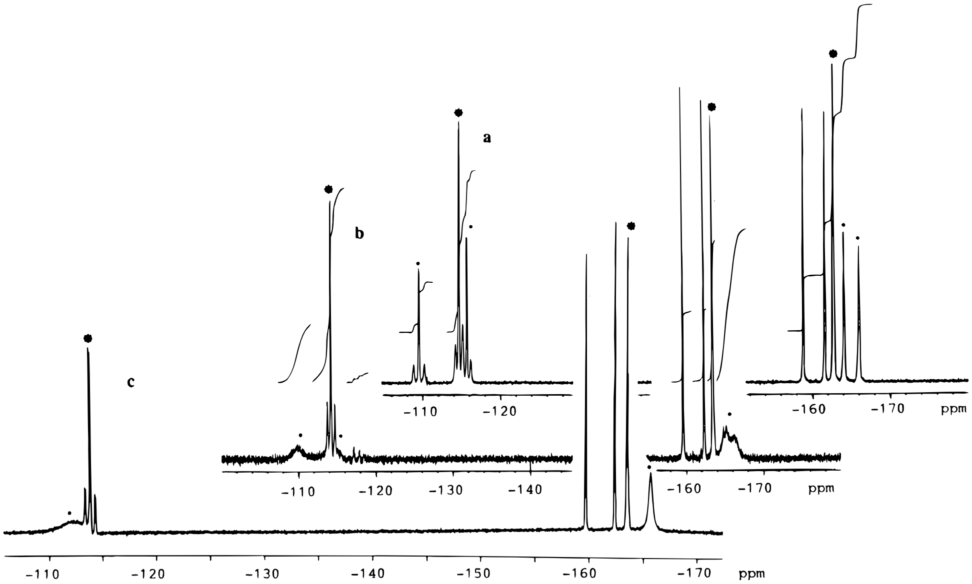


Figure 1. ^{19}F NMR spectra of complex $[(OC)(C_6F_5)_2Pt(\mu\text{-}C{=}CHPh)Pt(PPh_3)_2]$, **1**, in $CDCl_3$ at different temperatures: (a) −50 °C; (b) 20 °C; (c) 50 °C.

cis disposition for these ligands. The ^{1}H and ^{31}P NMR spectra of complex **1** can be readily interpreted on the basis of previous analysis of the NMR spectra for the analogous cationic $[Pt_2(\mu\text{-}C{=}CHPh)(C{\equiv}CPh)(PEt_3)_4][BF_4]$ and neutral $[Pt_2(\mu\text{-}C{=}CHPh)(C{\equiv}CPh)(PEt_3)_3X]$ and $[Pt_2(\mu\text{-}C{=}CHPh)(PEt_3)_3X_2]$ diplatinum complexes reported by Lukehart.[11,13,16] For complex **1**, the alkenylidene proton resonance appears as a doublet of doublets centered at 5.75 ppm due to $^4J(P-H)$ coupling to the two PPh_3 ligands coordinated to Pt(2) (see Scheme 1). On the basis of previous observations, the value of the two $^4J(P-H)$ coupling constants (26.3 and 8.3 Hz, respectively) suggest[11b,13] that complex **1** is isolated as the isomer shown in Scheme 1. The ^{31}P NMR spectrum shows two doublets with a $^2J(P_A-P_X)$ of 14 Hz, which is consistent with the presence of two inequivalent PPh_3 ligands. The resonance at 31.17 ppm with a normal[17] $^1J(Pt(2)-P_X)$ of 2593 Hz ($^2J(Pt(1)-P_X)$ not resolved) is assigned to the PPh_3 ligand in a nearly *cis* disposition to Pt(1). The signal at 35.95 ppm, assigned to the PPh_3 ligand nearly *trans* to Pt(1), shows two well-resolved Pt satellites: $^1J(Pt(2)-P_A) = 5534$ Hz and $^2J(Pt(1)-P_A) = 344$ Hz, respectively. These unusually large coupling constants compare well with those reported for the neutral $[Pt_2(\mu\text{-}C{=}CHPh)(C{\equiv}CPh)(PEt_3)_3X]$, $[Pt_2(\mu\text{-}C{=}CHPh)(PEt_3)_3X_2]$,[13,16] and $[X(PPh_3)Pt(\mu\text{-}CO)Pt(PPh_3)_2X]$ (X = Cl,[18a] Br[18b]) diplatinum complexes, all of which have been described as containing a platinum−platinum bond with some degree of mixed-valence character. A Pt(1)→Pt(2) formal Lewis acid−base interaction has also been proposed to rationalize the presence of a Pt−Pt bond in these types of compounds.[11,13,16] In addition, simulation of the ^{31}P NMR experimental spectrum using these assignements gives good agreement with the experimental spectrum.

The ^{19}F NMR spectral data are also informative. For the proposed structure, the two C_6F_5 groups are inequivalent and, in addition, the low symmetry makes the *o*-fluorine atoms (and the *m*-fluorine atoms as well), within each C_6F_5 ligand, inequivalent. Thus, for a static structure, the ^{19}F NMR spectrum should show a complex pattern with four *o*-, two *p*-, and four *m*-fluorine resonances, *i.e.* five different signals for each C_6F_5 group. The ^{19}F NMR spectra registered in $CDCl_3$ at different temperatures (−50, 20, and 50 °C) are shown in Figure 1. As can be observed, the inequivalence of the two C_6F_5 ligands can be easily inferred from the presence of two different triplets due to *p*-fluorine resonances. At low temperature (−50 °C) the spectrum shows the expected two *o*- and two *m*-fluorine signals for a rigid conformation of one of the two C_6F_5 groups. The only two (one *o*-F and one *m*-F) sharp resonances observed for the other C_6F_5 ligand clearly suggest the existence of a dynamic process. When the temperature is increased, the four resonances (two *o*-F and two *m*-F) of the former C_6F_5 group broaden and, finally, collapse (the *o*-signals practically disappear into the baseline) to only two at 50 °C. The observed spectrum at 50 °C can tentatively be explained by assuming the rotation of C_6F_5 rings around the $Pt-C_{ipso}(C_6F_5)$ bonds. Moreover, the different aspects of the signals for each one of the C_6F_5 rings (sharp and broad) in the *o*-F and *m*-F regions suggest that the energy barrier for this process is different in each ring. As a consequence, at low temperature (−50 °C) this process seems to be stopped for only one of the C_6F_5 rings. A similar behavior has been previously found in other complexes containing the "*cis*-$Pt(C_6F_5)_2(CO)$" fragment.[12a] Unfortunately, the ^{13}C NMR spectrum is not informative since only a complex pattern of carbon resonances in the aromatic region is observed.

The formation of **1** from *cis*-$[Pt(C_6F_5)_2(CO)(THF)]$ and *trans*-$[Pt(C{\equiv}CPh)H(PPh_3)_2]$ could involve an initial alkynylation of the "*cis*-$Pt(C_6F_5)_2(CO)$" fragment and simultaneous stabilization of the resulting unit by formation of a μ-acetylide hydride intermediate species of the type *cis,trans*-$[(OC)(C_6F_5)_2Pt(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CPh)PtH(PPh_3)_2]$ (**A**, Scheme 1) (as observed in the reaction

---

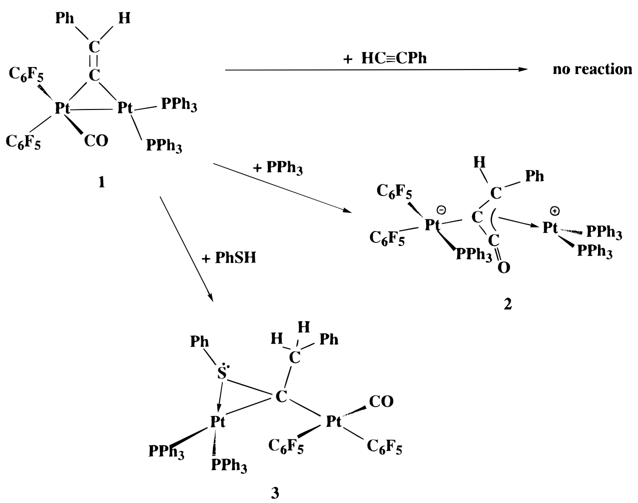
[15] Mastin, S. H. *Inorg. Chem.* **1974**, *13*, 1003.

[16] Baralt, E.; Lukehart, C. M. *Inorg. Chem.* **1990**, *29*, 2870.

[17] Pregosin, P. S.; Kunz, R. W. In *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes;* Diehl, P., Fluck, E., Kosfield, R., Eds.; Springer-Verlag: New York, 1979; Vol. 16.

[18] (a) Bender, R.; Braunstein, P.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Chem. Soc., Chem. Commun.* **1984**, 42. (b) Goodfellow, R. J.; Herbert, I. R.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1983**, 1386.

Scheme 2



between *cis*-[Pt(C_6F_5)$_2$(CO)(THF)] and platinum bis(alkynyl) complexes[12]) followed by isomerization to the *cis,cis* isomer and *cis* 1,2 addition of the Pt−H bond across the C−C triple bond, the last steps being similar to those proposed for the formation of the first example of this type of complex, [(PhC≡C)(PEt$_3$)$_2$Pt(*μ*-C=CHPh)-Pt(PEt$_3$)$_2$][BF$_4$].[11a]

Since one of the main interests in this type of dinuclear compound containing *μ*-hydrocarbyl ligands is justified principally by their posible chemical behavior at the bridging ligand, we decided to examine the chemical reactivity of **1**, in an attempt to induce (a) simple carbonyl−phosphine exchange, (b) carbon−carbon coupling at the *μ*-vinylidene ligand, and (c) addition to the carbon−carbon double bond. Complex **1** was treated separately with triphenylphosphine, phenylacetylene, and thiophenol. While no reaction was detected between **1** and phenylacetylene (room temperature, excess), compound **1** did react with PPh$_3$ or PhSH to give the new products **2** and **3** (Scheme 2), respectively.

Reaction with PPh$_3$. When an orange solution of **1** in CH$_2$Cl$_2$ was treated with PPh$_3$ (molar ratio 1:1), the color of the solution gradually turned yellow. Partial evaporation and addition of ethanol afforded yellow crystals of a compound, **2** (41% yield), which according to the elemental analysis corresponds apparently to an 1:1 adduct of the starting complex, **1**, and PPh$_3$. The IR spectrum revealed the presence of a new strong and broad absorption at 1885 cm^{-1}. The possibility that this was due to a carbonyl which had linked to the vinylidene ligand led us to carry out an X-ray diffraction study, which established that this was actually the case. The structure of **2** is presented in Figure 2a, with the atom-numbering scheme. Figure 2b provides a schematic view showing the central expanded unsaturated hydrocarbon fragment. Crystallographic data are collected in Table 1, and selected bond distances and angles are listed in Table 2.

The most interesting feature of this molecule is the presence of the new benzylideneketene bridging ligand *μ*-CHPhCCO, formed by a formal reductive coupling between the bridging vinylidene and the CO ligand. This new bridging ligand is connecting two separated platinum moieties "Pt(1)(C_6F_5)$_2$(PPh$_3$)" and "Pt(2)(PPh$_3$)$_2$" *via* the three carbon atoms C(9), C(1), and C(2). Pt(1), practically coplanar with the C(9)−C(1)−C(2) fragment [deviation 0.136(1) Å], is only *σ* bonded to the central carbon atom C(1). The Pt(1)−C(1) distance [2.07(2) Å] is identical, within the experimental error, to the other two Pt(1)−C(C_6F_5) [Pt(1)−C(10) 2.08(2) Å and Pt(1)−C(16) 2.05(2) Å] bond distances. Pt(2) is unsymmetrically η^3-bonded to the three carbon atoms of the hydrocarbon fragment, the Pt(2)−C(2) bond length [2.13(2) Å] being shorter than the Pt(2)−C(1) [2.26(2) Å] and Pt(2)−C(9) [2.34(2) Å] distances. The C−C distances and the angle at C(1) [C(2)−C(1)−C(9) 115(2)°] are similar to those formed in η^3-allyl−Pt systems.[19] In addition, the C(9)−O(1) bond length [1.15(2) Å] and the C(1)−C(9)−O(1) angle [162(2)°] are similar to those reported for μ^2,η^1-ketenyl complexes.[20] All these data suggest that the ligand is bonded to Pt(2) in a η^3-allylic form (see Scheme 2). The oxygen atom is practically coplanar with the central fragment C(9)−C(1)−C(2) [deviation 0.28(1) Å], and the C$_{ipso}$ carbon atom of the phenyl group C(3) deviates 0.88(2) Å. The two Pt(2)−P(PPh$_3$) distances are different [Pt(2)−P(2) 2.325(5) Å and Pt(2)−P(3) 2.291(5) Å], thus reflecting the asym-

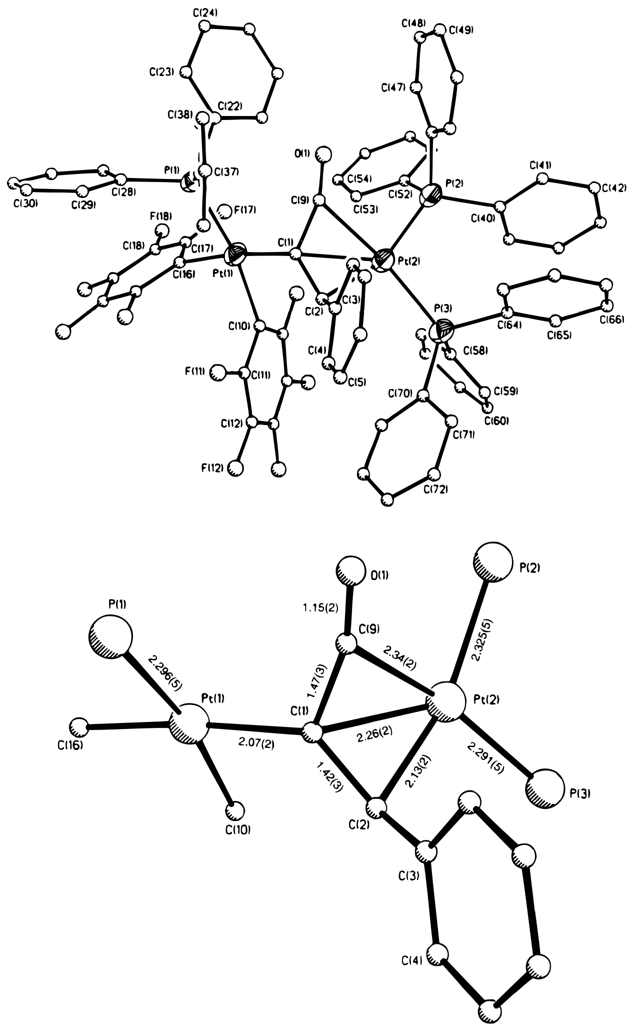


Figure 2. (a) Top: View of the structure of complex *cis,cis*-[(PPh$_3$)(C_6F_5)$_2$Pt(μ-η^1:η^3-CHPhCCO)Pt(PPh$_3$)$_2$], **2**, with the atom-numbering scheme. (b) Bottom: Schematic view of the central core of complex **2** with bond lengths in Å.

---

[19] Hartley, F. R. *Comprehensive Organometallic Chemistry;* Pergamon: Oxford, U.K., 1982; Vol. 6, p 721 and references therein.

[20] Geoffroy, G. L.; Bassner, S. L. *Adv. Organomet. Chem.* **1988**, *28*, 1.

Table 1. Crystal Data and Structure Refinement Parameters for Complexes 2·$^1/_2$(*n*-hexane) and 3

	2	3
empirical formula	$C_{78}H_{58}F_{10}OP_3Pt_2$	$C_{63}H_{43}F_{10}OP_2Pt_2S$
fw	1684.33	1490.15
temp	293(2) K	293(2) K
wavelength	1.541 84 Å	0.710 73 Å
crys system	triclinic	monoclinic
space group	$P\bar{1}$	Cc
unit cell dimens	$a = 12.668(3)$ Å $b = 14.201(3)$ Å $c = 20.704(4)$ Å $\alpha = 110.13(2)°$ $\beta = 90.00(2)°$ $\gamma = 94.59(2)°$	$a = 15.946(5)$ Å $b = 24.719(6)$ Å $c = 16.039(3)$ Å $\alpha = 90°$ $\beta = 93.01(2)°$ $\gamma = 90°$
V	3484.4(13) Å^3	6313(3) Å^3
Z	2	4
D (calcd)	1.605 Mg/m^3	1.568 Mg/m^3
abs coeff	8.654 mm^{-1}	4.578 mm^{-1}
$F(000)$	1650	2884
cryst size	0.14 × 0.35 × 0.36 mm	0.28 × 0.28 × 0.45 mm
θ range for data collcn	2.27−52.62°	1.52−25.43°
hkl ranges	−13 to 13, −14 to 13, 0 to 21	−19 to 19, 0 to 29, 0 to 19
reflcns collcd	8262	6183
indepdt reflcns	7981	6036
reflcns with $F_o > 4\sigma(F_o)$	5276	5120
refinement method	full-matrix l.s. on F^2	full-matrix l.s. on F^2
data/restraints/params	7981/9/804	6030/18/706
goodness-of-fit on F^2	0.994	1.027
R indices $[F_o > 4\sigma(F_o)]^a$	$R_1 = 0.0780$, w$R_2 = 0.1940$	$R_1 = 0.0409$, w$R_2 = 0.0878$
R indices (all data)^a	$R_1 = 0.1137$, w$R_2 = 0.2134$	$R_1 = 0.0540$, w$R_2 = 0.1029$
weighting params g_1, g_2	0.1415, 0.00	0.0486, 0.00
mean and max |shift/esd|, final cycle	0.003, 0.056	0.000, 0.001
largest diff peak and hole	2.089 and −2.563 e/Å^3	0.882 and −1.036 e/Å^3
absolute struct param		0.006(10)

[a] $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; w$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. Goodness-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$. $w = [\sigma^2(|F_o|) + (g_1P)^2 + g_2P]^{-1}$; $P = [\max(F_o^2;0) + 2F_c^2]/3$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 2·$^1/_2$(*n*-hexane)

Pt(2)−C(1)	2.26(2)	Pt(2)−C(2)	2.13(2)
Pt(2)−C(9)	2.34(2)	Pt(2)−P(3)	2.291(5)
Pt(2)−P(2)	2.325(5)	Pt(1)−C(1)	2.07(2)
Pt(1)−C(10)	2.08(2)	Pt(1)−C(16)	2.05(2)
Pt(1)−P(1)	2.296(5)	C(1)−C(2)	1.42(3)
C(1)−C(9)	1.47(3)	C(2)−C(3)	1.40(3)
C(9)−O(1)	1.15(2)		
C(1)−Pt(2)−C(2)	37.7(7)	C(1)−Pt(2)−C(9)	37.2(7)
C(2)−Pt(2)−C(9)	65.7(6)	C(1)−Pt(2)−P(3)	133.1(5)
C(2)−Pt(2)−P(3)	97.8(5)	C(9)−Pt(2)−P(3)	158.5(4)
C(1)−Pt(2)−P(2)	125.1(5)	C(2)−Pt(2)−P(2)	160.0(5)
C(9)−Pt(2)−P(2)	94.3(4)	P(3)−Pt(2)−P(2)	101.3(2)
C(1)−Pt(1)−C(10)	91.1(8)	C(1)−Pt(1)−C(16)	174.3(8)
C(10)−Pt(1)−C(16)	83.5(8)	C(1)−Pt(1)−P(1)	93.3(6)
C(10)−Pt(1)−P(1)	169.2(6)	C(16)−Pt(1)−P(1)	91.7(6)
Pt(2)−C(1)−Pt(1)	124.8(9)	Pt(2)−C(1)−C(2)	66.1(11)
Pt(1)−C(1)−C(2)	130(2)	Pt(2)−C(1)−C(9)	74.7(10)
Pt(1)−C(1)−C(9)	115.8(13)	C(2)−C(1)−C(9)	115(2)
Pt(2)−C(2)−C(3)	115.5(14)	C(1)−C(2)−C(3)	128(2)
Pt(2)−C(9)−C(1)	68.1(10)	Pt(2)−C(9)−O(1)	130.0(13)
C(1)−C(9)−O(1)	162(2)		

metry of the central hydrocarbon skeleton. The relative disposition of the C(9)−C(1)−C(2) fragment is such that the dihedral angles with the Pt(2)P(2)P(3) moiety and the coordination plane of Pt(1) [Pt(1)−P(1)−C(16)−C(10)−C(1)] are 121(1) and 139(1)°, respectively. The dihedral angle formed by the Pt(2)P(2)P(3) unit and the coordination plane of Pt(1) is 77.6(3)°. The long Pt(1)−Pt(2) distance (3.836 Å) indicates the absence of metal−metal bond.

The resulting unsaturated bridging ligand in **2** is very unusual. To our knowledge, the most closely related compound is the heterodinuclear complex $[(CO)_2CpMn\{\mu\text{-}C(CO)CHPh\}Fe(CO)_3]$, formed by the treatment of $[MnCp(CO)_2(C{=}CHPh)]$ with $[Fe_2(CO)_9]$, which has been formulated as containing a mangana−trimethylene−methane ligand bonded to an "Fe(CO)$_3$" group.[21]

The overall reaction between **1** and PPh$_3$ involves addition of PPh$_3$ ligand and insertion of CO into the μ-vinylidene ligand to produce a benzylideneketene ligand. The conversion of vinylidene to ketene is noteworthy in two additional respects. There are many examples of carbonylation (or insertion) of terminal carbene and carbyne ligands affording ketene and ketenyl complexes, in many cases promoted by strongly nucleophilic phosphines.[20,22] This well-known process has utility in organic synthesis[23] and has also been pointed out to be a key step of C−C bond formation in the hydrogenation of carbon monoxide to oxygenated compounds.[23b,24] However, the insertion of CO into a carbene bridging ligand is a rare process and the cases reported involve carbonylation or insertion of CO into a μ-methylene (μ-CH$_2$) group.[20,25] As far as we know, there is only one report in the literature of insertion of

---

(21) Andrianov, V. G.; Struchkov, Yu. T.; Kolobova, N. E.; Antonova, A. B.; Obezyuk, N. S. *J. Organomet. Chem* **1976**, *122*, C33.

(22) (a) Mayr, A.; Bastos, C. M. *Prog. Inorg. Chem.* **1992**, *40*, 1. (b) Mayr, A.; Lee, T. Y.; Kjelsberg, M. A.; Lee, K. S. *Organometallics* **1994**, *13*, 2512. (c) Mayr, A. *Comments Inorg. Chem.* **1990**, *10*, 227.

(23) (a) Anderson, B. A.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 8615. (b) Mitsudo, T.; Ishihara, A.; Kodokura, M.; Watanabe, Y. *Organometallics* **1986**, *5*, 238.

(24) (a) Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 2584. (b) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. (c) Henrici-Olivé, G.; Olivé, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136.

(25) (a) Chen, M. C.; Tsai, Y. J.; Chen, C. T.; Lin, Y. C.; Tseng, T. W.; Lee, G. H.; Wang, Y. *Organometallics* **1991**, *10*, 378 and references therein. (b) Ozawa, F.; Park, J. W.; Mackenzie, P. B.; Schaefer, W. P.; Henling, L. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 1319. (c) Nuccianore, D.; Taylor, N. J.; Carty, A. J.; Tiripicchio, A.; Tiripicchio-Camellini, M.; Sappa, E. *Organometallics* **1988**, *7*, 118 and references given therein.

CO into a μ-vinylidene bridging ligand.[26] However, in this case, both the μ-CCH_2 derivative and the methyleneketene μ-CH_2CCO complex exist in solution as a mixture of two isomers in equilibrium.[26] On the other hand, ketene[20,27] and vinylidene[4] ligands have been suggested as potential intermediates in CO reduction processes; therefore, their interconversion is relevant. Although there are several reports[28] showing the conversion of a free ketene to a μ-vinylidene, observation of the reverse process has not been reported.[29]

The NMR spectra of complex **2** in $CDCl_3$ are consistent with the structure found in the solid state. Thus, the ^{19}F NMR spectrum displays four *o*-, two *p*-, and four *m*- fluorine resonances as expected for the five inequivalent fluorine atoms in each one of the two nonequivalent C_6F_5 rings. The ^{31}P NMR spectrum exhibits only two resonances, but the intensity and pattern of the ^{195}Pt satellites of one of them indicates that two nonequivalent phosphorous nuclei have coincidental chemical shifts (δ 27.2 ppm, s, $^1J(Pt-P) = 3958$ Hz, 1P; 15.1 ppm, s, broad, $^1J(Pt-P) = 2546$ and 3960 Hz, 2P).

The ^1H NMR spectrum of **2** shows, in addition to several complex resonances in the 7.5−6.6 ppm range (see Experimental Section), two doublets at high field (δ 5.12 ppm, $J = 7.3$ Hz, $^1J(Pt-H) = 43.6$ Hz; 5.58 ppm, $J = 7.3$ Hz) which can be assigned to the benzylenic proton and to one *o*-phenyl proton of the CHPh fragment. The resonance of this *o*-phenyl proton appears at much higher field than that expected for a typical phenyl proton. This anomalous shielding could be attributed to the position of the *o*-proton just above the aromatic ring [C(70)−C(75)] of one of the phenyl groups of the PPh_3 ligands [distance H(4)−centroid of the ring = 2.842 Å].

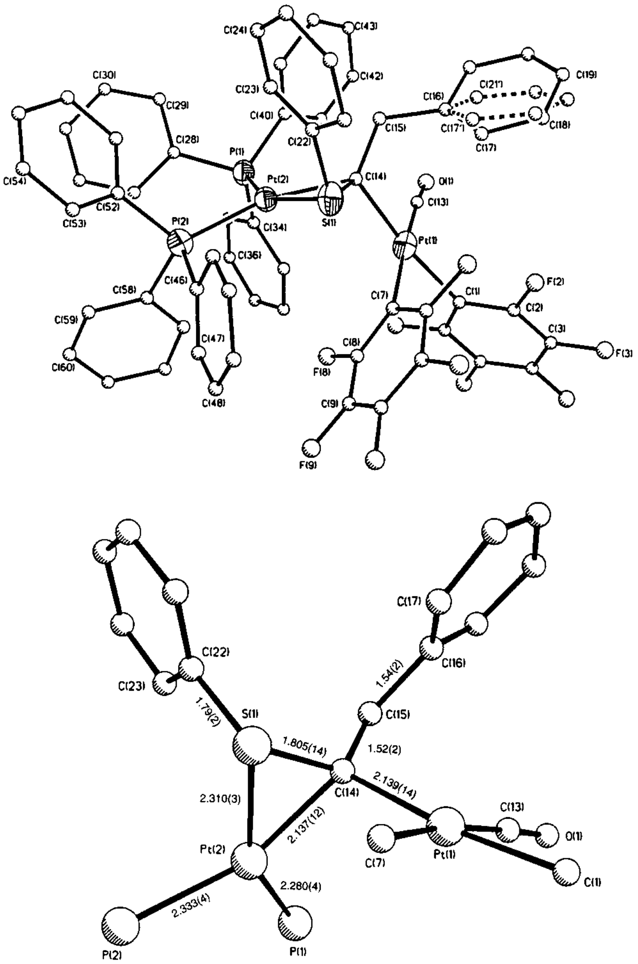


Figure 3. (a) Top: View of the structure of complex *cis,cis*-$[(PPh_3)_2Pt\{\mu-\eta^2(C,S):\eta^1(C)-C(SPh)(CH_2Ph)\}Pt(C_6F_5)_2(CO)]$, **3**, with the atom-numbering scheme. (b) Bottom: Schematic view of the central core of complex **3** with bond lengths in Å.

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

Pt(1)−C(1)	2.10(2)	Pt(1)−C(7)	2.07(2)
Pt(1)−C(13)	1.88(2)	Pt(1)−C(14)	2.139(14)
Pt(2)−S(1)	2.310(3)	Pt(2)−P(1)	2.280(4)
Pt(2)−P(2)	2.333(4)	Pt(2)−C(14)	2.137(12)
S(1)−C(14)	1.805(14)	S(1)−C(22)	1.79(2)
P(1)−C(28)	1.822(14)	P(1)−C(34)	1.799(13)
P(1)−C(40)	1.83(2)	P(2)−C(46)	1.86(2)
P(2)−C(52)	1.84(2)	P(2)−C(58)	1.841(13)
O(1)−C(13)	1.12(2)	C(14)−C(15)	1.52(2)
C(15)−C(16)	1.54(2)		

C(1)−Pt(1)−C(7)	87.5(6)	C(1)−Pt(1)−C(13)	84.8(7)
C(7)−Pt(1)−C(13)	171.3(7)	C(1)−Pt(1)−C(14)	173.0(6)
C(7)−Pt(1)−C(14)	95.8(6)	C(13)−Pt(1)−C(14)	92.3(7)
S(1)−Pt(2)−P(1)	151.14(13)	S(1)−Pt(2)−P(2)	101.78(13)
P(1)−Pt(2)−P(2)	106.45(13)	S(1)−Pt(2)−C(14)	47.7(4)
P(1)−Pt(2)−C(14)	104.7(4)	P(2)−Pt(2)−C(14)	148.8(4)
Pt(2)−S(1)−C(14)	61.1(4)	Pt(2)−S(1)−C(22)	104.9(6)
C(14)−S(1)−C(22)	109.6(8)	Pt(1)−C(13)−O(1)	174(2)
Pt(1)−C(14)−Pt(2)	110.3(6)	Pt(1)−C(14)−S(1)	110.9(7)
Pt(2)−C(14)−S(1)	71.2(5)	Pt(1)−C(14)−C(15)	113.8(9)
Pt(2)−C(14)−C(15)	123.0(9)	S(1)−C(14)−C(15)	120.9(11)
C(14)−C(15)−C(16)	115.8(13)		

Reaction with PhSH. A particularly interesting reaction of complex **1**, which is unprecedented for μ-vinylidene complexes, is the addition reaction observed with thiophenol. Complex **1** (0.1 mmol) is dissolved in neat PhSH (2 mL) to give immediatelly a pale yellow solution. Addition of *n*-hexane produces the precipitation of a yellow solid **3** (Scheme 2). Recrystallization from diethyl ether gives pale-yellow crystals of **3**, which were identified by elemental analysis as the 1:1 adduct. Similar results were obtained by treating **1** with 1 equiv of PhSH. A single-crystal diffraction analysis showed the presence of a (benzylthiophenoxy)methylene bridging ligand formed by the addition of PhSH to the carbon−carbon double bond of the μ-vinylidene ligand in **1**. Figure 3a shows a drawing of the molecular structure of **2**, and Figure 3b provides a schematic view of the central bridging ligand. Crystallographic data are collected in Table 1, and selected bond distances and angles are listed in Table 3. Within the (benzylthiophenoxy)methylene ligand, the bond lengths S−C [S(1)−C(14) 1.805(14) Å and S(1)−C(22) 1.79(2) Å] and the C(22)−S(1)−C(14) angle [109.6(8)°] are typical of sulfonium organic salts[30] and, moreover,

---

(26) Birk, R.; Berke, H.; Huttner, G.; Zsolnai, L. *Chem. Ber.* **1988**, *121*, 471.

(27) Loggenberg, P. M.; Carlton, L.; Copperthwaite, R. G.; Hutchings, G. J. *J. Chem. Soc., Chem. Commun.* **1987**, 541.

(28) (a) Mills, O. S.; Redhouse, A. D. *J. Chem. Soc. A* **1968**, 1282. (b) Young, D. A. *Inorg. Chem.* **1985**, *24*, 1492. See also: (c) Kreissl, F. R.; Eberl, K.; Uedelhoven, W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 860. (d) Eberl, K.; Uedelhoven, W.; Wolfgruber, W.; Kreissl, F. R. *Chem. Ber.* **1982**, *115*, 504. (e) Herrman, W. A.; Weber, C.; Ziegler, M. L.; Serhadli, O. *J. Organomet. Chem.* **1985**, *297*, 245.

(29) There is a recent report showing the interconversion between a bound ketene ligand and a terminal vinylidene group at a niobium center: Fermin, M. C.; Bruno, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 7511.

(30) Perozzi, E. F.; Paul, I. C. In *Chemistry of the Sulfonium Group*; Stirling, C. J. M., Patai, S., Eds.; Wiley: New York, 1981; p 15.

the C(14)−C(15) bond length of 1.52(2) Å is as expected for a C−C single bond. This ligand connects the two original organometallic fragments "*cis*-Pt(1)(C_6F_5)$_2$(CO)" and "Pt(2)(PPh_3)$_2$" present in **1** (Pt(1)$\cdots$Pt(2) = 4.11 Å), adopting a μ-σ(*C*):η^2(*C*,*S*) bonding mode. Thus, the alkylidene carbon, C(14), is bonded to both platinum atoms with identical bond lengths, within experimental error [Pt(1)−C(14) 2.139(14) Å; Pt(2)−C(14) 2.137(12) Å], and similar to those observed in binuclear heteroplatinum complexes containing μ-alkylidene ligands.[31] The C(15) and the S(1) atoms of the respective benzyl and thiophenoxy groups complete a distorted tetrahedral coordination on the alkylidene C(14) atom within which the angles vary from 71.2(5)° [Pt(2)−C(14)−S(1)] to 123.0(9)° [Pt(2)−C(14)−C(15)]. In addition, the sulfur atom is also bonded to Pt(2) yielding a platinathiirane cycle with a Pt(2)−S(1) bond distance [2.310(3) Å] similar to those found in other compounds with Pt−S bonds.[32]

It should be noted that both the alkylidene carbon atom C(14) and the sulfur atom S(1) are chiral centers and are of opposite configuration with both the *SR* and *RS* enantiomers present in the unit cell. The enantiomer drawn in Figure 4 has the *S* configuration about C(14) and *R* about S(1).

The Pt(2) atom completes its coordination sphere with two PPh_3 ligands. The shorter Pt(2)−P(1) distance [2.280(4) Å] is *trans* to the sulfur atom, and the longer Pt(2)−P(2) distance [2.333(4) Å] is *trans* to the alkylidene carbon atom C(14). These differences are comparable to those reported in complexes [Pt(PEt_3)$_2$(DHT-H)][PF_6],[32a] {Pd(PPh_3)Cl[S(Me)CH_2]},[33a] and {(PPh_3)$_2$Pd[S(Me)CH_2]}[PF_6],[33b] in which the M−P bond -*trans* to the carbon atom is longer than the M−P bond *trans* to the sulfur atom, and have been interpreted in terms of a stronger *trans* influence for carbon than for sulfur atoms.[34] The angle S(1)−Pt(2)−C(14) [47.7(4)°], similar to those of other three-membered (M−S−C) metallacyclic complexes,[33,35] is considerably smaller than the P(1)−Pt(2)−P(2) angle of 106.45(13)°, indicating a distorted square planar coordination for Pt(2). The dihedral angle between the S(1)−Pt(2)−C(14) and the Pt(2)−P(1)−P(2) planes is 10.8(3)°. However, the coordination around the platinum atom Pt(1) is less distorted and the dihedral angle between Pt(1)−C(1)−C(7) and Pt(1)−C(13)−C(14) planes is only 7.3(7)°. Finally, the dihedral angle formed by the best least-square planes around each platinum environment is 104.2(3)°.

In accord with the X-ray structure of complex **3**, the ^{1}H NMR spectrum shows, in addition to aromatic protons due to phenyl rings, an AB splitting pattern for the methylene protons of the benzyl group, which are nonequivalent (diastereotopic) due to the chirality of the quaternary carbon, C(14). One of the methylene signals appears as a well-resolved doublet at 3.54 ppm (*J*(H−H) = 17 Hz) and clearly displays a large value of the ^{3}*J*(Pt−H) of approximately 70 Hz, and the other appears as a doublet of doublets centered at 2.82 ppm (*J*(H−H) = 17 Hz and ^{4}*J*(P−H) = 5.4 Hz) due, probably, to a large distance coupling with P(2). The ^{31}P NMR spectrum exhibits the expected two signals. The peak at 19.7 ppm with the larger ^{1}*J*(Pt−P(1)) coupling constant (5055 Hz) can be assigned to the PPh_3 ligand *trans* to the sulfur atom [P(1)], and the peak at 19.9 ppm with the smaller ^{1}*J*(Pt−P(2)) coupling constant, to the PPh_3 ligand *trans* to the μ-alkylidene carbon atom C(14).

The ^{19}F NMR spectrum of **3**, at room temperature, shows a similar pattern to that observed for the starting complex **1** at low temperature (−50 °C). It shows the expected five signals (2 *o*-F, *p*-F, and 2 *m*-F; see Experimental Section) for a rigid conformation of one of the two C_6F_5 ligands. In this complex, examination of Figure 3 suggests that the C_6F_5 group *cis* to the bridging ligand is the most crowded and, probably, the rotation of this ring around the Pt−C bond is hindered. The remaining three signals (2:1:2) can be assigned to the less crowded C_6F_5 group *cis* to the CO ligand, and the observed pattern could be explained by assuming the rotation of this ring around the Pt−C bond. By a lowering of the temperature to −50 °C, the *o*-F and *m*-F resonances of this C_6F_5 ring only broaden, but they do not split in the expected two *o*-F and two *m*-F signals.

This reaction merits further consideration. MO calculations predict that electrophilic addition on a diplatinum symmetrical μ-vinylidene complex is frontier-orbital-controlled, which should therefore undergo electrophilic C_β attack.[10] In this respect, the formation of **3** from **1** and PhSH could be rationalized as a simple electrophilic addition to the C_β carbon atom of the vinylidene group in **1** and concomitant elimination of the formal Pt(1)→Pt(2) Lewis-base interaction by the coordination of the sulfur atom to Pt(2).

Conclusions

The present study extends knowledge on the chemistry of μ-vinylidene complexes. We have demostrated that the synthesis of a new neutral vinylidene-bridged dinuclear platinum complex [(OC)(C_6F_5)$_2$Pt(μ-C=CHPh)Pt(PPh_3)$_2$], **1**, is posible through a simple reaction between [*cis*-Pt(C_6F_5)$_2$(CO)(THF)] and the alkynyl−hydride mononuclear complex *trans*-[PtH(C≡CPh)(PPh_3)$_2$], supplementing those previously reported for Lukehart et al.[11] This complex provides the chance to study the influence of the nature of the ligands at the platinum centers on the reactivity of such complexes. It has been reported that the cationic [Pt_2(μ-C=CHPh)(C≡CPh)(PEt_3)$_4$](BF_4), **4**, reacts thermally or photochemically with halide or pseudohalide salts to form similar neutral compounds [Pt_2(μ-C=CHPh)(C≡CPh)(PEt_3)$_2$X], which further react with a protic acid and a second 1 equiv of nucleophile to give the neutral [Pt_2(μ-C=CHPh)(PEt_3)$_3$$X_2$] compounds by loss of phenylacetylene.[13] Very interesting is the unusual C−C reaction coupling of **4** with PhC≡CPh, under photolysis, to form a cationic diplatinum μ-η^1:η^3-butadienediyl complex.[3m] We have demonstrated that the simple μ-phenylethenylidene complex **1** shows some novel properties. Thus, reaction with PPh_3, under mild conditions, induces an unprecedent C−C coupling of the CO

---

[31] Ozawa, F.; Park, J. W.; Mackenzie, P. B.; Schaefer, W. P.; Henling, L. M.; Grubbs, R. M. *J. Am. Chem. Soc.* **1989**, 1319.

[32] (a) Glavee, G. N.; Daniels, L. M.; Angelici, R. J. *Organometallics* **1989**, *8*, 1856. (b) Cartner, A. M.; Fawcett, J.; Henderson, W.; Kemmit, R. D. W.; McKenna, P.; Russell, D. R. *J. Chem. Soc., Dalton Trans.* **1993**, 3755. (c) Usón, R.; Forniés, J.; Usón, M. A.; Tomás, M.; Ibáñez, M. A. *J. Chem. Soc., Dalton Trans.* **1994**, 401. (d) Mitchell, K. A.; Streveler, K. C.; Jensen, C. M. *Inorg. Chem.* **1993**, *32*, 2608.

[33] (a) Miki, K.; Kay, Y.; Yasuoka, N.; Nassai, N. *J. Organomet. Chem.* **1977**, *135*, 53. (b) Miki, K.; Kay, Y.; Yasuoka, N.; Kassai, N. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3639.

[34] (a) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335. (b) McWeeny, R.; Mason, R.; Towl, A. D. C. *Discuss. Faraday Soc.* **1969**, *47*, 20.

[35] Miller, D. C.; Angelici, R. J. *Organometallics* **1991**, *10*, 89.

ligand and the vinylidene moiety allowing the synthesis of the first μ-η^1:η^3 benzylidenketene dinuclear platinum complex **2**. On the other hand, thiophenol have been successfully incorporated into complex **1** via simple addition to the carbon−carbon double bond of the μ-C=CHPh. This addition increases the complexity of the ligand that bridges the metal centers, giving a dinuclear platinum complex which contains a μ-η^2(*C*,*S*):η^1(*C*) (benzylthiophenoxy)methylene bridging ligand.

Experimental Section

General Methods. Solvents were dried and purified by known procedures and distilled prior to use. Elemental analyses were performed with a Perkin-Elmer 240 microanalyzer. ^{1}H, ^{13}C, ^{31}P{^{1}H}, and ^{19}F NMR spectra were recorded on a Brucker ARX 300 spectrometer. Chemical shifts are given in ppm relative to external standars [SiMe$_4$, H$_3$PO$_4$ (85%), and CFCl$_3$]. Infrared spectra were run on a Perkin-Elmer 883 spectrometer using Nujol mulls between polyethylene sheets. Mass spectra were recorded on a VG Autospec spectrometer. The starting materials *cis*-[Pt(C$_6$F$_5$)$_2$(CO)(THF)][14b] and *trans*-[Pt(C≡CPh)H(PPh$_3$)$_2$][36] were prepared by published methods.

Preparation of [(OC)(C$_6$F$_5$)$_2$Pt(μ-C=CHPh)Pt(PPh$_3$)$_2$] (1). To a CH$_2$Cl$_2$ solution of *trans*-[Pt(C≡CPh)H(PPh$_3$)$_2$] (0.20 g, 0.24 mmol) was added, under N$_2$, 0.15 g (0.24 mmol) of *cis*-[Pt(C$_6$F$_5$)$_2$(CO)(THF)], resulting in an immediate color change of the solution from very pale yellow to deep orange. The mixture was stirred for *ca.* 15 h, and the solution was concentrated to small volume (~4 mL). Addition of ethanol (2 mL) yielded **1** (55%) as an orange solid. Anal. Calcd for C$_{57}$F$_{10}$H$_{36}$OP$_2$Pt$_2$: C, 49.69; H, 2.63. Found: C, 49.78; H, 2.60. IR (Nujol, cm^{-1}): ν(CO) 2083 (vs), ν(C$_6$F$_5$)$_{\text{x-sens}}$[14a] 807 (m), 795 (s). EI-MS: *m*/*z* 1378 [M]$^+$ (4%), 719 [Pt(PPh$_3$)$_2$]$^+$ (100%). ^{1}H NMR (CDCl$_3$, 16 °C): δ 7.38−7.15 (m, 35H, PPh$_3$, Ph), 5.75 (dd, C=CH, $^4J_{\text{P−H}}$ = 26.3 and 8.2 Hz). ^{31}P NMR (CDCl$_3$, 16 °C): δ(P$_A$) 35.95 (d, *J*(P$_A$−P$_X$) = 14 Hz, ^1J(Pt(2)−P$_A$) = 5534 Hz, ^2J(Pt(1)−P$_A$) = 344 Hz), δ(P$_X$) 31.17 (d, *J*(P$_A$−P$_X$) = 14 Hz, ^1J(Pt(2)−P$_X$) = 2593 Hz, ^2J(Pt(1)−P$_A$) not resolved). ^{19}F NMR (CDCl$_3$, −50 °C): δ −109.5 (1 F, ^3J(Pt−*o*-F) = 395 Hz), −114.7 (2F, ^3J(Pt−*o*-F) = 258 Hz), −115.7 (1F, ^3J(Pt−*o*-F) = 296 Hz), (d, *o*-F), −158.8 (1F), −161.5 (1F), (t, *p*-F), −162.7 (2F), −164.0 (1F), −166.0 (1F), (m, *m*-F). ^{19}F NMR (CDCl$_3$, 20 °C): δ −109.98 (m br, 1F), −114.3 (d, 2F, ^3J(Pt−*o*-F) = 267 Hz), −115.0 (m br, 1F), (*o*-F), −159.7 (1F), −162.4 (1 F), (t, *p*-F), −163.5 (m, 2F), −166.0 (m br, 2F), (*m*-F). ^{19}F NMR (CDCl$_3$, 50 °C): δ −112.6 (m br, 2F), −113.9 (d, 2F, ^3J(Pt−*o*-F) = 270 Hz), (*o*-F), −159.7 (1F), −162.4 (1F), (t, *p*-F), −163.5 (m, 2F), −165.7 (m br, 2F), (*m*-F). ^{13}C NMR (CDCl$_3$): only carbon resonances in the aromatic region are observed, δ 125.3−134.3 (Ph).

Preparation of *cis,cis*-[(PPh$_3$)(C$_6$F$_5$)$_2$Pt(μ-CHPhCCO)Pt(PPh$_3$)$_2$] (2). A mixture of **1** (0.140 g, 0.1 mmol) and PPh$_3$ (0.026 g, 0.1 mmol) in CH$_2$Cl$_2$ (20 mL) was stirred at room temperature for 17 h. The resulting yellow solution was filtered and concentrated to ~3 mL. Addition of ethanol caused the precipitation of **2** as a pale yellow microcrystalline solid. Yield: 41%. Anal. Calcd for C$_{75}$F$_{10}$H$_{51}$OP$_3$Pt$_2$: C, 54.88; H, 3.13. Found: C, 54.44; H, 3.13. IR (Nujol, cm^{-1}): ν(CO) 1885 (s, br), (1840 (s, br) in CH$_2$Cl$_2$ solution); ν(C$_6$F$_5$)$_{\text{x-sens}}$[14a] 789 (m), 775 (m). EI-MS: molecular peak not observed, *m*/*z* 719 [Pt(PPh$_3$)$_2$]$^+$ (100%). ^{1}H NMR (CDCl$_3$, 16 °C): δ 7.46, 7.31, 7.25, 7.05 and 6.92 (m, 46 H, Ph, PPh$_3$ and one *o*-H of the CHPh fragment), 6.69 (t, 1 *p*-H of CHPh), 6.56 (m, 2 *m*-H of CHPh), 5.57 (d, 1H, *J* = 7.6 Hz), 5.08 (d, 1 H, ^2J(Pt−H) = 43.6 Hz), (benzylenic and *o*-H of the CHPh). ^{31}P NMR (CDCl$_3$, 16 °C): δ 27.2 (s, 1P, ^1J(Pt−P) = 3958 Hz), 15.07 (s, br, 2P, ^1J(Pt−P) = 3960 and 2546 Hz). ^{19}F NMR (CD$_2$Cl$_2$, 16 °C): δ −113.17 (1 F, ^3J(Pt−*o*-F) = 353 Hz), −115.05 (1F, ^3J(Pt−*o*-F) = 347 Hz), −116.48 (1 F, ^3JPt-*o*-F = 373 Hz), −116.95 (1 F, ^3JPt-*o*-F = 361 Hz), (m, *o*-F), −162.47 (1F), −164.93 (1F), (t, *p*-F), −162.07 (1F); −163.22 (1F), −164.18 (1F), −165.19 (1F), (m, *m*-F). ^{13}C NMR (CDCl$_3$): δ 147−137 (C$_6$F$_5$), 125.3−134.1 (aromatic).

Preparation of *cis,cis*-[(PPh$_3$)$_2$Pt{μ-η^2(*C*,*S*):η^1(*C*)-C(SPh)(CH$_2$Ph)}Pt(C$_6$F$_5$)$_2$(CO)] (3). Method a. A mixture of **1** (0.14 g, 0.1 mmol) and 2 mL of PhSH was stirred at room temperature for 4 h. Then, *n*-hexane (10 mL) was added to the resulting yellow solution, causing the precipitation of a yellow solid, which was recrystallized from diethyl ether (yellow crystals, 36% yield). Anal. Calcd for C$_{63}$F$_{10}$H$_{42}$OP$_2$Pt$_2$S: C, 50.81; H, 2.84; S, 2.15. Found: C, 51.22; H, 3.26; S, 1.99. IR (Nujol, cm^{-1}): ν(CO) 2064 (vs); ν(C$_6$F$_5$)$_{\text{x-sens}}$[14a] 791 (m), 778 (m). EI-MS: molecular peak not observed, *m*/*z* 1321 [M − C$_6$F$_5$] (3%), 719 [Pt(PPh$_3$)$_2$]$^+$ (100%). ^{1}H NMR (CDCl$_3$, 16 °C): δ 7.61, 7.32, 7.08 (m, 40H, PPh$_3$ SPh, CH$_2$*Ph*); 3.54 (d, 1H, CH$_2$, ^2J(H−H) = 17 Hz, ^3J(Pt−H) = 70 Hz); 2.82 (dd, 1H, CH$_2$, ^2J(H−H) = 17 Hz, ^4J(P−H) = 5.4 Hz). ^{31}P NMR (CDCl$_3$, 16 °C): δ 19.87 (s, 1P, ^1J(Pt−P) = 2863 Hz); 19.69 (s, 1P, ^1J(Pt−P) = 5055 Hz). ^{19}F NMR (CDCl$_3$, 16 °C): δ −111.82 (1F, ^3J(Pt−*o*-F) = 427 Hz), −116.96 (1F, ^3J(Pt−*o*-F) = 358 Hz), −117.46 (2F, ^3J(Pt−*o*-F) = 279 Hz), (m, *o*-F), −162.33 (1F), −162.69 (1F), (t, *p*-F), −163.60 (1F), −164.54 (2F), −165.22 (1F), (m, *m*-F). ^{13}C NMR (CDCl$_3$): δ 153−135 (C$_6$F$_5$), 125.1−134.2 (aromatic), 49.9 (this signal could be tentatively assigned to the benzylic carbon CH$_2$).

Method b. To an orange solution of **1** (0.13 g, 0.09 mmol) in CH$_2$Cl$_2$ (10 mL) was added 10 μL (0.09 mmol) of PhSH to give, immediately, a pale yellow solution, which was stirred for 1 h. Evaporation of the solution to dryness and treatment with *n*-hexane (~5 mL) afforded **3** in 64% yield.

Crystal Structure Determination of *cis,cis*-[(PPh$_3$)(C$_6$F$_5$)$_2$Pt(μ-CHPhCCO)Pt(PPh$_3$)$_2$] (2) and *cis,cis*-[(PPh$_3$)$_2$Pt{μ-η^2(*C*,*S*):η^1(*C*)-C(SPh)(CH$_2$Ph)}Pt(C$_6$F$_5$)$_2$(CO)] (3). Suitable crystals of **2** and **3** for X-ray studies were obtained by slow diffusion at room temperature of *n*-hexane into an acetone solution of **2** and **3**, respectively. Data were purchased from Crystalytics Co.

Complex 2. A yellow crystal of 0.14 × 0.35 × 0.36 mm was sealed inside a thin-walled glass capillary with epoxy and mounted on a four-circle Nicolet (Siemens) autodiffractometer. Graphite-monochromated Cu Kα (λ = 1.541 84 Å) radiation was used. Unit cell constants were determined from 15 accurately centered reflections with 2θ > 45°. Data were collected at room temperature by the ω−2θ scan technique and corrected for Lorentz, polarization, absorption effects (ψ scan method, 7 reflections, maximum and minimum transmission factors = 1.000 and 0.303, respectively) and for the 22% decay that was observed during the data collection. No extinction correction was applied. The positions of the heavy atoms were determined from the Patterson map. The remaining atoms were located in successive Fourier syntheses. The H atoms of the phenyl groups were incorporated at calculated positions through the use of a riding model in which the C−H distance was fixed at 0.96 Å with a isotropic displacement parameter 1.5 times larger than that of the corresponding C atom. A site in the crystallographic asymmetric unit was found to be occupied by hexane, with an occupancy factor of 0.5. Loose geometrical restraints were applied to the C−C and C···C distances, and no hydrogen atoms of the solvent molecules were located. All non-hydrogen atoms except those of the solvent were refined with anisotropic displacement parameters. Final *R* factors were R_1 = 0.0780 (for 5276 data with $F_o > 4\sigma(F_o)$) and wR_2 = 0.2134 (for all data). There were six peaks higher than 1 e/Å^3 (2.09−1.03 e/Å^3) on the final difference Fourier map, and they were located close to the platinum atoms, without any chemical meaning. The highest hole is −2.563 e/Å^3. The high background is probably due to the poor quality of the data: high absorption and decay.

---

(36) Furlani, A.; Licoccia, S.; Russo, M. V.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1982**, 2449.

Complex 3. A single yellow crystal (approximate dimensions 0.28 × 0.28 × 0.28 mm) was mounted on a four-circle Nicolet (Siemens) autodiffractometer. Graphite-monochromated Mo Kα ($\lambda = 0.710\,73$ Å) radiation was used. Unit cell constants were determined from 15 accurately centered reflections with $2\theta > 21°$. The intensity data were collected by the ω scan techniqe at room temperatre. Six check reflections were measured every 300 min, and no loss of intensity was observed. Lorentz and polarization corrections were applied. Data reduction included an absorption correction (ψ scan method, 7 reflections, maximum and minimum transmission factors = 1.000 and 0.749, respectively). The positions of the platinum atoms were determined from the Patterson map. The remaining atoms were located in subsequent Fourier syntheses. One of the phenyl rings was found to be equally disordered over two positions, with the common C_{ipso} atom (C(16)). All non-hydrogen atoms, except those belonging to the disordered phenyl ring, were refined with anisotropic displacement parameters. Hydrogen atoms were added at calculated positions through the use of a riding model in which the C−H distance was fixed at 0.96 Å with the common isotropic factor refining at 0.079(11) Å^2. The final R factors were $R_1 = 0.0409$ (for 5108 data with $F_o > 4\sigma(F_o)$) and $wR_2 = 0.1029$ (for all data). The highest peak on the final difference Fourier map was 0.882 e/Å^3.

All the calculations were done on a Local Area VAX cluster (VAX/VMS V5.5) with the commercial package SHELXTL-PLUS[37] and the SHELXL-93 program.[38]

Acknowledgment. We thank the Comisión Interministerial de Ciencia y Tecnología (Spain) for financial support (Project PB92-0364) and for a grant to J.R.B.

Supporting Information Available: Tables of bond lengths and bond angles, anisotropic displacement parameters, and atom coordinates and U values for complexes **2** and **3** (18 pages). Ordering information is given on any current masthead page.

OM950891X

---

(37) SHELXTL-PLUS, Software Package for the Determination of Crystal Structures, Release 4.0, Siemens Analytical X-ray Instruments, Inc., Madison WI, 1990.

(38) Sheldrick, G. M. Shelxl-93 FORTRAN program for the refinement of crystal structures from diffraction data, University of Göttingen, 1993 (*J. Appl. Crystallogr.*, manuscript in preparation).