

# Selective Reactions of Functionalized Ruthenium(II) $\sigma$ -Alkynyl Complexes with Dicobalt Octacarbonyl and Tetracobalt Dodecacarbonyl: Synthesis of Cyclopentenone Derivatives *via* Intermolecular Pauson–Khand Reactions

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Treatment of  $[\text{Ru}\{\text{C}\equiv\text{CCPh}_2(\text{C}\equiv\text{CH})\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$  (**1**) with  $[\text{Co}_2(\text{CO})_8]$  leads to the formation of the adduct  $[\text{Ru}\{\text{C}\equiv\text{CCPh}_2(\mu_2\text{-}\eta^2\text{-C}\equiv\text{CH})\text{Co}_2(\text{CO})_6\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$  (**3**) through the selective coordination of the  $\text{Co}_2(\text{CO})_6$  fragment at the terminal alkyne group on **1**. Similarly, the enynyl complex  $[\text{Ru}\{\text{C}\equiv\text{CCH}=\text{CH}(\text{C}\equiv\text{CPh})\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$  (*(E,Z)*-**2**), prepared *via* a Wittig reaction from  $[\text{Ru}\{\text{C}\equiv\text{CCH}_2(\text{PPh}_3)\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$  (**5**) and phenylpropargyl aldehyde, also reacts with  $[\text{Co}_2(\text{CO})_8]$  to yield selectively the adduct  $[\text{Ru}\{\text{C}\equiv\text{CCH}=\text{CH}(\mu_2\text{-}\eta^2\text{-C}\equiv\text{CPh})\text{Co}_2(\text{CO})_6\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$  (*(E,Z)*-**6**). Protonation of complexes **3** and *(E,Z)*-**6** with  $\text{HBF}_4\cdot\text{Et}_2\text{O}$  affords the cationic vinylidene derivatives  $[\text{Ru}\{\text{C}=\text{C}(\text{H})\text{CPh}_2(\mu_2\text{-}\eta^2\text{-C}\equiv\text{CH})\text{Co}_2(\text{CO})_6\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{BF}_4]$  (**4**) and  $[\text{Ru}\{\text{C}=\text{C}(\text{H})\text{CH}=\text{CH}(\mu_2\text{-}\eta^2\text{-C}\equiv\text{CPh})\text{Co}_2(\text{CO})_6\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{BF}_4]$  (*(E,Z)*-**7**), respectively. Dicobalt adduct complexes **3** and *(E,Z)*-**6** undergo Pauson–Khand cyclization processes with strained cyclic alkenes (norbornadiene and norbornene) to afford regioselectively the tricyclic cyclopentenone derivatives **8a,b**, **9a,b**, *(E,Z)*-**10**, and **11**. *(E,Z)*-**6** reacts with  $[\text{Co}_4(\text{CO})_{12}]$  to give an unprecedented ruthenium(II) vinylidene complex containing a tetranuclear “butterfly” type cobalt cluster (**12**), which has been characterized by X-ray diffraction.

## Introduction

Metal-mediated cyclization reactions are becoming increasingly popular as tools for selective organic synthesis.<sup>1</sup> Indeed, the Pauson–Khand reaction, which affords cyclopentenones from the reaction of alkenes with alkynes in the presence of dicobalt octacarbonyl, represents one of the most expeditious ways to achieve functionalized cyclopentane derivatives.<sup>2</sup> Accordingly, this procedure has been successfully applied to the synthesis of a large variety of natural products.<sup>3</sup> This cyclopentenone formation reaction can be regarded as a formal  $[2 + 2 + 1]$  cycloaddition where the alkyne and alkene moieties serve as two-carbon components, whereas the carbonyl functionality is supplied from one of the

carbonyl ligands of the dicobalt unit. The currently accepted mechanistic pathway for this transformation, initially proposed by Magnus,<sup>4</sup> indicates the unambiguous intermediacy of the  $[\text{Co}_2(\text{CO})_6(\mu_2\text{-}\eta^2\text{-RC}\equiv\text{CR}')] \text{ complex.}^5$

The scope of this cycloaddition reaction with respect to the alkyne is considerable, and virtually all alkynes participate in this process. Although the intramolecular

(1) (a) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. (b) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1320. (c) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49. (d) Frühauf, H. W. *Chem. Rev.* **1997**, *97*, 523.

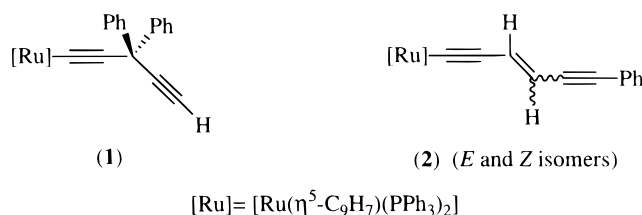
(2) Schore, N. E. in *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, U.K., 1991; Vol. 5, pp 1037–1064.

(3) See for example: (a) Exon, C.; Magnus, P. *J. Am. Chem. Soc.* **1983**, *105*, 2477. (b) Hua, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 3835. (c) Hua, D. H.; Coulter, M. J.; Badejo, I. *Tetrahedron Lett.* **1987**, *28*, 5465. (d) Billington, D. C.; Willison, D. *Tetrahedron Lett.* **1984**, *25*, 4041. (e) Schore, N. E.; Rowley, E. G. *J. Am. Chem. Soc.* **1988**, *110*, 5224. (f) Magnus, P.; Becker, D. P. *J. Am. Chem. Soc.* **1987**, *109*, 7945. (g) Johnstone, C.; Kerr, W. J.; Lange, U. *J. Chem. Soc., Chem. Commun.* **1995**, 459.

(4) (a) Magnus, P.; Exon, C.; Albaugh-Robertson, P. *Tetrahedron* **1985**, *41*, 5861. (b) Magnus, P.; Principe, L. M. *Tetrahedron Lett.* **1985**, *26*, 4851.

(5) The interaction of alkynes with  $[\text{Co}_2(\text{CO})_8]$  leading to  $[\text{Co}_2(\text{CO})_6(\mu_2\text{-}\eta^2\text{-RC}\equiv\text{CR}')] \text{ adducts has been recognized as one of the classical reactions in the field of organometallic chemistry: } \text{Dickson, R. S.; Fraser, P. J. } \textit{Adv. Organomet. Chem.} **1974**, *12*, 323.$

Chart 1



versions of this reaction give typically the best performances, the intermolecular reaction with strained alkenes occurs under milder conditions in the absence of any activator. Moreover, it has been observed that the presence of a nearby metal carbene moiety, probably activating the alkyne functionalization, may additionally promote the reaction, which proceeds under the lowest reported temperatures.<sup>6</sup>

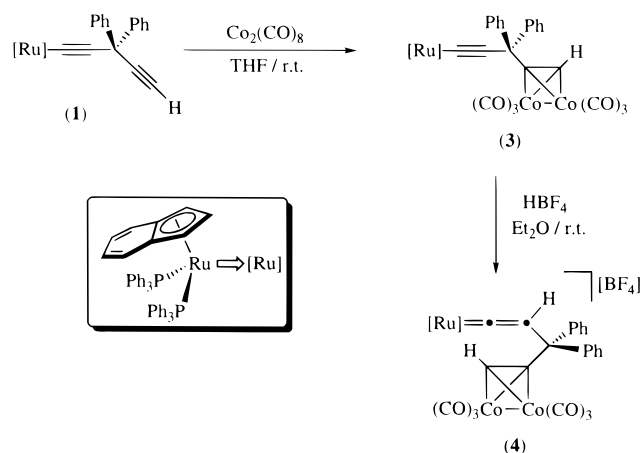
As part of our current research work on the reactivity of unsaturated carbene complexes containing the indenylruthenium(II) moiety  $[\text{Ru}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$  as metal auxiliary, we have described the synthesis of a large variety of functionalized ( $\sigma$ -alkynyl)ruthenium(II) complexes.<sup>7</sup> Since we are especially interested in exploiting the potential utility of these derivatives, we wondered about the possible effect of this metallic auxiliary on the Pauson–Khand type process. Thus, in this paper we describe the reactions of the ruthenium(II)  $\sigma$ -alkynyl derivatives **1** and **2** (Chart 1) with dicobalt octacarbonyl and the construction of the cyclopentenone framework resulting from the reaction of the ruthenium-alkyne-cobalt complexes with strained cyclic alkenes. Recently, related cyclopentenone derivatives have been also obtained by starting from iron(II)<sup>8</sup> and platinum(II)<sup>9</sup>  $\sigma$ -alkynyl complexes.

## Results and Discussion

**Interaction of Ruthenium(II)  $\sigma$ -Alkynyl Complexes with  $[\text{Co}_2(\text{CO})_8]$ .** Treatment of  $[\text{Ru}\{\text{C}\equiv\text{CPh}_2\text{-C}\equiv\text{CH}\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$ <sup>7g</sup> (**1**) with a slight excess of  $[\text{Co}_2(\text{CO})_8]$  in THF at room temperature generates the red adduct **3** (Scheme 1), which has been isolated after column chromatography in 76% yield.

As expected on the basis of steric effects, the spectroscopic data (IR and NMR) of complex **3** show that the coordination of the  $\text{Co}_2(\text{CO})_6$  fragment has occurred at the terminal alkyne group of the complex **1** (details are given in the Experimental Section). The infrared spectrum exhibits the typical carbonyl stretching fre-

Scheme 1



quencies for a  $[\text{Co}_2(\text{CO})_6(\mu_2\text{-}\eta^2\text{-RC}\equiv\text{CR}')] \text{ adduct}$  in the range 2020–2086  $\text{cm}^{-1}$ ,<sup>5</sup> overlapping the expected  $\nu(\text{C}\equiv\text{C})$  absorption band. The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra exhibit resonances in accordance with the proposed structure.<sup>10</sup> Significantly, in the  $^1\text{H}$  NMR spectra the low-field proton resonance from the  $\text{C}_2\text{H}$  group ( $\delta$  6.62 ppm), compared to that in the parent compound **1** ( $\delta$  2.45 ppm),<sup>7g</sup> is characteristic of cobalt  $\eta^2$ -alkyne complexes.<sup>9,11</sup> The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra exhibit the expected signals for the bridging  $\text{C}_2\text{H}$  unit as singlets in the range  $\delta$  80–120 ppm. The  $\text{C}_\alpha$  and  $\text{C}_\beta$  resonances appear as a triplet due to the coupling with the two equivalent phosphorus atoms ( $\delta$  99.97 ppm,  $^2J_{\text{CP}} = 21.8$  Hz) and a singlet at lower field, respectively (see Experimental Section).

Addition of electrophiles to  $\text{C}_\beta$  on  $\sigma$ -alkynyl complexes  $[\text{M}]\text{C}\equiv\text{CR}$  has been described as one of the most versatile entries into vinylidene complexes for a wide variety of systems.<sup>12</sup> Thus, the treatment of a solution of **3** in diethyl ether with an excess of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ , at room temperature, leads to the formation of the mono-substituted cationic vinylidene derivative **4** (Scheme 1), which has been isolated from the reaction mixture as an insoluble, air-stable tetrafluoroborate salt (75% yield). Complex **4** has been characterized by elemental analysis, conductance measurements, and NMR ( $^{31}\text{P}\{^1\text{H}\}$ ,  $^1\text{H}$ , and  $^{13}\text{C}\{^1\text{H}\}$ ) spectroscopy (see Experimental Section).

We have previously reported that alkynyl–phosphonio complexes  $[\text{Ru}\{\text{C}\equiv\text{CCH}(\text{R})(\text{PR}_3)\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$  ( $\text{R} = \text{H}, \text{Ph}$ ) are excellent substrates for Wittig reactions, leading to the formation of new double carbon–carbon bonds.<sup>7c,e</sup> Thus, treating a THF solution of the alkynyl–phosphonio complex **5** ( $\text{R} = \text{H}, \text{PR}_3 = \text{PPh}_3$ ) with 1 equiv of  $\text{Li}^n\text{Bu}$  at  $-20^\circ\text{C}$ , adding phenylpropargyl aldehyde, and warming the mixture to room temperature resulted in the formation of the enynyl complex **2** (Scheme 2). This compound was obtained as

(6) (a) Camps, F.; Moretó, J. M.; Ricart, S.; Viñas, J. M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1470. (b) Jordi, L.; Ricart, S.; Viñas, J. M.; Moretó, J. M. *Organometallics* **1997**, *16*, 2808. (c) Kretschick, O.; Nieger, M.; Dötter, K. H. *Chem. Ber.* **1997**, *130*, 507.

(7) (a) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Lastra, E.; Borge, J.; García-Granda, S. *Organometallics* **1994**, *13*, 745. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Lastra, E. *J. Organomet. Chem.* **1994**, *474*, C27. (c) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Borge, J.; García-Granda, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2495. (d) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J.; García-Granda, S. *Organometallics* **1996**, *15*, 2137. (e) Houbrechts, S.; Clays, K.; Persoons, A.; Cadierno, V.; Gamasa, M. P.; Gimeno, J. *Organometallics* **1996**, *15*, 5266. (f) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 3178. (g) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; López-González, M. C.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 4453.

(8) Akita, M.; Terada, M.; Ishii, N.; Hirakawa, H.; Moro-oka, Y. *J. Organomet. Chem.* **1994**, *473*, 175.

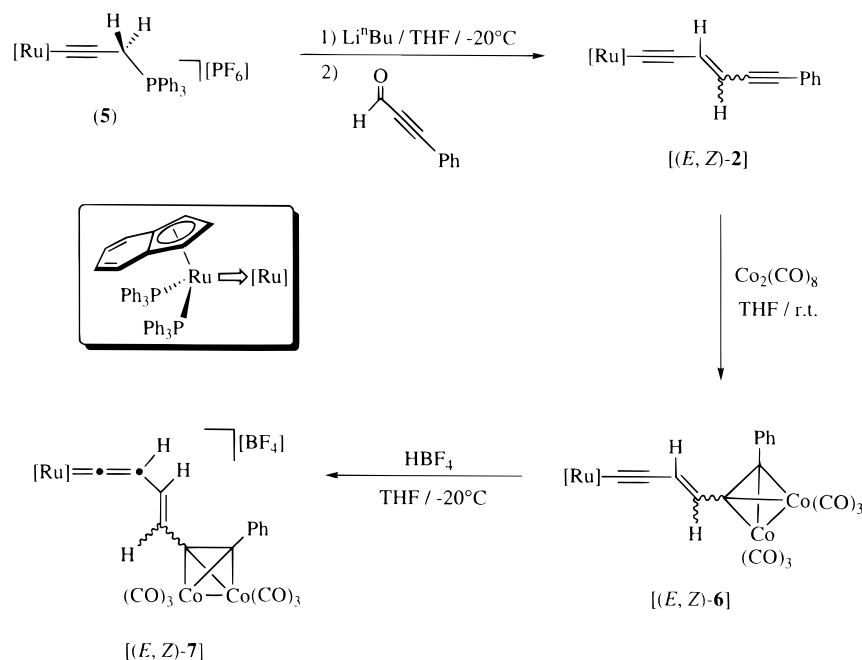
(9) Lewis, J.; Lin, B.; Raithby, P. R. *Transition Met. Chem.* **1995**, *20*, 569.

(10) (a) Gamasa, M. P.; Gimeno, J.; Martín-Vaca, B. M.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. *Organometallics* **1994**, *13*, 4045. (b) Gamasa, M. P.; Gimeno, J.; Godefroy, I.; Lastra, E.; Martín-Vaca, B. M.; García-Granda, S.; Gutiérrez-Rodríguez, A. *J. Chem. Soc., Dalton Trans.* **1995**, 1901.

(11) See for example: (a) Holmes, A. B.; Jennings-White, C. L. D.; Schulthess, A. H.; Akinde, B.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1979**, 840. (b) Holmes, A. B.; Jones, G. E. *Tetrahedron Lett.* **1980**, *21*, 3111.

(12) For a general review see: Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.

Scheme 2



a nonseparable mixture of the *E* and *Z* stereoisomers (ca. 1/2) in 79% yield.

The structure of the conjugated chain on **2** was ascertained from the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopic data. Thus, the olefinic protons appear as doublets ( $J_{\text{HH}} = 15.3$  (*E*) and 10.3 Hz (*Z*)) in the range  $\delta$  5.72–7.51 ppm. The coordinated triple bond shows a considerable polarization. While  $\text{C}_\alpha$  in  $^{13}\text{C}\{^1\text{H}\}$  NMR falls within the aromatic region, the corresponding  $\text{C}_\beta$  appears at  $\delta$  116.23 ppm for both isomers. Singlet signals of the noncoordinated  $\text{C}\equiv\text{C}$  and the olefinic carbons have been assigned using DEPT experiments in the range  $\delta$  91.61–110.56 ppm (see Experimental Section for details).

Similarly to complex **1** coordination of the  $\text{Co}_2(\text{CO})_6$  fragment on **2** takes place selectively on the less sterically hindered (and probably electronically richer)  $\text{C}\equiv\text{C}$  bond, leading to the formation of complex **6** (68% yield), isolated as a green solid (Scheme 2). The *E/Z* stereoisomer ratio on **6** is the same as that found in the parent enynyl compound **2** (ca. 1/2). Analytical and spectroscopic data (IR and  $^{31}\text{P}\{^1\text{H}\}$ ,  $^1\text{H}$ , and  $^{13}\text{C}\{^1\text{H}\}$  NMR) are in accordance with the proposed formulation (see Experimental Section for details).

Similarly to the case for complex **3** the protonation of complex **6** with  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ , in THF at  $-20^\circ\text{C}$ , takes place selectively on the  $\text{C}_\beta$  of the enynyl chain, leading to the formation of the cationic alkenyl–vinylidene derivative **7** (68% yield; *E/Z* ca. 1/2) (Scheme 2). The presence of the vinylidene moiety was identified, as usual, on the basis of the low-field triplet resonance in  $^{13}\text{C}\{^1\text{H}\}$  NMR of the carbene carbon  $\text{Ru}=\text{C}_\alpha$  (*E*, 357.10 ppm,  $^2J_{\text{CP}} = 15.6$  Hz; *Z*, 357.31 ppm;  $^2J_{\text{CP}} = 15.3$  Hz; assigned by taking into account the signal intensity).

The formation of **7** clearly indicates the higher nucleophilic character of the  $\text{C}_\beta$  atom of the enynyl moiety compared to that of the olefinic carbons. It is well-known that  $[\text{Co}_2(\text{CO})_6]$ -stabilized propargylium ions can be easily obtained by electrophilic additions on  $\text{Co}_2(\text{CO})_6$ -

( $\mu_2$ - $\eta^2$ -1,3-enyne) complexes.<sup>13</sup> Furthermore, these derivatives now play a burgeoning role in organic synthesis.<sup>14</sup>

**Synthesis of ( $\sigma$ -Alkynyl)ruthenium(II) Complexes Containing Cyclopentenone Fragments via Pauson–Khand Reactions.** The reactions between the dicobalt adducts **3** and **6** with strained cyclic alkenes have been examined in order to explore their utility for the construction of cyclopentenone frameworks. Thus, the treatment of complex **3** with norbornadiene and norbornene at  $85^\circ\text{C}$  results in the formation of the tricyclic cyclopentenone derivatives **8a** (72%) and **8b** (69%), respectively (Scheme 3).

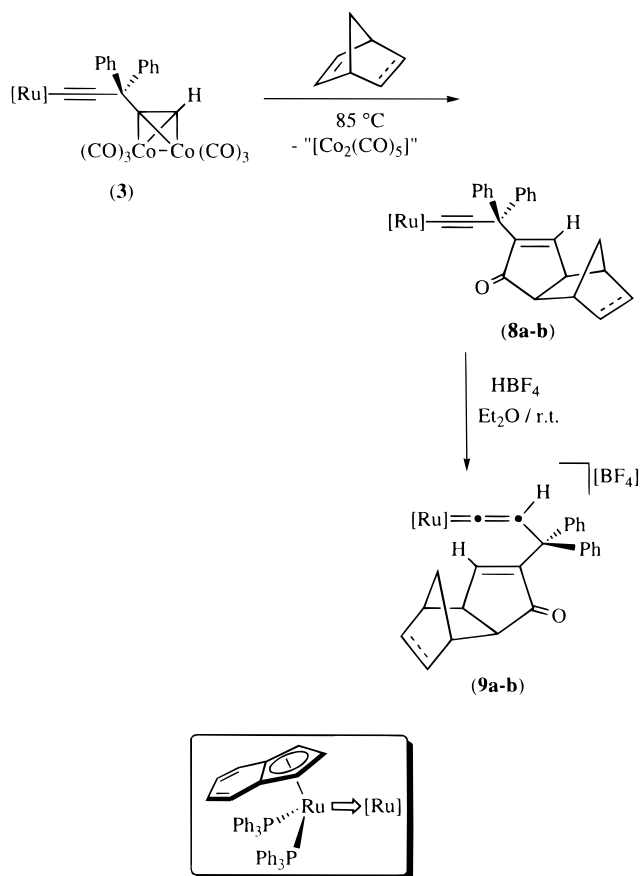
The proposed structures for compounds **8a,b** in which the bulky  $[\text{Ru}(\text{C}\equiv\text{CPh}_2)(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$  fragment is placed at the  $\alpha$ -position of the cyclopentenone rings, are usually observed in other Pauson–Khand cycloadditions starting from analogous terminal alkyne dicobalt adducts.<sup>2</sup> Complexes **8a,b** have been analytically and spectroscopically characterized.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra display two doublet signals (AB system) (**8a**, 53.13 and 53.56 ppm ( $^2J_{\text{PP}} = 33.9$  Hz); **8b**, 52.73 and 53.21 ppm ( $^2J_{\text{PP}} = 33.7$  Hz)). The nonequivalence of the phosphorus nuclei is due to the presence of chiral carbon atoms on the added cycloalkane.

$^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra are in agreement with the presence of the tricyclic cyclopentenone fragments (details are given in the Experimental Section). The most remarkable feature in the  $^1\text{H}$  NMR spectra is the presence of doublet signals in the range  $\delta$  2.01–2.31 ppm, corresponding to the CH protons of the cyclopentenone ring. The values of the chemical shift and coupling constants (ca.  $J_{\text{HH}} = 5.0$  Hz) for these new bridgehead protons indicate that the cyclopentenone ring is fused to the norbornadiene and norbornene

(13) (a) Nicholas, K. M. *Acc. Chem. Res.* **1987**, *20*, 207. (b) Elamouri, H.; Gruselle, M. *Chem. Rev.* **1996**, *96*, 1077 and references cited therein.

(14) Mukai, C.; Hanaoka, M. *Synlett* **1996**, 11 and references cited therein.

Scheme 3



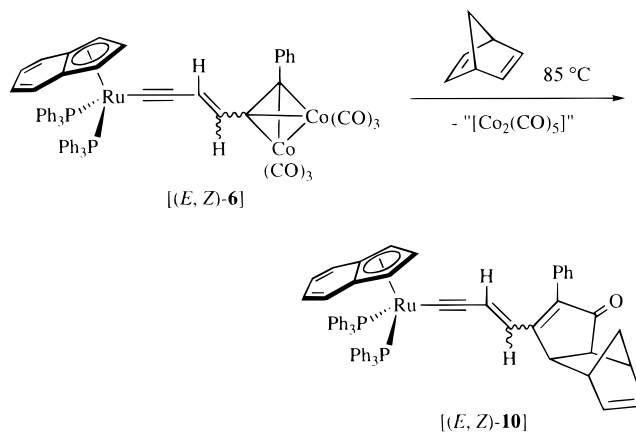
skeleton in an *exo* fashion.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra display characteristic triplet ( $^2J_{\text{CP}} = 23.2$  Hz) resonances for the Ru–C $_{\alpha}$  carbon nucleus at  $\delta$  97.17 (**8a**) and 96.68 (**8b**) ppm. The C $_{\beta}$  and C $_{\gamma}$  nuclei resonate as two singlets at *ca.*  $\delta$  114 and 54 ppm, respectively. The CH and CH $_2$  carbon atoms of the tricyclic units appear as high-field singlets ( $\delta$  28.64–55.82 ppm), while those of the olefinic and C=O groups resonate at lower fields, in the ranges  $\delta$  155.84–161.52 and 204.78–205.93 ppm, respectively.

As the stereochemistry of the fusion of the two rings was found to follow the general trend, being in *exo* fashion, the regiochemistry for the mutual arrangement of the alkene and the alkyne turned out to be that predicted: the ketone carbonyl in the final product binds the most crowded end of the triple bond.<sup>2</sup> This was concluded from the low-field chemical shift for the olefinic proton and also from that for the corresponding C $_{\beta}$  atom in their  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra (*ca.* 7.50 and 161.50 ppm), respectively, in both **8a** and **8b**.

The corresponding vinylidene derivatives containing the tricyclic cyclopentenone fragments have been synthesized through the protonation in Et $_2$ O of the  $\sigma$ -alkynyl complexes **8a,b** with tetrafluoroboric acid at room temperature. The treatment leads to the formation of the desired tetrafluoroborate complexes **9a,b** isolated as brown stable solids (71 and 69%, respectively) (Scheme 3). The presence of the vinyldiene moiety in **9a,b** is clearly confirmed by  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy (see Experimental Section for spectroscopic data).

It is worth mentioning that vinyldiene complexes **9a,b** can not be directly obtained by starting from complex

Scheme 4



**4**. Thus, the treatment of **4** with norbornadiene or norbornene led to the formation of the neutral  $\sigma$ -alkynyl complexes **8a,b** probably due to a deprotonation of the vinylidene complex **4** in the reaction media.

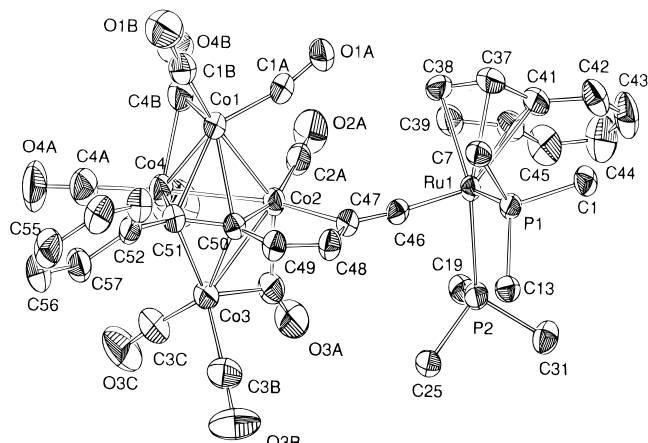
In order to find out to what extent the molecular design of the ( $\sigma$ -alkynyl)ruthenium(II)–dicobalt starting complexes may affect these cycloaddition reactions the behavior of the enynyl complex **6** (*E* + *Z*) toward norbornadiene and norbornene has been also explored. Thus, the reaction of **6** with norbornadiene at 85 °C affords, after column chromatographic purification, the orange cyclopentenone complexes (*E*)-**10** (16%) and (*Z*)-**10** (49%) (Scheme 4).

$^{31}\text{P}\{^1\text{H}\}$  NMR spectra of complexes (*E*)-**10** and (*Z*)-**10** display, similarly to those of complexes **8a,b**, two doublet resonances (*ca.*  $^2J_{\text{PP}} = 30$  Hz) of the diastereotopic phosphorus nuclei at *ca.*  $\delta$  51 ppm. Moreover, IR spectra show the expected  $\nu(\text{C}\equiv\text{C})$  and  $\nu(\text{C}=\text{O})$  absorption bands. An *exo* fusion between the norbornadiene skeletons and the cyclopentenone rings is again found as deduced from the coupling constants ( $J_{\text{HH}} = 5.6$  (*E*) and 5.8 Hz (*Z*)) displayed by the CH protons of the fusion carbons of the cyclopentenone rings. In order to elucidate the resulting regiochemistry, we carried out some  $^1\text{H}$  NMR Eu(III) shifting experiments.<sup>15</sup> Thus, the addition of variable amounts of [Eu(tfn) $_3$ ]<sup>16</sup> to solutions of complexes (*E*)-**10** and (*Z*)-**10** in CDCl $_3$  was found mainly to shift the phenyl proton resonances to lower field. These results indicated that the phenyl group is, in both cases, placed at the  $\alpha$ -position of the cyclopentenone ring.  $^{13}\text{C}\{^1\text{H}\}$  NMR data are also in accordance with the proposed structures (see Experimental Section for details).

The reaction of adduct **6** with norbornene proceeds, however, in a different way (Scheme 5). Thus, the treatment of **6** with norbornene at 85 °C yields the new enynyl complex **11** (42%), identified by comparison of its spectroscopic data to those shown by the analogous complex (*Z*)-**10** (see Experimental Section) along with the *E* stereoisomer of **2** probably generated from the loss of the Co $_2$ (CO) $_6$  fragment in the parent complex **6**.

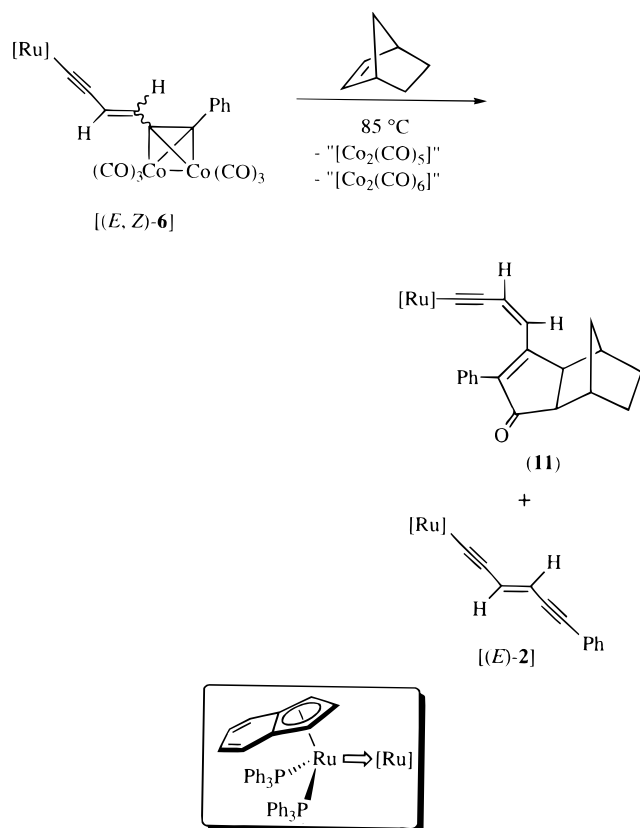
(15) It is well-known that when lanthanide complexes are added to solutions of organic compounds containing heteroatoms they cause a shift of the proton resonances: (a) Cotton, S. *Lanthanides & Actinides*; MacMillan Physical Science Series; Oxford University Press: New York, 1991. (b) *Lanthanide Shift Reagents in Stereochemical Analysis*; Morrill, T. C., Ed.; VCH: Weinheim, Germany, 1986.

(16) tfn = 1,1,1,2,2,3,3,7,7,8,8,9,9,9-tetradecafluoro-4,6-nonanedionate.



**Figure 1.** ORTEP view of the structure of complex **12**. For clarity, aryl groups of the triphenylphosphine ligands are omitted.

### Scheme 5



In contrast, when this reaction is performed in refluxing THF, the new complex **12** (10%), isolated as a green air-stable solid, is formed along with **11** (33%) and (*E*)-**2** (21%). Complex **12** has been characterized by an X-ray crystallographic study, and its molecular structure is shown in Figure 1. Selected bond distances and angles are listed in Table 1.

Complex **12** consists of an unprecedented vinylideneruthenium(II) fragment, displaying the typical three-legged piano-stool geometry, which is attached to the tetranuclear cobalt cluster  $\text{Co}_4(\text{CO})_9$ . The Ru atom is bonded to the  $\eta^5$ -indenyl group, the P(1) and P(2) atoms of the phosphines, and a carbon atom (C(46)) of the unsaturated vinylidene chain. The interligand angles P(1)–Ru–P(2), C(46)–Ru–P(1) and C(46)–Ru–P(2) and

**Table 1.** Selected Bond Distances (Å) and Bond Angles (deg) for Complex **12**

Distances			
Ru–C* <sup>a</sup>	1.924	Co(1)–C(51)	2.106(2)
Ru–P(1)	2.3584(8)	Co(4)–C(51)	2.014(2)
Ru–P(2)	2.3539(8)	Co(2)–C(50)	1.979(2)
Ru–C(46)	1.884(2)	Co(2)–Co(4)	2.6311(10)
C(46)–C(47)	1.281(3)	Co(2)–Co(1)	2.4542(8)
C(47)–C(48)	1.451(3)	Co(2)–Co(3)	2.4665(8)
C(48)–C(49)	1.331(3)	Co(2)–C(47)	2.076(2)
C(49)–C(50)	1.457(3)	Co(3)–Co(4)	2.4204(7)
C(50)–C(51)	1.408(3)	Co(3)–C(50)	2.048(2)
Co(1)–Co(4)	2.4463(7)	Co(3)–C(51)	2.118(2)
Co(1)–C(50)	2.098(2)		
Angles			
C*–Ru–C(46)	122.88(7)	C(50)–C(51)–C(52)	126.8(2)
C*–Ru–P(1)	118.31(2)	C(46)–C(47)–Co(2)	121.2(3)
C*–Ru–P(2)	125.38(2)	C(48)–C(47)–Co(2)	108.3(2)
P(1)–Ru–P(2)	102.90(3)	Co(4)–Co(1)–Co(2)	64.95(2)
C(46)–Ru–P(2)	88.62(7)	Co(1)–Co(2)–Co(3)	92.48(2)
C(46)–Ru–P(1)	90.44(7)	Co(1)–Co(2)–Co(4)	57.38(2)
Ru–C(46)–C(47)	175.3(2)	Co(3)–Co(2)–Co(4)	56.58(2)
C(46)–C(47)–C(48)	131.0(2)	Co(4)–Co(3)–Co(2)	65.14(2)
C(47)–C(48)–C(49)	119.7(2)	Co(3)–Co(4)–Co(1)	93.82(2)
C(48)–C(49)–C(50)	115.9(2)	Co(3)–Co(4)–Co(2)	58.27(2)
C(49)–C(50)–C(51)	134.9(2)	Co(1)–Co(4)–Co(2)	57.67(2)

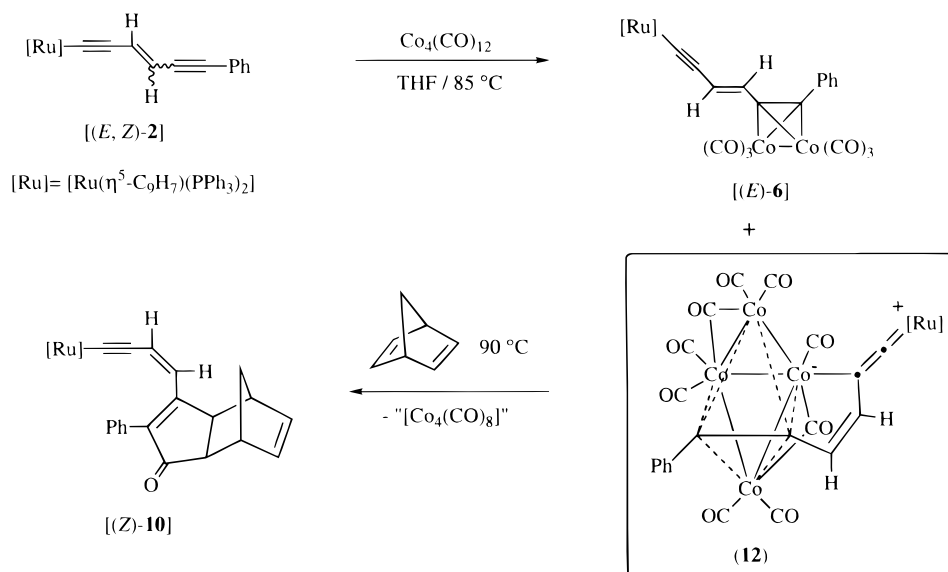
<sup>a</sup> C\* = centroid of C(37), C(38), C(39), C(40), and C(41).

those between the centroid C\* and the legs show typical values of a pseudooctahedron. The unsaturated chain consisting of the carbon atoms C46–C47–C48–C49–C50–C51 is linked to a tetranuclear “butterfly” type cobalt cluster through the terminal triple bond C(50)–C(51) in such a way that the C–C bond is nearly parallel to the hinge of the butterfly (see Figure 1). A similar arrangement is shown in the structures of the well-known tetranuclear complexes  $[\text{Co}_4(\text{CO})_{10}(\mu_4\text{-}\eta^2\text{-RC}\equiv\text{CR}^*)]$ .<sup>17</sup>

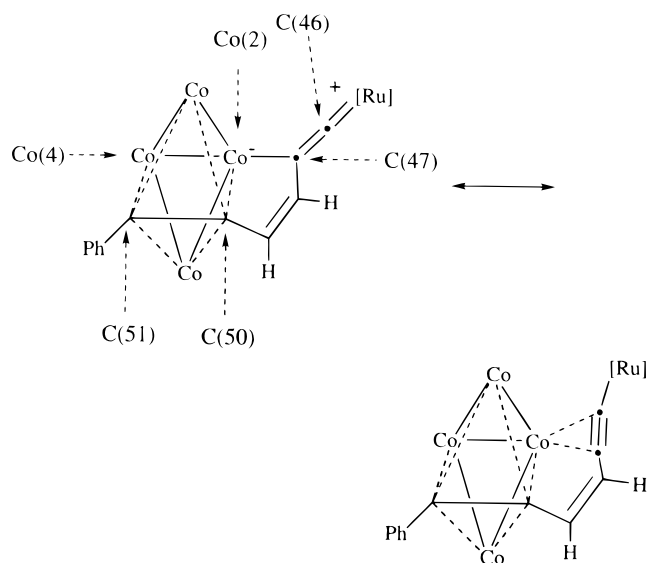
The Co–Co distances are similar and are close (average 2.4837 Å) to those of the metal lattice (2.50 Å), the hinge bond of the butterfly (Co(2)–Co(4) = 2.6311(10) Å) being longer (*ca.* 0.18 Å) than the rest (see Table 1). The bonding of the alkyne to the tetranuclear cluster can be formally described as consisting of two  $\sigma$ -bonds (C(50)–Co(2) and C(51)–Co(4)) and a delocalized four-center–two-electron  $\pi$ -bonding system between C(50), C(51), Co(1), and Co(3). In accordance with this description, the former carbon–cobalt distances (1.979(2) and 2.014(2) Å, respectively) are significantly shorter than those implied in the  $\pi$ -bond (average 2.0925 Å). The Co(2) atom is also bound to the  $\text{C}_\beta$  atom C(47) of the vinylidene group with a bond length of 2.076(2) Å, which is consistent with the presence of a single metal–carbon bond. The vinylidene ligand is bound to ruthenium in a nearly linear fashion, with an Ru–C(46)–C(47) angle of 175.3(2)°. The Ru–C(46) and C(46)–C(47) bond lengths of 1.884(2) and 1.281(3) Å, respectively, are larger than those observed in analogous indenylruthenium(II) vinylidene complexes.<sup>7a,f,10a</sup> These distances seem to indicate an effective contribution of an  $\eta^2$ -alkyne canonical form (Chart 2). In fact, the Co(2) and C(46) atoms are located at a relatively short distance (2.940 Å), and a bonding interaction between

(17) See for example: (a) Dahl, L. F.; Smith, D. L. *J. Am. Chem. Soc.* **1962**, *84*, 2450. (b) Gervasio, G.; Rossetti, R.; Stanghellini, P. L. *Organometallics* **1985**, *4*, 1612. (c) Osella, D.; Ravera, M.; Nervi, C.; Housecroft, C. E.; Raithby, P. R.; Zanello, P.; Laschi, F. *Organometallics* **1991**, *10*, 3253.

## Scheme 6



## Chart 2



these two atoms cannot be discarded. Moro-oka and co-workers have recently reported a similar bonding interaction in the binuclear vinylidene complex  $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}=\text{C}=\text{CH}(\text{Fp})]$  ( $\text{Fp} = \text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$ ) with a distance of 2.866(6) Å.<sup>18</sup> The contribution of this canonical form in the bonding to the cluster is consistent with the chemical shifts observed for the  $\text{C}_\alpha$  and  $\text{C}_\beta$  atoms in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (see Experimental Section). The  $\text{C}(48)\text{--}\text{C}(49)$  bond length of 1.331(3) Å is consistent with the presence of a double  $\text{C}\text{--}\text{C}$  bond.

The formation of complex **12** can be understood as the result of the reaction of  $(Z)\text{-}6$  with 1 equiv of the fragment  $\text{Co}_2(\text{CO})_6$  or  $\text{Co}_2(\text{CO})_5$ , which is eliminated in the process of formation of complexes  $(E)\text{-}2$  and **11**, respectively (Scheme 5). It is interesting to note that the atypical interaction of the  $\text{C}_\beta$  atom  $\text{C}(47)$  with the  $\text{Co}(2)$  atom arises from the  $Z$  configuration of the enynyl chain, which probably also is promoting the formation of complex **11** from  $(Z)\text{-}6$  (for the  $E$  isomer the metal

alkynyl moiety would be too far away to allow such an interaction). Probably, this cisoid arrangement may also favor the proton abstraction observed in the reaction of the vinylidene complex **4** with norbornadiene and norbornene (see above), affording the alkynyl complexes **8a,b**. Such an arrangement of the vinylidene group would locate one of the unsaturated cobalt atoms (generated during the Pauson–Khand cycloaddition) in the proximity of the hydrogen atom of the vinylidene group.

The presence of the tetranuclear cobalt fragment in the structure of complex **12** suggests that it could be directly obtained from the reaction of the enynyl complex **2** with  $[\text{Co}_4(\text{CO})_{12}]$ . Accordingly, when a mixture of **2** and  $[\text{Co}_4(\text{CO})_{12}]$  was heated under reflux in THF for 2 h, complex **12** was obtained, after column chromatography, in 44% yield (Scheme 6), also with the  $E$  isomer of complex **6**.<sup>19</sup>

It is worth mentioning that vinylidene complex **12** is also active in Pauson–Khand reactions. Thus, treatment of **12** with norbornadiene leads finally to the formation of  $(Z)\text{-}10$  in almost quantitative yield (Scheme 6). However, a longer reaction time (90 min) and a higher temperature (90 °C) are required with respect to the reaction starting from enynyl complex **6**. This seems to indicate that complex **12** is not an intermediate in these cycloaddition processes, and only by loss of a  $\text{Co}_2(\text{CO})_4$  unit (more forcing reaction conditions) may the process be reconducted to the same intermediate involved in the conventional Pauson–Khand reaction.

The behavior of adducts **3** and **6** with a large variety of unstrained alkenes has been also studied. However, the displacement of the coordinated alkyne by the alkenes takes place instead to give the parent complexes **1** and **2**, respectively, even in the presence of amine  $N$ -oxides.<sup>20</sup>

(19) It has been previously reported that  $[\text{Co}_2(\text{CO})_6(\mu_2\text{-}\eta^2\text{-RC}\equiv\text{CR})]$  adducts can be obtained from the reactions of alkynes with  $\text{Co}_4(\text{CO})_{12}$ : Dickson, R. S.; Tailby, G. R. *Aust. J. Chem.* **1970**, *23*, 229.

(20) Amine  $N$ -oxides have been shown to promote Pauson–Khand reactions in a wide range of examples: (a) Billington, D. C.; Kerr, W. J.; Pauson, P. L. *J. Organomet. Chem.* **1988**, *341*, 181. (b) Gordon, A. R.; Johnstone, C.; Kerr, W. J. *Synlett* **1995**, 1083. (c) Kerr, W. J.; Kirk, G. G.; Middlemiss, D. *Synlett* **1995**, 1085 and references cited therein.

(18) Akita, M.; Ishii, N.; Takabuchi, A.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1994**, *13*, 258.

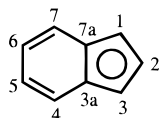
## Experimental Section

The manipulations were performed under dry nitrogen using vacuum-line and standard Schlenk techniques. All reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by standard methods and distilled under nitrogen before use. The complexes  $[\text{Ru}\{\text{C}\equiv\text{CPh}_2(\text{C}\equiv\text{CH})\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$ ,<sup>76</sup>  $[\text{Ru}\{\text{C}\equiv\text{CCH}_2(\text{PPh}_3)\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]^{76}$  and  $\text{Co}_4(\text{CO})_{12}$ <sup>21</sup> were prepared by following the methods reported in the literature.

Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. The conductivities were measured at room temperature, in *ca.*  $10^{-3}$  mol dm<sup>-3</sup> acetone solutions, with a Jenway PCM3 conductimeter. The C and H analyses were carried out with a Perkin-Elmer 240-B microanalyzer. NMR spectra were recorded on a Bruker AC300 instrument at 300 MHz (<sup>1</sup>H), 121.5 MHz (<sup>31</sup>P), or 75.4 MHz (<sup>13</sup>C) using SiMe<sub>4</sub> or 85% H<sub>3</sub>PO<sub>4</sub> as standard. DEPT experiments were carried out for all the complexes. <sup>1</sup>H-<sup>1</sup>H COSY and <sup>1</sup>H-<sup>13</sup>C HMQC experiments were carried out for (*E*)-**6**, (*Z*)-**6**, and **9a**.

Legend for indenyl skeleton:

The numbering system for the indenyl skeleton is as follows:



**Synthesis of  $[\text{Ru}\{\text{C}\equiv\text{CPh}_2(\mu^2\text{-}\eta^2\text{-C}\equiv\text{CH})\text{Co}_2(\text{CO})_6\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$  (**3**).**  $[\text{Co}_2(\text{CO})_8]$  (0.513 g, 1.5 mmol) was added at room temperature to a solution of  $[\text{Ru}\{\text{C}\equiv\text{CPh}_2(\text{C}\equiv\text{CH})\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$  (**1**; 0.956 g, 1 mmol) in 30 mL of THF, and the resulting solution was stirred for 1 h. The solvent was then removed *in vacuo* and the red solid residue transferred to an Alox I chromatography column. Elution with diethyl ether gave a red band which was collected and evaporated to give the desired compound. Yield (%), IR (THF;  $\nu(\text{C}\equiv\text{O})$ , cm<sup>-1</sup>), and NMR spectroscopic data are as follows: 76; 2020, 2048, 2086; <sup>31</sup>P{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>)  $\delta$  51.72 (s) ppm; <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>)  $\delta$  4.68 (d, 2H,  $J_{\text{HH}} = 1.6$  Hz, H-1,3), 5.51 (t, 1H,  $J_{\text{HH}} = 1.6$  Hz, H-2), 6.43 (m, 2H, H-4,7 or H-5,6), 6.62 (s, 1H, CH), 6.86–7.67 (m, 42H, Ph and H-4,7 or H-5,6) ppm; <sup>13</sup>C{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>)  $\delta$  55.77 (s, C<sub>7</sub>), 72.97 (s, C-1,3), 80.37 (s, CH), 96.10 (s, C-2), 99.97 (t, <sup>2</sup> $J_{\text{CP}} = 21.8$  Hz, Ru-C<sub>α</sub>), 110.89 (s, C-3a,7a), 115.89 and 117.07 (s, C and C<sub>β</sub>), 124.12 (s, C-4,7 or C-5,6), 125.95–148.71 (m, Ph and C-4,7 or C-5,6), 200.66 (s, C=O) ppm.  $\Delta\delta(\text{C-3a,7a}) = -19.81$ . Anal. Calcd for RuC<sub>68</sub>H<sub>48</sub>O<sub>6</sub>Co<sub>2</sub>P<sub>2</sub>: C, 65.76; H, 3.89. Found: C, 65.42; H, 3.77.

**Synthesis of  $[\text{Ru}\{\text{C}\equiv\text{C}(\text{H})\text{CPh}_2(\mu^2\text{-}\eta^2\text{-C}\equiv\text{CH})\text{Co}_2(\text{CO})_6\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{BF}_4]$  (**4**).** To a stirred solution of the alkynyl complex **3** (1.24 g, 1 mmol) in 100 mL of diethyl ether, at room temperature, was added a dilute solution of HBF<sub>4</sub>·Et<sub>2</sub>O in diethyl ether dropwise. Immediately, an insoluble solid precipitated but the addition was continued until no further solid was formed. The solution was then decanted and the brown solid washed with diethyl ether (3 × 20 mL) and vacuum-dried. Yield (%), IR (THF;  $\nu(\text{C}\equiv\text{O})$ , cm<sup>-1</sup>), conductivity (acetone, 20 °C,  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>), and NMR spectroscopic data are as follows: 75; 2026, 2052, 2090; <sup>31</sup>P{<sup>1</sup>H} ((CD<sub>3</sub>)<sub>2</sub>CO)  $\delta$  37.33 (s) ppm; <sup>1</sup>H ((CD<sub>3</sub>)<sub>2</sub>CO)  $\delta$  4.69 (t, 1H, <sup>4</sup> $J_{\text{HP}} = 1.9$  Hz, Ru=C=CH), 5.43 and 7.24 (m, 2H each, H-4,7 and H-5,6), 5.52 (d, 2H,  $J_{\text{HH}} = 2.9$  Hz, H-1,3), 6.46 (t, 1H,  $J_{\text{HH}} = 2.9$  Hz, H-2), 6.69–7.59 (m, 41H, Ph and CH) ppm; <sup>13</sup>C{<sup>1</sup>H} ((CD<sub>3</sub>)<sub>2</sub>CO)  $\delta$  56.75 (s, C<sub>7</sub>), 80.63 (s, CH), 81.82 (s, C-1,3), 100.37 (s, C-2), 115.73 (s, C), 119.25 (s, C-3a,7a), 124.60 and 128.67 (s, C-4,7 and C-5,6), 124.76 (s, C<sub>β</sub>), 129.38–146.38 (m, Ph), 200.52 (s, C=O), 342.52 (t, <sup>2</sup> $J_{\text{CP}} = 15.8$  Hz, Ru=C<sub>α</sub>) ppm.  $\Delta\delta(\text{C-3a,7a}) =$

–11.45. Anal. Calcd for RuC<sub>68</sub>H<sub>49</sub>O<sub>6</sub>F<sub>4</sub>Co<sub>2</sub>P<sub>2</sub>B: C, 61.42; H, 3.71. Found: C, 60.93; H, 3.91.

**Synthesis of  $[\text{Ru}\{\text{C}\equiv\text{CCH}=\text{CH}(\text{C}\equiv\text{CPh})\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$  [(*E,Z*)-**2**].** To a solution of  $[\text{Ru}\{\text{C}\equiv\text{CCH}_2(\text{PPh}_3)\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$  (**5**; 1.186 g, 1 mmol) in 25 mL of THF, kept at –20 °C, was added a solution of Li<sup>n</sup>Bu (1.6 M in hexane, 0.625 mL, 1 mmol). After the addition was complete, the color of the solution had changed from yellow to violet. The reaction mixture was stirred for 15 min; phenylpropargyl aldehyde (0.366 mL, 3 mmol) was added, and after this mixture was warmed to room temperature it was stirred for 30 min. The solvent was then removed *in vacuo* and the orange solid residue transferred to an Alox I chromatography column. Elution with hexane/diethyl ether (1/1) gave complex **2** as a mixture of stereoisomers *E/Z* (1/2). Yield: 79%. Anal. Calcd for RuC<sub>57</sub>H<sub>44</sub>P<sub>2</sub>: C, 76.75; H, 4.97. Found: C, 76.13; H, 4.81. IR (KBr;  $\nu(\text{C}\equiv\text{C})$ , cm<sup>-1</sup>), and NMR spectroscopic data are as follows. *E*: 2038, 2140; <sup>31</sup>P{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>)  $\delta$  51.57 (s) ppm; <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>)  $\delta$  4.69 (d, 2H,  $J_{\text{HH}} = 2.2$  Hz, H-1,3), 5.57 (t, 1H,  $J_{\text{HH}} = 2.2$  Hz, H-2), 6.14 (d, 1H,  $J_{\text{HH}} = 15.3$  Hz, =CH), 6.28 and 6.65 (m, 2H each, H-4,7 and H-5,6), 6.88–7.51 (m, 36H, Ph and =CH) ppm; <sup>13</sup>C{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>)  $\delta$  75.19 (s, C-1,3), 91.61 and 92.65 (s, C≡C), 95.47 (s, C-2), 109.58 (s, C-3a,7a), 110.56 (s, =CH), 116.23 (s, C<sub>β</sub>), 123.14–138.63 (m, Ph, C-4,7, C-5,6, =CH and Ru-C<sub>α</sub>) ppm.  $\Delta\delta(\text{C-3a,7a}) = -21.12$ . *Z*: 2038, 2182; <sup>31</sup>P{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>)  $\delta$  50.84 (s) ppm; <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>)  $\delta$  4.78 (d, 2H,  $J_{\text{HH}} = 2.6$  Hz, H-1,3), 5.72 (d, 1H,  $J_{\text{HH}} = 10.3$  Hz, =CH), 6.02 (t, 1H,  $J_{\text{HH}} = 2.6$  Hz, H-2), 6.28 and 6.65 (m, 2H each, H-4,7 and H-5,6), 6.88–7.51 (m, 34H, Ph and =CH), 7.67 (d, 2H,  $J_{\text{HH}} = 7.6$  Hz, Ph) ppm; <sup>13</sup>C{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>)  $\delta$  75.19 (s, C-1,3), 92.46 and 92.52 (s, C≡C), 96.90 (s, C-2), 108.39 (s, =CH), 109.99 (s, C-3a,7a), 116.23 (s, C<sub>β</sub>), 123.14–138.63 (m, Ph, C-4,7, C-5,6, =CH and Ru-C<sub>α</sub>) ppm.  $\Delta\delta(\text{C-3a,7a}) = -20.71$ .

**Synthesis of  $[\text{Ru}\{\text{C}\equiv\text{CCH}=\text{CH}(\mu^2\text{-}\eta^2\text{-C}\equiv\text{CPh})\text{Co}_2(\text{CO})_6\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$  [(*E,Z*)-**6**].**  $[\text{Co}_2(\text{CO})_8]$  (0.513 g, 1.5 mmol) was added at room temperature to a solution of  $[\text{Ru}\{\text{C}\equiv\text{CCH}=\text{CH}(\text{C}\equiv\text{CPh})\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$  [(*E,Z*)-**2**; 0.892 g, 1 mmol) in 30 mL of THF and the resulting solution stirred for 1 h. The solvent was then removed *in vacuo* and the green solid residue transferred to an Alox I chromatography column. Elution with diethyl ether gave a green band, which was collected and evaporated to give complex **6** as a mixture of stereoisomers *E/Z* (1/2). Yield: 68%. IR (THF;  $\nu(\text{C}\equiv\text{O})$ , cm<sup>-1</sup>):

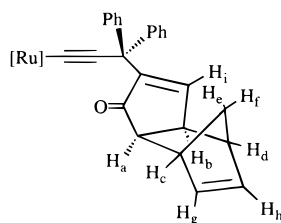
2017, 2047, 2083. Anal. Calcd for RuC<sub>63</sub>H<sub>54</sub>O<sub>6</sub>Co<sub>2</sub>P<sub>2</sub>: C, 63.69; H, 4.58. Found: C, 63.39; H, 4.22. NMR spectroscopic data are as follows. *E*: <sup>31</sup>P{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>)  $\delta$  49.65 (s) ppm; <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>)  $\delta$  4.71 (m, 2H, H-1,3), 5.66 (m, 1H, H-2), 6.10 (m, 2H, H-4,7 or H-5,6), 6.46–7.92 (m, 39H, Ph, CH=CH and H-4,7 or H-5,6) ppm; <sup>13</sup>C{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>)  $\delta$  75.13 (s, C-1,3), 90.46 and 93.22 (s, C), 95.55 (s, C-2), 110.26 (s, C-3a,7a), 117.72 (s, C<sub>β</sub>), 123.18 and 126.11 (s, C-4,7 and C-5,6), 124.70 (s, =CH), 127.48–139.95 (m, Ph and =CH), 143.74 (t, <sup>2</sup> $J_{\text{CP}} = 23.9$  Hz, Ru-C<sub>α</sub>), 200.39 (s, C=O) ppm.  $\Delta\delta(\text{C-3a,7a}) = -20.44$ . *Z*: <sup>31</sup>P{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>)  $\delta$  50.77 (s) ppm; <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>)  $\delta$  4.76 (m, 2H, H-1,3), 5.91 (m, 1H, H-2), 6.25 (m, 2H, H-4,7 or H-5,6), 6.46–7.92 (m, 39H, Ph, CH=CH and H-4,7 or H-5,6) ppm; <sup>13</sup>C{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>)  $\delta$  75.13 (s, C-1,3), 93.49 and 93.84 (s, C), 95.55 (s, C-2), 109.80 (s, C-3a,7a), 118.36 (s, C<sub>β</sub>), 120.31 and 124.05 (s, =CH), 123.18 and 126.11 (s, C-4,7 and C-5,6), 127.48–139.95 (m, Ph and Ru-C<sub>α</sub>), 201.16 (s, C=O) ppm.  $\Delta\delta(\text{C-3a,7a}) = -20.90$ .

**Synthesis of  $[\text{Ru}\{\text{C}\equiv\text{C}(\text{H})\text{CH}=\text{CH}(\mu^2\text{-}\eta^2\text{-C}\equiv\text{CPh})\text{Co}_2(\text{CO})_6\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{BF}_4]$  (*E,Z*)-**7**.** To a solution of the enynyl complex (*E,Z*)-**6** (1.188 g, 1 mmol) in 50 mL of THF, at room temperature, was added dropwise an excess of a diluted solution of HBF<sub>4</sub>·Et<sub>2</sub>O in diethyl ether (*ca.* 3 mmol). The resulting solution was stirred at room temperature for 30 min. The solvent was then removed *in vacuo* and the black solid obtained washed with diethyl ether (3 × 20 mL) and vacuum-dried. Complex **7** was obtained as a mixture of stereoisomers *E/Z* (1/2). Yield (%), IR (THF;  $\nu(\text{C}\equiv\text{O})$ , cm<sup>-1</sup>), and conductivity (acetone, 20 °C,  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>) data are as follows: 68; 2086,

(21) King, R. B. In *Organometallic Syntheses*; Eisch, J. J., King, R. B., Eds.; Academic Press: New York, 1965, Vol I, p 98.

2051, 2021; 108. Anal. Calcd for  $\text{RuC}_{63}\text{H}_{45}\text{O}_6\text{F}_4\text{Co}_2\text{P}_2\text{B}$ : C, 59.78; H, 3.58. Found: C, 59.02; H, 3.72. NMR spectroscopic data are as follows.  $E$ :  $^{31}\text{P}\{^1\text{H}\}$  ( $(\text{CD}_3)_2\text{CO}$ )  $\delta$  41.98 (s) ppm;  $^1\text{H}$  ( $(\text{CD}_3)_2\text{CO}$ )  $\delta$  5.82–5.87 (m, 4H, H-1,3, H-2 and  $\text{Ru}=\text{C}=\text{CH}$ ), 6.44 (m, 2H, H-4,7 or H-5,6), 6.67 (d, 1H,  $J_{\text{HH}} = 14.4$  Hz,  $=\text{CH}$ ), 6.98–7.76 (m, 38H, Ph,  $=\text{CH}$  and H-4,7 or H-5,6) ppm;  $^{13}\text{C}\{^1\text{H}\}$  ( $(\text{CD}_3)_2\text{CO}$ )  $\delta$  86.88 (s, C-1,3), 93.19 and 93.46 (s, C), 99.34 (s, C-2), 115.02 (s, C-3a,7a), 118.55, 121.36 and 122.37 (s,  $\text{CH}=\text{CH}$  and  $\text{C}_\beta$ ), 123.73–138.80 (m, Ph, H-4,7 and H-5,6), 200.37 (s,  $\text{C}=\text{O}$ ), 357.10 (t,  $^2J_{\text{CP}} = 15.6$  Hz,  $\text{Ru}=\text{C}_\alpha$ ) ppm.  $\Delta\delta(\text{C-3a,7a}) = -15.68$ .  $Z$ :  $^{31}\text{P}\{^1\text{H}\}$  ( $(\text{CD}_3)_2\text{CO}$ )  $\delta$  40.81 (s) ppm;  $^1\text{H}$  ( $(\text{CD}_3)_2\text{CO}$ )  $\delta$  5.82–5.87 (m, 4H, H-1,3, H-2 and  $\text{Ru}=\text{C}=\text{CH}$ ), 6.44 (m, 2H, H-4,7 or H-5,6), 6.57 (d, 1H,  $J_{\text{HH}} = 9.8$  Hz,  $=\text{CH}$ ), 6.98–7.76 (m, 38H, Ph,  $=\text{CH}$  and H-4,7 or H-5,6) ppm;  $^{13}\text{C}\{^1\text{H}\}$  ( $(\text{CD}_3)_2\text{CO}$ )  $\delta$  84.95 and 90.95 (s, C), 86.53 (s, C-1,3), 99.52 (s, C-2), 115.42 (s, C-3a,7a), 116.35, 118.77 and 121.32 (s,  $\text{CH}=\text{CH}$  and  $\text{C}_\beta$ ), 123.73–138.80 (m, Ph, C-4,7 and C-5,6), 200.37 (s,  $\text{C}=\text{O}$ ), 357.31 (t,  $^2J_{\text{CP}} = 15.3$  Hz,  $\text{Ru}=\text{C}_\alpha$ ) ppm.  $\Delta\delta(\text{C-3a,7a}) = -15.28$ .

**Reaction of  $[\text{Ru}\{\text{C}=\text{CCPh}_2(\mu^2-\eta^2-\text{C}\equiv\text{CH})\text{Co}_2(\text{CO})_6\}(\eta^5-\text{C}_9\text{H}_7)(\text{PPh}_3)_2$  (**3**) with Norbornadiene.** A solution of complex **3** (1.242 g, 1 mmol) in 20 mL of norbornadiene was heated at 85 °C for 30 min. The solvent was then removed *in vacuo* and the orange solid residue transferred to an Alox I chromatography column. Elution with  $\text{CH}_2\text{Cl}_2$  gave complex **8a** (orange band). The labeling scheme is as follows:



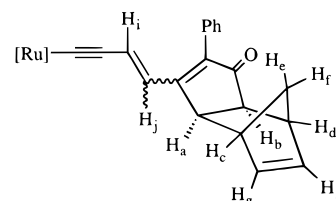
Yield (%), IR (KBr;  $\nu(\text{C}=\text{O})$ ,  $\nu(\text{C}\equiv\text{C})$ ,  $\text{cm}^{-1}$ ), and NMR spectroscopic data are as follows: 72; 1700, 2075;  $^{31}\text{P}\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  53.13 (d,  $^2J_{\text{PP}} = 33.9$  Hz,  $\text{PPh}_3$ ), 53.56 (d,  $^2J_{\text{PP}} = 33.9$  Hz,  $\text{PPh}_3$ ) ppm;  $^1\text{H}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  1.32 (d, 1H,  $J_{\text{HH}} = 8.8$  Hz,  $\text{H}_e$  or  $\text{H}_f$ ), 1.47 (d, 1H,  $J_{\text{HH}} = 8.8$  Hz,  $\text{H}_c$  or  $\text{H}_d$ ), 2.20 (d, 1H,  $J_{\text{HH}} = 5.0$  Hz,  $\text{H}_a$ ), 2.31 (m, 2H,  $\text{H}_b$  and  $\text{H}_c$  or  $\text{H}_d$ ), 2.93 (m, 1H,  $\text{H}_c$  or  $\text{H}_d$ ), 4.64 (m, 2H, H-1 and H-3), 5.40 (m, 1H, H-2), 5.90 (m, 2H,  $\text{H}_g$  and  $\text{H}_h$ ), 6.48 (m, 2H, H-4, H-5, H-6, or H-7), 6.79–7.82 (m, 43H, Ph,  $\text{H}_i$  and H-4, H-5, H-6, or H-7) ppm;  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  42.03 (s,  $\text{CH}_e\text{H}_f$ ), 43.97, 44.31, 46.53, and 54.24 (s,  $\text{CH}_a$ ,  $\text{CH}_b$ ,  $\text{CH}_c$ , and  $\text{CH}_d$ ), 54.16 (s,  $\text{C}_\gamma$ ), 73.84 and 74.21 (s, C-1 and C-3), 96.08 (s, C-2), 97.17 (t,  $^2J_{\text{CP}} = 23.2$  Hz,  $\text{Ru}-\text{C}_\alpha$ ), 110.20 and 110.76 (s, C-3a and C-7a), 114.56 (s,  $\text{C}_\beta$ ), 123.93–147.27 (m, Ph, C-4, C-5, C-6 and C-7), 137.50 and 138.43 (s,  $=\text{CH}_g$  and  $=\text{CH}_h$ ), 156.90 (s,  $=\text{C}$ ), 161.49 (s,  $=\text{CH}_i$ ), 204.78 (s,  $\text{C}=\text{O}$ ) ppm.  $\Delta\delta(\text{C-3a,7a}) = -20.22$ . Anal. Calcd for  $\text{RuC}_{70}\text{H}_{56}\text{P}_2\text{O}$ : C, 78.12; H, 5.24. Found: C, 78.47; H, 5.44.

**Reaction of  $[\text{Ru}\{\text{C}=\text{CCPh}_2(\mu^2-\eta^2-\text{C}\equiv\text{CH})\text{Co}_2(\text{CO})_6\}(\eta^5-\text{C}_9\text{H}_7)(\text{PPh}_3)_2$  (**3**) with Norbornene.** A solution of complex **3** (1.242 g, 1 mmol) in 20 mL of norbornene was heated at 85 °C for 30 min. The solvent was then removed *in vacuo* and the orange solid residue transferred to an Alox I chromatography column. Elution with  $\text{CH}_2\text{Cl}_2$  gave complex **8b** (orange band). Yield (%), IR (KBr;  $\nu(\text{C}=\text{O})$ ,  $\nu(\text{C}\equiv\text{C})$ ,  $\text{cm}^{-1}$ ), and NMR spectroscopic data are as follows: 69; 1706, 2071;  $^{31}\text{P}\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  52.73 (d,  $^2J_{\text{PP}} = 33.7$  Hz,  $\text{PPh}_3$ ), 53.21 (d,  $^2J_{\text{PP}} = 33.7$  Hz,  $\text{PPh}_3$ ) ppm;  $^1\text{H}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  0.74–1.31 (m, 6H,  $\text{CH}_2$ ), 1.84 (m, 1H,  $\text{H}_c$  or  $\text{H}_d$ ), 2.01 (d, 1H,  $J_{\text{HH}} = 5.0$  Hz,  $\text{H}_a$ ), 2.12 (m, 1H,  $\text{H}_b$ ), 2.44 (m, 1H,  $\text{H}_c$  or  $\text{H}_d$ ), 4.65 (m, 2H, H-1 and H-3), 5.41 (m, 1H, H-2), 6.50 (m, 2H, H-4, H-5, H-6, or H-7), 6.80–7.83 (m, 41H, Ph,  $\text{H}_i$ , and H-4, H-5, H-6, or H-7), 7.59 (d, 2H,  $J_{\text{HH}} = 7.5$  Hz, Ph) ppm;  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  28.64, 29.50, and 31.97 (s,  $\text{CH}_2$ ), 38.92, 39.48, 47.63, and 55.82 (s,  $\text{CH}_a$ ,  $\text{CH}_b$ ,  $\text{CH}_c$ , and  $\text{CH}_d$ ), 53.88 (s,  $\text{C}_\gamma$ ), 73.86 and 74.26 (s, C-1 and C-3), 96.18 (s, C-2), 96.68 (t,  $^2J_{\text{CP}} = 23.2$  Hz,  $\text{Ru}-\text{C}_\alpha$ ), 110.18 and 110.71 (s,

C-3a and C-7a), 114.65 (s,  $\text{C}_\beta$ ), 123.94–147.38 (m, Ph, C-4, C-5, C-6, and C-7), 155.84 (s,  $=\text{C}$ ), 161.52 (s,  $=\text{CH}_i$ ), 205.93 (s,  $\text{C}=\text{O}$ ) ppm.  $\Delta\delta(\text{C-3a,7a}) = -20.25$ . Anal. Calcd for  $\text{RuC}_{70}\text{H}_{58}\text{P}_2\text{O}$ : C, 77.97; H, 5.42. Found: C, 77.15; H, 5.63.

**Synthesis of Vinylidene Complexes 9a,b.** To a stirred solution of the corresponding alkynyl complex **8a,b** (1 mmol) in 100 mL of diethyl ether, at room temperature, was added dropwise a dilute solution of  $\text{HBF}_4\cdot\text{Et}_2\text{O}$  in diethyl ether. Immediately, an insoluble solid precipitated, but the addition was continued until no further solid was formed. The solution was then decanted and the brown solid washed with diethyl ether (3  $\times$  20 mL) and vacuum-dried. Yield (%), IR (KBr;  $\nu(\text{BF}_4)$ ,  $\nu(\text{C}=\text{O})$ ,  $\text{cm}^{-1}$ ), conductivity (acetone, 20 °C;  $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ), and NMR spectroscopic data are as follows. Anal. Calcd for  $\text{RuC}_{70}\text{H}_{57}\text{F}_4\text{P}_2\text{BO}$ : (**9a**) C, 72.22; H, 4.93. Found: C, 71.98; H, 4.87. **9a**: 71; 1060, 1694; 112;  $^{31}\text{P}\{^1\text{H}\}$  ( $\text{CDCl}_3$ )  $\delta$  35.87 (d,  $^2J_{\text{PP}} = 22.8$  Hz,  $\text{PPh}_3$ ), 37.16 (d,  $^2J_{\text{PP}} = 22.8$  Hz,  $\text{PPh}_3$ ) ppm;  $^1\text{H}$  ( $\text{CDCl}_3$ )  $\delta$  0.93 (d, 1H,  $J_{\text{HH}} = 9.0$  Hz,  $\text{H}_e$  or  $\text{H}_f$ ), 1.28 (d, 1H,  $J_{\text{HH}} = 9.0$  Hz,  $\text{H}_e$  or  $\text{H}_f$ ), 2.45 (d, 1H,  $J_{\text{HH}} = 4.7$  Hz,  $\text{H}_a$ ), 2.74 and 2.81 (m, 1H each,  $\text{H}_c$  and  $\text{H}_d$ ), 2.90 (m, 1H,  $\text{H}_b$ ), 5.30 (m, 2H, H-1 and H-3), 5.38 (m, 2H, H-4, H-5, H-6 or H-7), 5.70 (s, 1H,  $\text{Ru}=\text{C}=\text{CH}$ ), 6.23 (m, 2H, H-2 and  $\text{H}_g$  or  $\text{H}_h$ ), 6.34 (m, 1H,  $\text{H}_g$  or  $\text{H}_h$ ), 6.58–7.45 (m, 43H, Ph,  $\text{H}_i$ , and H-4, H-5, H-6 or H-7) ppm;  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{CDCl}_3$ )  $\delta$  41.39 (s,  $\text{CH}_e\text{H}_f$ ), 43.56 and 44.11 (s,  $\text{CH}_c$  and  $\text{CH}_d$ ), 46.42 and 53.59 (s,  $\text{CH}_a$  and  $\text{CH}_b$ ), 52.64 (s,  $\text{C}_\gamma$ ), 79.95 and 80.04 (s, C-1 and C-3), 99.50 (s, C-2), 115.95 (s,  $\text{C}_\beta$ ), 116.59 and 118.40 (s, C-3a and C-7a), 122.95, 123.70, 127.04 and 127.11 (s, C-4, C-5, C-6, and C-7), 127.85–153.44 (m, Ph,  $=\text{CH}_g$ , and  $=\text{CH}_h$ ), 153.44 (s,  $=\text{C}$ ), 162.09 (s,  $=\text{CH}_i$ ), 207.23 (s,  $\text{C}=\text{O}$ ), 340.25 (t,  $^2J_{\text{CP}} = 15.8$  Hz,  $\text{Ru}=\text{C}_\alpha$ ) ppm.  $\Delta\delta(\text{C-3a,7a}) = -13.20$ . Anal. Calcd for  $\text{RuC}_{70}\text{H}_{59}\text{F}_4\text{P}_2\text{BO}$ : (**9b**) C, 72.10; H, 5.09. Found: C, 72.30; H, 5.15; 119; **9b**: 69; 1060, 1691;  $^{31}\text{P}\{^1\text{H}\}$  ( $\text{CDCl}_3$ )  $\delta$  36.03 (d,  $^2J_{\text{PP}} = 22.5$  Hz,  $\text{PPh}_3$ ), 37.11 (d,  $^2J_{\text{PP}} = 22.5$  Hz,  $\text{PPh}_3$ ) ppm;  $^1\text{H}$  ( $\text{CDCl}_3$ )  $\delta$  0.73 (d, 1H,  $J_{\text{HH}} = 9.8$  Hz,  $\text{H}_e$  or  $\text{H}_f$ ), 0.88 (d, 1H,  $J_{\text{HH}} = 9.8$  Hz,  $\text{H}_e$  or  $\text{H}_f$ ), 1.34 (m, 2H,  $\text{CH}_2$ ), 1.60 (m, 2H,  $\text{CH}_2$ ), 2.20 and 2.29 (m, 1H each,  $\text{H}_c$  and  $\text{H}_d$ ), 2.33 (d, 1H,  $J_{\text{HH}} = 4.7$  Hz,  $\text{H}_a$ ), 2.74 (m, 1H,  $\text{H}_b$ ), 5.32 (m, 4H, H-1, H-3, and H-4, H-5, H-6, or H-7), 5.68 (s, 1H,  $\text{Ru}=\text{C}=\text{CH}$ ), 6.20 (m, 1H, H-2), 6.52–7.44 (m, 43H, Ph,  $=\text{CH}_i$ , and H-4, H-5, H-6, or H-7) ppm;  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{CDCl}_3$ )  $\delta$  28.19, 29.18, and 31.53 (s,  $\text{CH}_2$ ), 38.55, 39.51, 47.00, and 55.07 (s,  $\text{CH}_a$ ,  $\text{CH}_b$ ,  $\text{CH}_c$ , and  $\text{CH}_d$ ), 52.52 (s,  $\text{C}_\gamma$ ), 79.98 and 80.08 (s, C-1 and C-3), 99.50 (s, C-2), 116.07 (s,  $\text{C}_\beta$ ), 116.67 and 118.30 (s, C-3a and C-7a), 123.01 and 123.69 (s, C-4, C-5, C-6, or C-7), 127.02–143.90 (m, Ph and C-4, C-5, C-6, or C-7), 152.62 (s,  $=\text{C}$ ), 162.65 (s,  $=\text{CH}_i$ ), 208.63 (s,  $\text{C}=\text{O}$ ), 340.20 (t,  $^2J_{\text{CP}} = 15.8$  Hz,  $\text{Ru}=\text{C}_\alpha$ ) ppm.  $\Delta\delta(\text{C-3a,7a}) = -13.21$ .

**Reaction of  $[\text{Ru}\{\text{C}=\text{CCH}=\text{CH}(\mu^2-\eta^2-\text{C}\equiv\text{CPh})\text{Co}_2(\text{CO})_6\}(\eta^5-\text{C}_9\text{H}_7)(\text{PPh}_3)_2$  (**6**) with Norbornadiene.** A solution of (*E*)-**6** (1.188 g, 1 mmol) in 20 mL of norbornadiene was heated at 85 °C for 30 min. The solvent was then removed *in vacuo* and the orange solid residue transferred to an Alox I chromatography column. Initial elution with diethyl ether gave an orange band, from which the enynyl complex (*E*)-**10** was obtained by solvent removal. Further purification by elution with a hexane/methanol (4/1) mixture gave an orange solution, from which the enynyl complex (*Z*)-**10** was obtained. The labeling scheme is as follows:



Anal. Calcd for  $\text{RuC}_{65}\text{H}_{52}\text{P}_2\text{O}$  (*E*)-**10**: C, 77.13; H, 5.18. Found: C, 77.32; H, 5.23. Yield (%), IR (KBr;  $\nu(\text{C}=\text{O})$ ,  $\nu(\text{C}\equiv\text{C})$ ,  $\text{cm}^{-1}$ ), and NMR spectroscopic data are as follows: *E*: 1692,



2041;  $^{31}\text{P}\{\text{H}\}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  51.63 (d,  $^2J_{\text{PP}} = 30.5$  Hz,  $\text{PPh}_3$ ), 51.91 (d,  $^2J_{\text{PP}} = 30.5$  Hz,  $\text{PPh}_3$ ) ppm;  $^1\text{H}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  1.24 (d, 1H,  $J_{\text{HH}} = 9.5$  Hz,  $\text{H}_e$  or  $\text{H}_f$ ), 1.38 (d, 1H,  $J_{\text{HH}} = 9.5$  Hz,  $\text{H}_e$  or  $\text{H}_f$ ), 2.29 (m, 1H,  $\text{H}_c$ ), 2.35 and 2.79 (d, 1H each,  $J_{\text{HH}} = 5.6$  Hz,  $\text{H}_a$  and  $\text{H}_b$ ), 3.10 (m, 1H,  $\text{H}_d$ ), 4.66 and 4.70 (m, 1H each, H-1 and H-3), 5.63 (m, 1H, H-2), 5.90 and 5.98 (m, 1H each,  $\text{H}_g$  and  $\text{H}_h$ ), 6.30 (m, 2H, H-4, H-5, H-6, or H-7), 6.59–6.65 (m, 4H, Ph and  $\text{H}_i$  or  $\text{H}_j$ ), 6.81–7.48 (m, 34H, Ph, and H-4, H-5, H-6, or H-7), 8.38 (d, 1H,  $J_{\text{HH}} = 15.4$  Hz,  $\text{H}_i$  or  $\text{H}_j$ ) ppm;  $^{13}\text{C}\{\text{H}\}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  42.99 (s,  $\text{CH}_e\text{H}_f$ ), 44.41 (s,  $\text{CH}_c$ ), 45.17 (s,  $\text{CH}_d$ ), 50.92 and 53.97 (s,  $\text{CH}_a$  and  $\text{CH}_b$ ), 75.85 (s, C-1 and C-3), 96.43 (s, C-2), 109.96 and 110.44 (s, C-3a and C-7a), 118.33 (s,  $\text{C}_\beta$ ), 123.07 and 123.15 (s,  $\text{CH}_i$  and  $\text{CH}_j$ ), 123.58, 123.91, 126.55 and 126.81 (s, C-4, C-5, C-6 and C-7), 125.17 (t,  $^2J_{\text{CP}} = 24.6$  Hz, Ru– $\text{C}_\omega$ ), 128.21–139.55 (m, Ph), 138.54 and 138.91 (s,  $\text{CH}_g$  and  $\text{CH}_h$ ), 141.38 and 164.20 (s, C=C), 207.89 (s, C=O) ppm.  $\Delta\delta$  (C-3a,7a) = –20.50. Anal. Calcd for  $\text{RuC}_{65}\text{H}_{52}\text{P}_2\text{O}$  ((*Z*)-**10**): C, 77.13; H, 5.18. Found: C, 77.74; H, 5.14. **Z**: 49; 1674, 2027;  $^{31}\text{P}\{\text{H}\}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  51.35 (d,  $^2J_{\text{PP}} = 30.0$  Hz,  $\text{PPh}_3$ ), 51.69 (d,  $^2J_{\text{PP}} = 30.0$  Hz,  $\text{PPh}_3$ ) ppm;  $^1\text{H}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  1.37 (d, 1H,  $J_{\text{HH}} = 9.1$  Hz,  $\text{H}_e$  or  $\text{H}_f$ ), 1.50 (d, 1H,  $J_{\text{HH}} = 9.1$  Hz,  $\text{H}_e$  or  $\text{H}_f$ ), 2.43 and 2.85 (d, 1H each,  $J_{\text{HH}} = 5.8$  Hz,  $\text{H}_a$  and  $\text{H}_b$ ), 2.88 (m, 1H,  $\text{H}_c$ ), 3.14 (m, 1H,  $\text{H}_d$ ), 4.70 (m, 2H, H-1 and H-3), 5.57 (m, 1H, H-2), 6.02 (m, 2H,  $\text{H}_g$  and  $\text{H}_h$ ), 6.30 and 6.68 (m, 2H each, H-4, H-5, H-6, and H-7), 6.85–7.38 (m, 35H, Ph,  $\text{H}_i$  and  $\text{H}_j$ ), 7.57 (d, 2H,  $J_{\text{HH}} = 7.1$  Hz, Ph) ppm;  $^{13}\text{C}\{\text{H}\}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  43.55 (s,  $\text{CH}_e\text{H}_f$ ), 44.75 (s,  $\text{CH}_d$ ), 46.20 (s,  $\text{CH}_c$ ), 47.16 and 53.71 (s,  $\text{CH}_a$  and  $\text{CH}_b$ ), 76.14 (s, C-1 and C-3), 96.00 (s, C-2), 110.37 and 110.73 (s, C-3a and C-7a), 120.70 (s,  $\text{C}_\beta$ ), 123.77, 124.00, 126.96, and 127.16 (s, C-4, C-5, C-6, and C-7), 125.88 and 127.28 (s,  $\text{CH}_i$  and  $\text{CH}_j$ ), 127.47–139.14 (m, Ph), 138.50 and 139.01 (s,  $\text{CH}_g$  and  $\text{CH}_h$ ), 140.35 and 167.32 (s, C=C), 141.26 (t,  $^2J_{\text{CP}} = 24.6$  Hz, Ru– $\text{C}_\omega$ ), 204.73 (s, C=O) ppm.  $\Delta\delta$ (C-3a,7a) = –20.15.

**Reaction of  $[\text{Ru}\{\text{C}\equiv\text{CCH}=\text{CH}(\mu^2\text{-}\eta^2\text{-C}\equiv\text{CPh})\text{Co}_2(\text{CO})_6\}\text{-}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2$ ] ((*E,Z*)-**6**) with Norbornene.** A solution of (*E,Z*)-**6** (1.188 g, 1 mmol) in 20 mL of norbornene was heated at 85 °C for 90 min. The solvent was then removed *in vacuo* and the brown solid residue transferred to an Alox I chromatography column. Initial elution with diethyl ether gave an orange band, from which the precursor complex (*E*)-**2** was isolated. Further purification by elution with a hexane/methanol (4/1) mixture gave an orange solution, from which the enynyl complex **11** was obtained. Yield (%), IR (KBr;  $\nu(\text{C}=\text{O})$ ,  $\nu(\text{C}\equiv\text{C})$ ,  $\text{cm}^{-1}$ ), and NMR spectroscopic data are as follows: 42; 1674, 2027;  $^{31}\text{P}\{\text{H}\}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  51.32 (d,  $^2J_{\text{PP}} = 30.5$  Hz,  $\text{PPh}_3$ ), 51.60 (d,  $^2J_{\text{PP}} = 30.5$  Hz,  $\text{PPh}_3$ ) ppm;  $^1\text{H}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  0.81 (d, 1H,  $J_{\text{HH}} = 9.9$  Hz,  $\text{H}_e$  or  $\text{H}_f$ ), 1.10 (m, 2H,  $\text{CH}_2$ ), 1.29 (d, 1H,  $J_{\text{HH}} = 9.9$  Hz,  $\text{H}_e$  or  $\text{H}_f$ ), 1.36 (m, 2H,  $\text{CH}_2$ ), 2.27 and 2.63 (d, 1H each,  $J_{\text{HH}} = 5.8$  Hz,  $\text{H}_a$  and  $\text{H}_b$ ), 2.39 (m, 1H,  $\text{H}_c$ ), 2.66 (m, 1H,  $\text{H}_d$ ), 4.70 (m, 2H, H-1 and H-3), 5.59 (m, 1H, H-2), 6.30 and 6.66 (m, 2H each, H-4, H-5, H-6, and H-7), 6.86–7.36 (m, 35H, Ph,  $\text{H}_i$ , and  $\text{H}_j$ ), 7.59 (d, 2H,  $J_{\text{HH}} = 7.5$  Hz, Ph) ppm;  $^{13}\text{C}\{\text{H}\}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  28.97 (s,  $\text{CH}_2$ ), 29.65 (s,  $\text{CH}_2$ ), 32.63 (s,  $\text{CH}_2$ ), 39.10 (s,  $\text{CH}_d$ ), 40.72 (s,  $\text{CH}_c$ ), 47.17 and 54.69 (s,  $\text{CH}_a$  and  $\text{CH}_b$ ), 75.46 (s, C-1 and C-3), 95.38 (s, C-2), 109.71 and 110.05 (s, C-3a and C-7a), 119.92 (s,  $\text{C}_\beta$ ), 123.09, 123.30, 125.45, 126.32, 124.69, and 126.66 (s, C-4, C-5, C-6, C-7,  $\text{CH}_i$ , and  $\text{CH}_j$ ), 127.11–138.82 (m, Ph and =C), 140.39 (t,  $^2J_{\text{CP}} = 24.3$  Hz, Ru– $\text{C}_\omega$ ), 167.51 (s, =C), 205.58 (s, C=O) ppm.  $\Delta\delta$ (C-3a,7a) = –20.82. Anal. Calcd for  $\text{RuC}_{65}\text{H}_{54}\text{P}_2\text{O}$ : C, 76.98; H, 5.37. Found C, 76.01; H, 5.31.

**Synthesis of Complex 12.**  $\text{Co}_4(\text{CO})_{12}$  (0.858 g, 1.5 mmol) was added to a solution of  $[\text{Ru}\{\text{C}\equiv\text{CCH}=\text{CH}(\text{C}\equiv\text{CPh})\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$  ((*E,Z*)-**2**; 0.892 g, 1 mmol) in 30 mL of THF and the resulting solution refluxed for 2 h. The solvent was then removed *in vacuo* and the green solid residue transferred to an Alox I chromatography column. Elution with diethyl ether gave a green band which from which (*E*)-**6** was obtained. Further purification by elution with a diethyl ether/dichloromethane (3/1) mixture gave a new green band, which was collected and evaporated to dryness to produce pure cluster

Table 2. Crystallographic Data for Complex 12

chem formula	$\text{C}_{66}\text{H}_{44}\text{O}_9\text{P}_2\text{Co}_4\text{Ru}$
<i>a</i> , Å	11.107(2)
<i>b</i> , Å	15.564(5)
<i>c</i> , Å	17.896(4)
$\alpha$ , deg	97.55(2)
$\beta$ , deg	90.25(1)
$\gamma$ , deg	109.69(2)
mol wt	1379.74
<i>Z</i>	2
<i>V</i> , Å <sup>3</sup>	2883.6(12)
<i>D</i> <sub>calcd</sub> , g cm <sup>-3</sup>	1.589
<i>F</i> (000)	1388
radiation	Mo K $\alpha$ ( $\lambda = 0.710$ 69 Å)
monochromator	graphite
temp, K	293(2)
space group	<i>P</i> $\bar{1}$
cryst syst	triclinic
cryst size, mm	0.22 $\times$ 0.32 $\times$ 0.43
$\mu$ , mm <sup>-1</sup>	1.50
$\theta$ range, deg	1.15–24.98
index ranges for data collecn	–13 $\leq h \leq$ 13 –18 $\leq k \leq$ 18 0 $\leq l \leq$ 21
no. of rflns measd	10 239
no. of indep rflns	9882 ( $R(\text{int})^a = 0.0134$ )
refinement method	full-matrix least-squares on <i>F</i> <sup>2</sup>
no. of data/restraints/params	9882/0/740
goodness of fit on <i>F</i> <sup>2</sup>	1.040
final <i>R</i> factors $R(I > 2\sigma(I))$	<i>R</i> 1 = 0.0240, <i>wR</i> 2 = 0.0557
final <i>R</i> factors <i>R</i> (all data)	<i>R</i> 1 = 0.0376, <i>wR</i> 2 = 0.0607

$$^a R_{\text{int}} = \sum(I - \langle I \rangle) / \sum I$$

complex **12**. Yield (%), IR (THF;  $\nu(\text{C}\equiv\text{O})$ ,  $\text{cm}^{-1}$ ), and NMR spectroscopic data are as follows: 44; 1845, 1958, 2000, 2031, 2049;  $^{31}\text{P}\{\text{H}\}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  40.37 (s) ppm;  $^1\text{H}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  4.88 (d, 1H,  $J_{\text{HH}} = 5.7$  Hz, =CH), 5.50 (m, 5H, H-2, H-1,3, and H-4,7 or H-5,6), 6.21 (d, 1H,  $J_{\text{HH}} = 5.7$  Hz, =CH), 6.92–7.57 (m, 37H, Ph and H-4,7 or H-5,6) ppm;  $^{13}\text{C}\{\text{H}\}$  ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  76.55 (s, C-1,3), 95.46 (s, C-2), 116.29 (s, C-3a,7a), 121.34 (s, C), 123.79 (s, C-4,7 or C-5,6), 127.06 and 139.79 (s, CH=CH), 127.44–152.74 (m, Ph and C-4,7 or C-5,6), 157.39 (t,  $^3J_{\text{CP}} = 8.8$  Hz,  $\text{C}_\beta$ ), 169.46 (s, C), 209.66 and 213.67 (bs, C=O), 279.21 (t,  $^2J_{\text{CP}} = 18.1$  Hz, Ru= $\text{C}_\omega$ ) ppm.  $\Delta\delta$ (C-3a,7a) = –14.41. Anal. Calcd for  $\text{RuC}_{66}\text{H}_{44}\text{O}_9\text{Co}_4\text{P}_2$ : C, 57.45; H, 3.21. Found: C, 56.95; H, 3.59.

**X-ray Diffraction Study.** Data collection, crystal, and refinement parameters are collected in Table 2. The unit cell parameters were obtained from the least-squares fit of 25 reflections (with  $\theta$  between 16 and 20°). Graphite-monochromated Mo K $\alpha$  radiation was used. Data were collected on an Enraf-Nonius CAD4 diffractometer with the  $\omega$ – $2\theta$  scan technique and a variable scan rate, with a maximum scan time of 60 s per reflection. No decay of standards was observed. Lorentz, polarization, and absorption (empirical  $\psi$  scan, maximum and minimum transmission factors 0.9991 and 0.8491) corrections were applied, and the data were reduced to  $|F_o|$  values.

The structure was solved by SHELX-86.<sup>22</sup> Isotropic full-matrix least-squares refinement on  $|F_o|^2$  using SHELXL93<sup>23</sup> converged to *R* = 0.08. Finally, all hydrogen atoms were geometrically placed. During the final stages of the refinement, the positional parameters and the anisotropic thermal parameters of the non-H atoms were refined. The geometrically placed hydrogen atoms were isotropically refined with a common thermal parameter, riding on their parent atoms. The function minimized was  $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ ;

(22) Sheldrick, G. M. SHELX86. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Clarendon Press: Oxford, U.K., 1985.

(23) Sheldrick, G. M. SHELXL93. In *Crystallographic Computing 6*; Flack, P., Parkanyi, P., Simon, K., Eds.; IUCr/Oxford University Press: Oxford, U.K., 1993.

$w = 1/[\sigma^2(F_o^2) + (0.0260P)^2]$ , where  $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$  with  $\sigma^2(F_o^2)$  from counting statistics. No constraint or restraint was used during the refinement. The excellent final  $R$  values obtained suggest the exceptional quality of the initial data set.

The maximum shift to esd ratio in the last full-matrix least-squares cycle was 0.003. The final difference Fourier map showed no peaks higher than  $0.28 \text{ e } \text{Å}^{-3}$  nor deeper than  $-0.40 \text{ e } \text{Å}^{-3}$ . Atomic scattering factors were taken from ref 24. Geometrical calculations were made with SHELXL93.<sup>23</sup> The crystallographic plots were made with ZORTEP. All calculations were made at the "Institut de Ciencia de Materials de Barcelona" on a DEC-ALPHA computer and a VOBIS portable PC.

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(24) *International Tables for X-Ray Crystallography*, Kynoch Press: Birmingham, U.K. 1974; Vol. IV.

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**Supporting Information Available:** Crystal structure data for **12**, including tables of atomic and thermal parameters, bond distances, and bond angles (12 pages). Ordering information is given on any current masthead page.

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