Synthesis, Reactivity, and Catalytic Activity of Triangular ZrM_2 (M = Rh, Ir) Early−Late Heterobimetallic Complexes

Marc A. F. Hernandez-Gruel, Jesús J. Pérez-Torrente, Miguel A. Ciriano,*
Angel B. Rivas, Fernando J. Lahoz, Isabel T. Dobrinovitch, and Luis A. Oro*

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón,
Universidad de Zaragoza-CSIC, 50009-Zaragoza, Spain

Received November 19, 2002

Reactions of the zirconium−sulfide metallocene anion $[Cp^{tt}_2ZrS_2]^{2-}$ ($Cp^{tt} = \eta^5$-1,3-di-*tert*-butylcyclopentadienyl) with $[\{M(\mu\text{-}Cl)(diolefin)\}_2$ gave the d^0-d^8 complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{M(diolefin)\}_2]$ (M = Rh, diolefin = 2,5-norbornadiene (nbd) (**1**), 1,5-cyclooctadiene (cod); M = Ir, diolefin = cod) with a triangular ZrM_2 core capped by two symmetrical μ_3-sulfido ligands. The rhodium complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(diolefin)\}_2]$ (diolefin = tetrafluorobenzobarrelene (tfbb), nbd, cod) can also be prepared by the additive-deprotonation reactions of the mononuclear [Rh(acac)(diolefin)] (diolefin = nbd, tfbb) and the dinuclear $[\{Rh(\mu\text{-}OH)(cod)\}_2]$ complexes with $[Cp^{tt}_2Zr(SH)_2]$. These compounds exist as two rotamers in solution due to a hindered rotation of the cyclopentadienyl rings and the relative disposition of the substituents of the Cp^{tt} groups in the sandwich moiety. The reaction of $[Cp^{tt}_2Zr(SH)_2]$ with [Ir(acac)(cod)] gave the complex $[Cp^{tt}(acac)Zr(\mu_3\text{-}S)_2\{Ir(cod)\}_2]$ (**5**) with release of HCp^{tt} and coordination of acetylacetonate to the zirconium center. Carbonylation of compounds **1** and **5** yielded $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**6**) and $[Cp^{tt}(acac)Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}_2]$, respectively, while the complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{M(CO)_2\}_2]$ (M = Rh, Ir) resulted also from the reaction of $[Cp^{tt}_2Zr(SH)_2]$ with $(PPh_3Bz)[MCl_2(CO)_2]$ in the presence of triethylamine. Reactions of the carbonyl complexes with 1 molar equiv of bis(diphenylphosphino)methane (dppm) gave the cisoid complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{M(CO)\}_2(\mu\text{-}dppm)]$ (M = Rh (**9**), Ir) with evolution of carbon monoxide. Monodentate phosphites, $P(OMe)_3$ and $P(OPh)_3$, react with **6** to give mixtures of the transoid and cisoid isomers $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)(P(OR)_3)\}_2]$, which also exhibit a restricted rotation of the Cp^{tt} rings. The molecular structures of complexes **6** and **9** have been determined by X-ray diffraction methods. Compound **6** in the presence of P-donor ligands, $P(OMe)_3$, $P(OPh)_3$, and PPh_3, is a precursor of the catalyst for the hydroformylation of oct-1-ene under mild conditions of pressure and temperature. No Zr−Rh synergic effect is observed in this case, and the precursor breaks down after catalysis.

Introduction

Transition-metal−sulfur complexes have attracted considerable attention due to the possible relevance to the active sites of metalloenzymes and industrial processes by metal−sulfide catalysts.[1] Sulfido clusters containing metals of groups 8−10 display a wide potential in homogeneous catalysis,[2] owing both to their structural diversity and to the strong bridging ability of sulfido ligands to prevent the fragmentation of the metal−sulfur framework.[3] In addition, new reactivity patterns are expected from the combination of widely divergent transition metals in mixed-metal sulfido clusters. Early−late heterobimetallic (ELHB) complexes, containing both electron-poor early transition metals and electron-rich late transition metals in close proximity, should provide multimetallic reaction sites to explore the cooperative heterometallic activation of small molecules and to search for the synergism between the metals in both catalytic[4,5] and stoichiometric reactions.[6]

The rational construction of sulfur-bridge ELHB complexes requires the design of building blocks suitable

---

* To whom correspondence should be addressed. Fax: 34 976761143. E-mail: M.A.C., mciriano@posta.unizar.es; L.A.O., oro@posta.unizar.es.

(1) (a) *Transition Metal Sulfur Chemistry: Biological and Industrial Significance*; Stiefel, E. I., Matsumoto, K., Eds.; American Chemical Society: Washington, DC, 1996. (b) Startsev, A. N. *Catal. Rev.-Sci. Eng.* **1995**, *37*, 353. (c) Ogino, H.; Inomata, S.; Tobita, H. *Chem. Rev.* **1998**, *98*, 2083. (d) Beinert, H.; Holm, R. H.; Münck, E. *Science* **1997**, *277*, 653.

(2) (a) Masui, D.; Kochi, T.; Tang, Z.; Ishii, Y.; Mizobe, Y.; Hidai, M. *J. Organomet. Chem.* **2001**, *620*, 69. (b) Masui, D.; Ishii, Y.; Hidai, M. *Chem. Lett.* **1998**, 717. (c) Wakabayashi, T.; Ishii, Y.; Ishikawa, K.; Hidai, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2123. (d) Wakabayashi, T.; Ishii, Y.; Murata, T.; Mizobe, Y.; Hidai, M. *Tetrahedron Lett.* **1995**, *36*, 5585. (e) Rakowski DuBois, M. *Chem. Rev.* **1989**, *89*, 9.

(3) (a) Fedin, V. P.; Seo, M. S.; Saysell, D. M.; Dybtsev, D. N.; Elsegood, M. R. J.; Clegg, W.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **2002**, 138. (b) Seino, H.; Arai, Y.; Iwata, N.; Hagao, S.; Mizobe, Y.; Hidai, M. *Inorg. Chem.* **2001**, *40*, 1677. (c) Yuki, M.; Okazaki, M.; Ogino, H. *Organometallics* **2001**, *20*, 1762. (d) Kuwata, S.; Kabashima, S.; Ishii, Y.; Hidai, M. *J. Am. Chem. Soc.* **2001**, *123*, 3826. (e) Che, C. M.; Xia, B. H.; Huang, J. S.; Chan, C. K.; Zhou, Z. Y.; Cheung, K. K. *Chem. Eur. J.* **2001**, *7*, 3998. (f) Hidai, M.; Kuwata, S.; Mizobe, Y. *Acc. Chem. Res.* **2000**, *33*, 46. (g) Xu, F.; Chen, Y. M.; Yang, S. Y.; Sun, W. H.; Yu, K. B. *Transition Met. Chem.* **2000**, *25*, 108. (h) Kabashima, S.; Kuwata, S.; Ueno, K.; Shiro, M.; Hidai, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 1128. (i) Tatsumi, K.; Kawaguchi, H.; Inoue, Y.; Nakamura, A.; Cramer, R. E.; Golen, J. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 763.

10.1021/om0209576 CCC: \$25.00
Publication on Web 02/19/2003

for a stepwise synthetic approach. Recently, it has been established that hydrosulfido[3f,7] and hydroxo metal complexes[8] are appropriate to synthesize ELHB complexes. In this context, we have shown that the deprotonations of the bis(hydrosulfido)titanium complex $[Cp_2Ti(SH)_2]$ with d^8 rhodium and iridium compounds lead to d^0-d^8 sulfido-bridged complexes.[9] Thus, the reactions of $[Cp_2Ti(SH)_2]$ with $[\{Rh(\mu\text{-}OMe)(diolefin)\}_2]$ gave the tetranuclear heterobimetallic clusters $[CpTi(\mu_3\text{-}S)_3\{Rh(diolefin)\}_3]$ (diolefin = cod, tfbb),[10] with a corner-sulfido voided incomplete cubane structure, probably through the cubane cluster $[(CpTi)_2(\mu_3\text{-}S)_4\{Rh(diolefin)\}_2$.[11] However, this reaction carried out in the presence of water and after carbonylation afforded the oxo−sulfido cluster $[(CpTi)_2(\mu_4\text{-}O)(\mu_3\text{-}S)_4Rh_4(CO)_6]$ with an incomplete double-fused cubane structure.[12] In contrast, the additive deprotonation of $[Cp_2Ti(SH)_2]$ with the diolefin complexes [M(acac)(diolefin)] (M = Rh, Ir; diolefin = cod, tfbb) resulted in the formation of the heterotrinuclear complexes $[Cp(acac)Ti(\mu_3\text{-}S)_2\{M(diolefin)\}_2]$ with elimination of cyclopentadiene.[13] Moreover, these syntheses may be complicated further by the transference of sulfido ligands between the metal centers, such as was found in the reactions of $[Cp_2Ti(SH)_2]$ with the carbonyl complexes $[M(acac)(CO)_2]$ to give the ion-pair compounds $[Cp_2Ti(acac)][M_3(\mu_3\text{-}S)_2(CO)_6]$ (M = Rh, Ir).[13]

Preliminary experiments with the related zirconium hydrosulfido complex $[Cp_2Zr(SH)_2]$ resulted in extensive sulfido transfer to the d^8 metal centers, the trimetallic complexes $[M_3(\mu\text{-}S)_2(\mu\text{-}H)(cod)_3]$ and the anionic clusters $[M_3(\mu_3\text{-}S)_2(CO)_6]^-$ (M = Rh, Ir) being the outcome of these reactions. We reasoned that the known dimerization[14] of $[Cp_2Zr(SH)_2]$ with extrusion of H_2S probably complicated these reactions. To overcome this problem in the syntheses of ELHB complexes containing zirconium, we envisaged that the use of a bulkier zirconium−metallocene hydrosulfido compound could avoid the undesirable reactions. For this purpose we explored successfully[15,16] the capability of $[Cp^{tt}{}_2Zr(SH)_2]$ (Cp^{tt} = η^5-1,3-di-*tert*-butylcyclopentadienyl) to generate a sulfido metalla ligand. Herein we report on the controlled construction of diolefin and carbonyl complexes containing the core "$Zr(\mu_3\text{-}S)_2M_2$" as well as replacement reactions on the carbonyl complexes by P-donor ligands. In addition, the hydroformylation of oct-1-ene under mild conditions using the catalyst precursor $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ is also described.

Results

Syntheses of the Heterotrinuclear Diolefin Complexes. The double deprotonation of $[Cp^{tt}{}_2Zr(SH)_2]$ with *n*-BuLi (in a 1:2 molar ratio) in diethyl ether at temperatures under 0 °C generated the zirconium−sulfide metallocene anion $[Cp^{tt}{}_2ZrS_2]^{2-}$ in situ. Reactions of these solutions with the complexes $[\{M(\mu\text{-}Cl)(diolefin)\}_2]$ gave the d^0-d^8 ELHB complexes $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{M(diolefin)\}_2]$ (M = Rh, diolefin = 2,5-norbornadiene (nbd) (**1**), diolefin = 1,5-cyclooctadiene (cod) (**3**); M = Ir, diolefin = cod (**4**)) with a triangular $ZrRh_2$ or $ZrIr_2$ core capped by two μ_3-sulfido ligands. The reactions are almost quantitative at temperatures under −20 °C, but a partial decomposition occurs if the reactions are carried out at room temperature, which is particularly noticeable for the iridium complex.

Alternatively, the acidity of the hydrosulfido ligands in $[Cp^{tt}{}_2Zr(SH)_2]$ facilitates the direct synthesis by using other mono- and dinuclear rhodium complexes that avoid the use of *n*-BuLi. Thus, the reaction of $[Cp^{tt}{}_2Zr(SH)_2]$ with 2 molar equiv of [Rh(acac)(nbd)] in methanol gave compound **1** in good yield, while **1** can be also obtained from the reaction of $[Cp^{tt}{}_2Zr(SH)_2]$ with $[\{Rh(\mu\text{-}Cl)(nbd)\}_2]$ in the presence of NEt_3 (Scheme 1). The related compound $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{Rh(tfbb)\}_2]$ (**2**) was cleanly obtained as an orange solid in excellent yield by addition of methanol to a solid mixture of $[Cp^{tt}{}_2Zr(SH)_2]$ with 2 molar equiv of [Rh(acac)(tfbb)]. However, the additive-deprotonation reactions are not appropriate for the preparation of the related 1,5-cyclooctadiene complexes $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{M(cod)\}_2]$ (**3**, **4**), since the formation of these complexes competes with the transference of the sulfido ligands to the d^8 metal centers. Thus, the reactions of $[Cp^{tt}{}_2Zr(SH)_2]$ with $[\{Rh(\mu\text{-}OMe)$-

---

(4) (a) Takayama, C.; Yamaguchi, Y.; Mise, T., Suzuki, N. *J. Chem. Soc., Dalton Trans.* **2001**, 948. (b) Yamaguchi, Y.; Suzuki, N.; Mise, T.; Wakatsuki, Y. *Organometallics* **1999**, *18*, 996. (c) Wheatley, N.; Kalck, P. *Chem. Rev.* **1999**, *99*, 3379. (d) Lindenberg, F.; Shribman, T.; Sieler, J.; Hey-Hawkins, E.; Eisen, M. S. *J. Organomet. Chem.* **1996**, *515*, 19. (e) Hostetler, M. J.; Butts, M. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 2743. (f) Hostetler, M.; Butts, M. D.; Bergman, R. G. *Organometallics* **1993**, *12*, 65. (g) Kalck, P.; Serra, C.; Machet, C.; Broussier, R.; Gautheron, B.; Delmas, G.; Trouve, G.; Kubicki, M. *Organometallics* **1993**, *12*, 1021. (h) Hostetler, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 8621.

(5) (a) Casado, M. A., Pérez-Torrente, J. J. Ciriano, M. A.; Oro, L. A.; Orejón, A.; Claver, C. *Organometallics* **1999**, *18*, 3035. (b) Dickson, R. S.; Bowen, J.; Campi, E. M.; Jackson, W. R.; Jonasson, C. A. M.; McGrath, F. J.; Paslow, D. J.; Polas, A.; Renton, P.; Gladiali, S. *J. Mol. Catal. A: Chem.* **1999**, *150*, 133. (c) Trzeciak, A. M.; Ziólkowski, K. J.; Choukroun, R. *J. Mol. Catal.* **1996**, *110*, 135. (d) Choukroun, R.; Dahan, F.; Gervais, D.; Rifaï, C. *Organometallics* **1990**, *9*, 1982. (e) Gelmini, L.; Stephan, D. W. *Organometallics* **1988**, *7*, 849. (f) Gelmini, L.; Stephan, D. W. *Organometallics* **1988**, *7*, 849. (g) Senocq, F.; Randrialimanana, C.; Thorez, A.; Kalck, Ph.; Choukroun, R.; Gervais, D. *J. Mol. Catal.* **1986**, *35*, 213. (h) Choukroun, R.; Gervais, D.; Jaud, J.; Kalck, P.; Senocq, F. *Organometallics* **1986**, *5*, 67.

(6) (a) Lutz, M.; Haukka, M.; Pakkanen, T. A.; Gade, L. H. *Organometallics* **2001**, *20*, 2631. (b) Fulton, J. R.; Hanna, T. A.; Bergman, R. G. *Organometallics* **2000**, *19*, 602, (c) Gade, L. H.; Memmler, H.; Kauper, U.; Schneider, A.; Fabre, S.; Bezougli, I.; Lutz, M.; Galka, C.; Scowen, I. J.; McPartlin. M. *Chem. Eur. J.* **2000**, *6*, 692. (d) Aubart, M. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 1793. (e) Bahhmutov, V. I.; Viseaux, M.; Baudry, D.; Dormond, A.; Richard, P. *Inorg. Chem.* **1996**, *35*, 7316. (f) Hanna, T.; Baranger, A. M.; Bergman, R. G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 653. (g) Stephan, D. W.; Nadasdi, T. T. *Coord. Chem. Rev.* **1996**, *147*, 147. (h) Baranger, A. M.; Hanna, T. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 10041. (i) Hanna, T. A.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 11363. (j) Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 3822. (k) Casey, C. P. *J. Organomet. Chem.* **1990**, *400*, 205. (l) Stephan, D. W. *Coord. Chem. Rev.* **1989**, *95*, 41.

(7) Kuwata, S.; Hidai, M. *Coord. Chem. Rev.* **2001**, *213*, 211.

(8) (a) Fandos, R.; Hernández, C.; Otero, A.; Rodriguez, A.; Ruiz, M. J. *Organometallics* **1999**, *18*, 2718. (b) Fandos, R.; Fierro, J. L. G.; Kubicki, M. M.; Otero, A.; Terreros, P.; Vivar-Cerrato, M. A. *Organometallics* **1995**, *14*, 2162. (c) Selent, D.; Ramm, M. *J. Organomet. Chem.* **1995**, *485*, 135. (d) Selent, D.; Pickardt, J.; Claus, P. *J. Organomet. Chem.* **1994**, *468*, 131.

(9) Atencio, R.; Casado, M. A.; Ciriano, M. A.; Lahoz, F. J.; Pérez-Torrente, J. J.; Tiripicchio, A.; Oro, L. A. *J. Organomet. Chem.* **1996**, *514*, 103.

(10) Casado, M. A.; Ciriano, M. A.; Edwards, A. J.; Lahoz, F. J.; Oro, L. A.; Pérez-Torrente, J. J. *Organometallics* **1999**, *18*, 3025.

(11) Ameniya, T.; Kuwata, S.; Hidai, M. *Chem. Commun.* **1999**, 711.

(12) Casado, M. A.; Ciriano, M. A.; Edwards, A. J.; Lahoz, F. J.; Pérez-Torrente, J. J.; Oro, L. A. *Organometallics* **1998**, *17*, 3414.

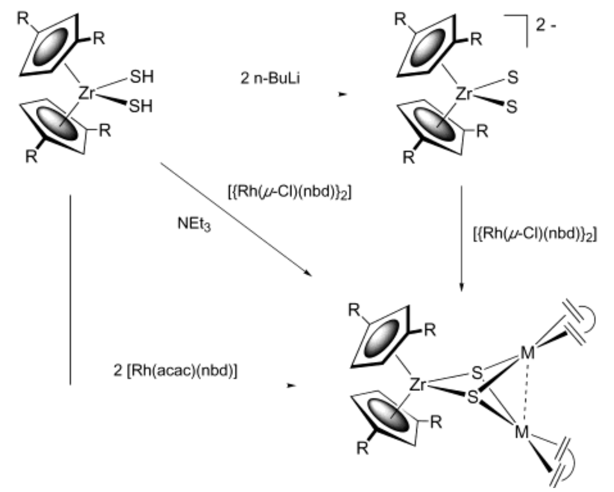
(13) Casado, M. A.; Pérez-Torrente, J. J.; Ciriano, M. A.; Edwards, A. J.; Lahoz, F. J.; Oro, L. A. *Organometallics* **1999**, *18*, 5299.

(14) Parkin, G. *Prog. Inorg. Chem.* **1998**, *47*, 1.

(15) Hernandez-Gruel, M. A. F.; Pérez-Torrente, J. J.; Ciriano, M. A.; López, J. A.; Lahoz, F. J.; Oro, L. A. *Eur. J. Inorg. Chem.* **1999**, 2047.

(16) Hernandez-Gruel, M. A. F.; Pérez-Torrente, J. J.; Ciriano, M. A.; Lahoz, F. J.; Oro, L. A. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2769.

Scheme 1



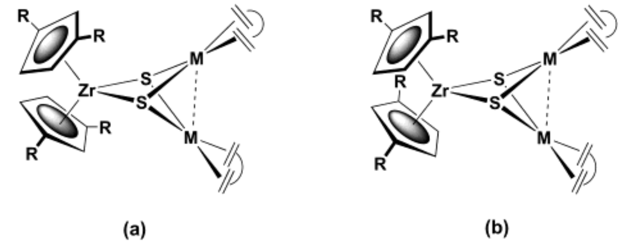


Figure 1. The two limiting rotamers observed in solution for the complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{M(diolefin)\}_2]$: (a) eclipsed rotamer ($C_{2v}$ symmetry); (b) staggered rotamer (C_s symmetry).

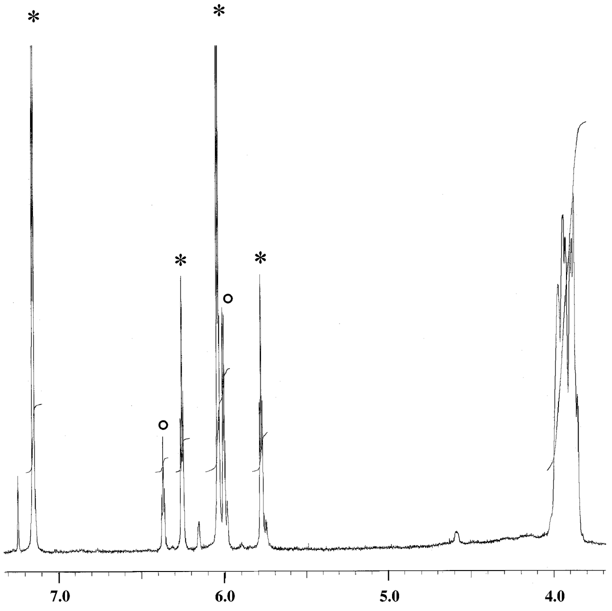


Figure 2. Part of the ^1H NMR spectrum of $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Ir(cod)\}_2]$ (**4**) in $CDCl_3$, showing the signals of the cyclopentadienyl and olefinic protons of cod (∗, staggered rotamer; ○, eclipsed rotamer). Residual resonances are due to $CHCl_3$ and decomposition products.

(cod)}$_2$], [Rh(acac)(cod)], and $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$ in the presence of NEt_3 gave non separable mixtures of **3** and the known[17] hydride trirhodium complex $[Rh_3(\mu\text{-}S)_2(\mu\text{-}H)(cod)_3]$ in variable amounts. Nevertheless, a straightforward and clean synthesis of $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(cod)\}_2]$ (**3**) consisted of the reaction of $[Cp^{tt}_2Zr(SH)_2]$ with $[\{Rh(\mu\text{-}OH)(cod)\}_2]$ in methanol at room temperature. However, the identical reaction of $[Cp^{tt}_2Zr(SH)_2]$ with 1 molar equiv of $[\{Ir(\mu\text{-}OH)(cod)\}_2]$ in tetrahydrofuran/methanol gave the triiridium hydride complex $[Ir_3(\mu\text{-}S)_2(\mu\text{-}H)(cod)_3]$,[18] which was isolated in 90% yield. On the other hand, the reaction of $[Cp^{tt}_2Zr(SH)_2]$ with 2 molar equiv of [Ir(acac)(cod)] in diethyl ether afforded the new complex $[Cp^{tt}(acac)Zr(\mu_3\text{-}S)_2\{Ir(cod)\}_2]$ (**5**) with $[Ir_3(\mu\text{-}S)_2(\mu\text{-}H)(cod)_3]$ as an impurity; complex **5** could be isolated pure as a dark blue solid by recrystallization.

Characterization of the Heterotrinuclear Diolefin Complexes and Their Rotamers in Solution. Elemental analyses, mass spectra, and molecular weight data of compounds **1**−**5** were found in accordance with the proposed formulas, except for compound **4**, which gave unsatisfactory elemental analyses due presumably to incomplete combustion. Complexes **1** and **2** were found to exist in solution as two species which were unambiguously identified as two rotamers by ^1H, $^{13}C\{^1H\}$, and two-dimensional NMR techniques (vide infra). Both rotamers differ in the spatial disposition of the *tert*-butyl groups of both Cp^{tt} rings in the sandwich moiety and correspond to the limiting eclipsed (**a**) and fully staggered (**b**) conformations, respectively (Figure 1). In the eclipsed rotamer (**a**) the *tert*-butyl groups of both Cp^{tt} rings are positioned toward the front of the metallocene “clamshell”, while in the fully staggered rotamer (**b**) the *tert*-butyl groups of one of the Cp^{tt} rings are directed toward the back of the metallocene clamshell.

The rotamers of the compounds **1** and **2** interconvert in solution, producing an equilibrium mixture in which the eclipsed rotamers **1a** (60%) and **2a** (55%) predominate. This interconversion was verified by a saturation transfer experiment on the nbd complex **1**. Both rotamers **3a (**15%) and **3b** (85%) were detected for the cod complex **3** on monitoring the reaction by ^1H NMR, but the staggered rotamer was the sole species isolated for complex **3**. A mixture of both rotamers **4b** and **4a** containing mainly the staggered isomer **4b** (80%) could be isolated for the iridium complex **4**. A remarkable observation is that the eclipsed isomer **4a** decomposes in $CDCl_3$ at room temperature over a period of 4 h, which allowed the isolation of the staggered isomer **4b** pure. A further observation is that the staggered rotamers of the cod complexes **3** and **4** do not evolve to the eclipsed rotamers for a period of 24 h in solution.

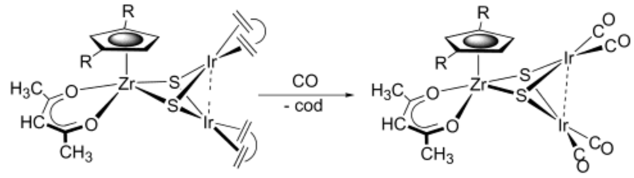
The identification of the rotamers is simple by NMR methods, since the eclipsed rotamer **a** (C_{2v} symmetry) possesses equivalent Cp^{tt} rings, while they are inequivalent for the staggered isomer **b** (C_s symmetry). For example, the eclipsed minor isomer **4a** displays two resonances, at δ 6.37 and 6.00 ppm, for the cyclopentadienyl protons and a singlet for the *tert*-butyl groups in the ^1H NMR spectrum (Figure 2). The staggered rotamer **4b** displays four resonances for the cyclopentadienyl protons and two singlets for the *tert*-butyl groups. Moreover, the resonances at δ 6.25 and 6.04 ppm correspond to the Cp^{tt} ligand with the *t*-Bu groups directed toward the $ZrRh_2$ core, while the signals at δ 7.15 and 5.78 ppm are due to the cyclopentadienyl protons of the Cp^{tt} ligand with the *t*-Bu groups directed

---

[17] Arif, A. M.; Hefner, J. G.; Jones, R. A.; Koschmieder, S. U. *Polyhedron* **1988**, *7*, 561.

[18] Bright, T. A.; Jones, R. A.; Koschmieder, S. U.; Nunn, C. M. *Inorg. Chem.* **1988**, *27*, 3819.

Scheme 2



5 **8**

away from the $ZrRh_2$ core. The pattern of resonances for the cyclopentadienyl protons of the Cp^{tt} ligands of both rotamers **1a**, **2a** and **1b**, **2b** in the ^1H NMR spectra follows a trend similar to that observed for complex **1**. Again we note the unusual chemical shifts of one of the Cp^{tt} rings of the staggered isomer, as previously observed.[16] The number of signals from the *tert*-butyl groups and the auxiliary nbd and tfbb ligands in the $^{13}C\{^1H\}$ and ^1H NMR spectra corroborate the identification and symmetry of both rotamers. For example, the eclipsed rotamers (**1a**, **2a**) display two doublets for the olefinic carbons in the $^{13}C\{^1H\}$ NMR spectra, while the staggered rotamer **2b** shows four signals for the olefinic carbons, in agreement with the lower symmetry. This assignment is evident for the complexes $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{M(cod)\}_2]$ (**3**, **4**), for which the staggered rotamers **b** were isolated pure.

Complex **5** shows the molecular ion at *m*/*z* 1032, and its ^1H NMR spectrum displays a 1:1:2 ratio for the Cp^{tt}, acac, and cod ligands, in agreement with the proposed formulation. The ^1H and the $^{13}C\{^1H\}$ NMR spectra (the full assignment of the signals has been done with the help of the $^{13}C-^1H$ HETCOR spectrum) indicate the presence of a plane of symmetry containing the $ZrIr_2$ core, which intersects both the acac and Cp^{tt} groups, relating both halves. In addition, the chemical shifts of the signals for the cyclopentadienyl protons (at δ 7.02 and 5.47) indicate that the *t*-Bu groups are directed away from the $ZrIr_2$ core (Scheme 2).

Synthesis and Characterization of the Carbonyl Complexes. Carbonylation of $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{Rh(nbd)\}_2]$ (**1**) under atmospheric pressure in benzene gave the carbonyl complex $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**6**), which was isolated as an emerald green microcrystalline solid in good yield. Complex **6** is a remarkably stable compound that can be synthesized directly in excellent yields by reacting $[Cp^{tt}{}_2Zr(SH)_2]$ with a variety of rhodium−carbonyl complexes. Thus, the reactions of $[Cp^{tt}{}_2Zr(SH)_2]$ with 2 molar equiv of $[Rh(acac)(CO)_2]$ in diethyl ether, with $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ in the presence of a slight excess of NEt_3 in dichloromethane, and with $[\{Rh(\mu\text{-}pz)(CO)_2\}_2]$ gave **6** in yields greater than 90%. The related carbonyl complex $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}_2]$ (**7**) was obtained from the reaction of $[Cp^{tt}{}_2Zr(SH)_2]$ with 2 molar equiv of the anionic complex $[IrCl_2(CO)_2]^-$ in the presence of a slight excess of NEt_3. Under similar experimental conditions, complex **6** was obtained from $(PPh_3Bz)[RhCl_2(CO)_2]$ in 92% yield.

The $ZrRh_2$ core of the compound $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**6**) has been established by X-ray diffraction methods, and the molecular structure is depicted in Figure 3(see below). The spectroscopic data indicate that complexes **6** and **7** have closely related structures, since a similar pattern of resonances is observed in both the $^{13}C\{^1H\}$ and ^1H NMR spectra, in agreement with the C_{2v} symmetry found for **6** in the solid state. We also note the free rotation of the Cp^{tt} rings in complexes **6** and **7**, which is fast on the time scale of $^{13}C\{^1H\}$ and ^1H NMR. Accordingly, the four equivalent carbonyl ligands give one signal in the $^{13}C\{^1H\}$ NMR spectra, and both Cp^{tt} ligands are equivalent. In addition, both complexes display three strong ν(CO) bands for the terminal carbonyl groups in the IR spectra, in agreement with the C_{2v} symmetry of the molecules.

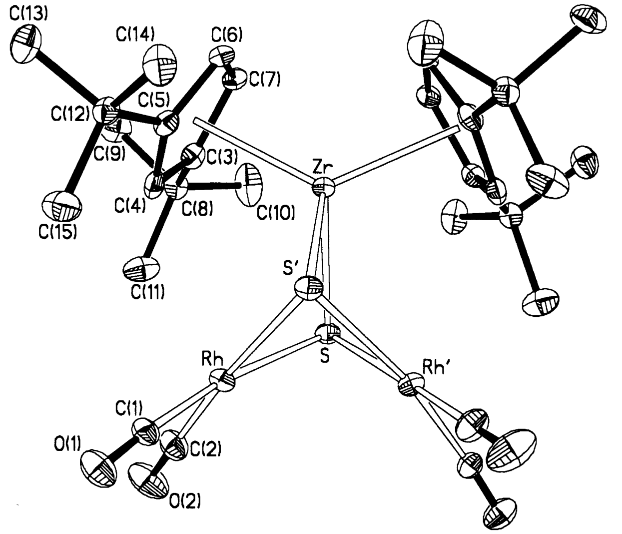


Figure 3. Molecular structure of $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**6**).

The carbonylation of $[Cp^{tt}(acac)Zr(\mu_3\text{-}S)_2\{Ir(cod)\}_2]$ (**5**) under atmospheric pressure gave the carbonyl complex $[Cp^{tt}(acac)Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}_2]$ (**8**), which was isolated as a golden microcrystalline solid in good yield. The spectroscopic information is compatible with the expected C_s structure resulting from the replacement of each diolefin ligand in **5** by two carbonyl groups (Scheme 2). Interestingly, all the carbonyl groups are isochronous in the $^{13}C\{^1H\}$ NMR spectrum, which shows a strong singlet at δ 174.3 ppm. In addition, **8** displays three strong ν(CO) absorptions in the IR spectrum, as found for the related titanium complexes $[Cp(acac)Ti(\mu_3\text{-}S)_2\{M(CO)_2\}_2]$ (M = Rh, Ir).[13]

Replacement Reactions of the Carbonyl Complexes. Carbonyl replacement reactions by P-donor ligands take place quickly at room temperature with evolution of carbon monoxide. The reaction of complex $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**6**) with 1 molarequiv of dppm in dichloromethane gave a dark green solution of the compound $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)\}_2(\mu\text{-}dppm)]$ (**9**), which was isolated as a dark green or black microcrystalline solid in excellent yield. Analogously, the complex $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)\}_2(\mu\text{-}dppm)]$ (**10**) was isolated as an orange crystalline solid from the reaction of $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}_2]$ (**7**) with 1 molar equiv of dppm.

Complexes **9** and **10** were characterized by elemental analyses, FAB+ mass spectra, and NMR spectroscopy. In addition, the molecular structure of $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)\}_2(\mu\text{-}dppm)]$ (**9**) was determined by X-ray diffraction methods and the molecular diagram is shown in Figure 4. It is noteworthy that the $ZrRh_2$ core is maintained after the replacement of two carbonyl groups by the dppm ligand, which bridges the rhodium atoms with a cisoid arrangement. The ^1H, $^{13}C\{^1H\}$, and

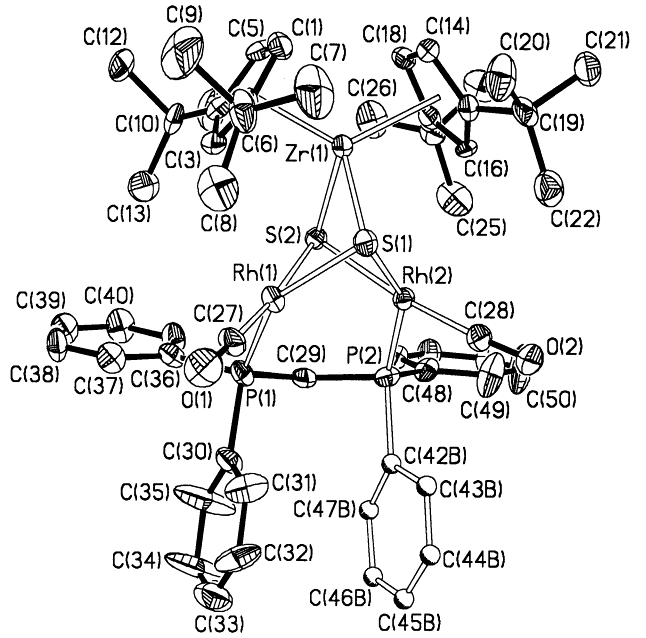


Figure 4. View of the molecular structure of $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)\}_2(\mu\text{-dppm})]$ (**9**). One of the phenyl rings of the dppm ligand is disordered (C(42B)−C(47B)).

$^{31}P\{^1H\}$ NMR spectra of **9** and **10** reveal the existence of a plane of symmetry in the molecules, which contains the Zr and both sulfido ligands and intersects the M−M vector. This plane is the cause of the equivalence of the carbonyl ligands, the P-donor atoms of the dppm ligand, and the Cp^{tt} ligands, but the protons in each cyclopentadienyl ring are inequivalent, in agreement with the C_s symmetry found in the solid state for **9**; both complexes also display two strong ν(CO) bands for the terminal carbonyls. Although the spectroscopic data suggest that compounds **9** and **10** have identical structures, the broadening of the signals observed in the NMR spectra of **9** at room temperature indicates some kind of fluxionality for the rhodium complex.

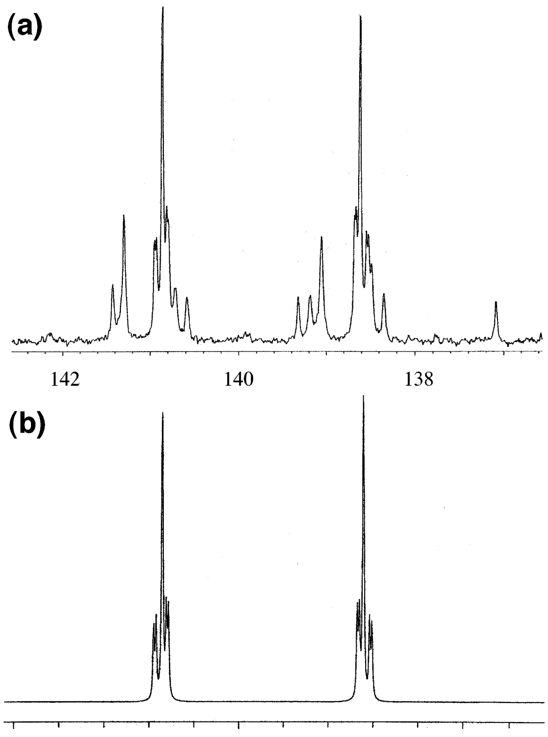
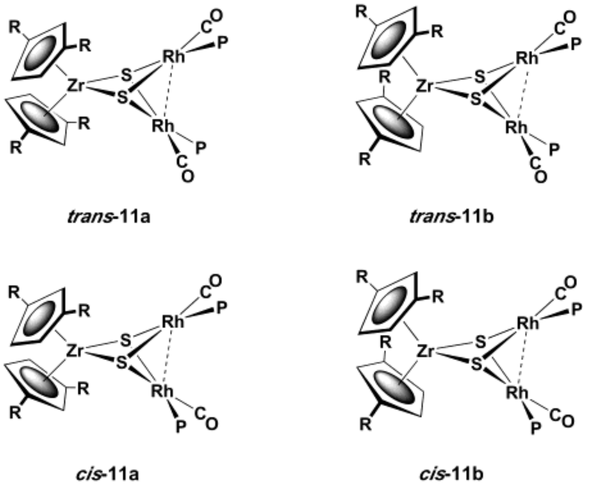


Figure 5. (a) $^{31}P\{^1H\}$ NMR spectrum of $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)(P(OMe)_3)\}_2]$ (**11**), showing the presence of the cis/trans isomers with the corresponding rotamers. (b) Calculated $^{31}P\{^1H\}$ NMR spectrum for the AA′XX′ spin system observed for the eclipsed rotamer of the trans isomer (*trans*-**11a**).



trans-**11a** *trans*-**11b**

cis-**11a** *cis*-**11b**

Figure 6. Cis/trans isomers of the compounds $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)(P(OR)_3)\}_2]$ (**11**, **12**) with the corresponding eclipsed and staggered rotamers.

The reaction of $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**6**) with 2 molar equiv of $P(OMe)_3$ gave the complex $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)(P(OMe)_3)\}_2]$ (**11**) with evolution of carbon monoxide. The compound was isolated as a green apple microcrystalline solid in good yield. Although the FAB+ mass spectrum of **11** showed the mass of the molecular ion, the ^1H NMR spectrum is complicated and evidences a nonselective replacement of the carbonyl ligands by the monodentate P-donor ligands. This and the $^{31}P\{^1H\}$ NMR spectrum (Figure 5a) can be rationalized by assuming the existence of the cisoid and transoid isomers, resulting from the relative disposition of the $P(OMe)_3$ ligands along with a restricted rotation of the Cp^{tt} rings for both isomers (Figure 6). The main species is the eclipsed rotamer *trans*-**11a** (of C_2 symmetry), which displays an AA′XX′ spin system centered at δ 139.7 ppm. This signal correlates well with the calculated spectrum (Figure 5b) using the parameters reported in the Experimental Section. The doublet centered at δ 140.2 ppm corresponds to the eclipsed rotamer *cis*-**11a** (C_s symmetry). Finally, the minor staggered rotamers *trans*-**11b** and *cis*-**11b** give rise to four doublets, as expected, due to their lack of symmetry. It is noticeable that the transoid isomer is much more abundant than the cisoid isomer, while the eclipsed rotamer is largely predominant for the trans isomer, and both rotamers are roughly in the same proportion for the cis isomer.

The unselective replacement of carbonyl ligands in **6** is also observed in the reaction with other monodentate P-donor ligands. Thus, reaction of **6** with 2 molar equiv of $P(OPh)_3$ in toluene gave the complex $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)(P(OPh)_3)\}_2]$ (**12**), which was isolated as a green microcrystalline solid in good yield. When this reaction is performed in $CDCl_3$ and monitored by $^{31}P\{^1H\}$ NMR, a cis/trans mixture of isomers is evident. Although the transoid isomer is much more abundant than the cisoid isomer, the eclipsed rotamers predominate over the

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 6

Rh···Rh′	2.8397(7)	Zr−S	2.5214(11)
Rh···Zr	3.3302(7)	Zr−C(3)	2.591(4)
Rh−S	2.3769(11)	Zr−C(4)	2.621(4)
Rh− S′	2.4096(11)	Zr−C(5)	2.639(4)
Rh−C(1)	1.868(5)	Zr−C(6)	2.505(4)
Rh−C(2)	1.858(5)	Zr−C(7)	2.484(4)
		Zr−G*	2.272(2)
S−Rh−S′	84.18(4)	S−Zr−S′	79.02(5)
S−Rh−C(1)	170.76(14)	S−Zr−G*	111.97(6)
S′−Rh- C(1)	91.97(14)	S−Zr−G′*	107.88(6)
S−Rh−C(2)	89.47(15)	G-Zr−G′*	127.62(7)
S′−Rh-C(2)	173.15(15)		
C(1)−Rh−C(2)	93.9(2)		
Rh−S−Rh′	72.77(3)	Rh−C(1)−O(1)	176.7(4)
Rh−S−Zr	85.61(3)	Rh−C(2)−O(2)	177.8(4)
Rh−S′−Zr	84.93(3)		

*G and G′ represent the centroids of the cyclopentadienyl ligands.

staggered ones in both isomers. The eclipsed rotamer *trans*-**12a** displays the expected AA′XX′ spin system, while the eclipsed rotamer *cis*-**12a** shows a doublet at δ 121.0 ppm ($^1J_{Rh-P}$ = 294 Hz) in the $^{31}P\{^1H\}$ NMR spectrum. On the other hand, the staggered rotamer *trans*-**12b** displays an ABXY spin system and the rotamer *cis*-**12b** shows two broad doublets at δ 121.8 and 117.8 ppm with $^1J_{Rh-P}$ coupling constants of 290 and 298 Hz, respectively. Interestingly, the isolated product contains only the trans isomer (*trans*-**12a** and *trans*-**12b**), as deduced from the $^{31}P\{^1H\}$ NMR spectrum, indicating that both isomers possess different solubilities. Similarly, the IR spectrum (toluene) of the isolated compound displays only two broad ν(CO) bands at 1995 (m) and 1981 (s) cm^{-1}.

Molecular Structures of [$Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2$] (6) and [$Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)\}_2(\mu\text{-dppm})$] (9). Good-quality monocrystals for X-ray diffraction were grown by slow diffusion of *n*-hexane into a saturated dichloromethane solution of compound **6** at room temperature. Under these experimental conditions the complex crystallized out as the water solvate. In fact, we have observed that the crystallization process is considerably facilitated by the presence of water. Nevertheless, all the attempts to grow good-quality water-free crystals of **6** were unsuccessful.

As proposed from spectroscopic data, complexes **6** and **9** are trinuclear with a triangular $ZrRh_2$ core capped by two μ_3-sulfido ligands; the central skeleton formed by the metals and the sulfur atoms makes up a trigonal bipyramid. The two molecules are structurally analogous, with the sole difference being the substitution of one carbonyl at each Rh by a P atom of the bridging dppm ligand. Figures 3 and 4 represent the molecular structures of **6** and **9** together with the atomic labeling schemes, while Tables 1 and 2 collect selected bond distances and angles.

In both complexes the Zr atoms exhibit distorted pseudo-tetrahedral geometries, being bonded to two bridging sulfur atoms and to two η^5-Cp^{tt} rings. The Zr−Cp^{tt}(centroid) distances, 2.272(2) Å in **6** and 2.302(3) and 2.297(3) Å in **9**, are comparable to the observed values in the closely related heterotrimetallic complex [$Cp^{tt}_2Zr(\mu_3\text{-}S)_2Ir(CO)_2Rh(cod)$] (2.290(9) and 2.290(13) Å)[16] and longer than the reported distances in mononuclear zirconium thiolate complexes containing unsubstituted Cp rings (range 2.203(3)−2.220(1) Å).[19]

The angles centered on the Zr with the centroids of the Cp^{tt} ligands (G(1)−Zr−G(2) = 127.62(7)° in **6** and 126.75(10)° in **9**) are significantly larger than the typical value for a tetrahedral geometry, most probably due to the presence of the bulky *tert*-butyl substituents. The relative dispositions of the Cp^{tt} substituents in both complexes are eclipsed and are on the side of the trinuclear core, favoring a G(1)−Zr−G(2) angle smaller than that described in the related Zr−Ir−Rh complex,[16] 129.8(4)°, where the Cp^{tt} rings exhibit a staggered disposition. In fact, the angles G(1)−Zr−G(2) in **6** and **9** are at the lower end of mononuclear zirconium thiolate complexes of the type $Cp_2Zr(SR)_2$ (range 127.7(3)−130.4(1)°).[19]

While complex **6** presents a crystallographically imposed C_{2v} symmetry, and therefore only one value for the Zr−S distance (2.5214(11) Å), in **9** the two Zr−S bond lengths are different, 2.460(1) and 2.507(1) Å, reflecting the relative asymmetry of the molecule. However, these bond distances in both complexes are comparable to those reported in the Zr−Ir−Rh analogue (2.506(3) and 2.519(3) Å).[16] The angles S−Zr−G (mean

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 9[a]

Rh(1)···Zr(1)	3.3378(11)	3.2963(10)	Rh(2)···Zr(1)	3.3219(10)	3.3638(10)
Rh(1)···Rh(2)	2.7399(9)	2.7410(9)			
Rh(1)−P(1)	2.255(2)	2.246(2)	Rh(2)−P(2)	2.257(2)	2.248(2)
Rh(1)−S(1)	2.440(2)	2.467(2)	Rh(2)−S(1)	2.414(2)	2.408(2)
Rh(1)−S(2)	2.422(2)	2.396(2)	Rh(2)−S(2)	2.437(2)	2.450(2)
Rh(1)−C(27)	1.818(9)	1.827(9)	Rh(2)−C(28)	1.837(9)	1.789(9)
Zr(1)−S(1)	2.461(2)	2.458(2)	Zr(1)−S(2)	2.507(2)	2.507(2)
Zr(1)−G(1)[b]	2.295(4)	2.310(4)	Zr(1)−G(2)[b]	2.302(4)	2.292(4)
P(1)−Rh(1)−S(1)	149.44(8)	147.66(8)	P(2)−Rh(2)−S(1)	147.45(8)	150.47(8)
P(1)−Rh(1)−S(2)	85.53(8)	85.53(8)	P(2)−Rh(2)−S(2)	87.71(8)	87.78(7)
P(1)−Rh(1)−C(27)	96.8(3)	96.3(3)	P(2)−Rh(2)−C(28)	96.0(3)	95.5(3)
S(1)−Rh(1)−S(2)	84.42(7)	84.39(7)	S(1)−Rh(2)−S(2)	84.63(7)	84.50(7)
S(1)−Rh(1)−C(27)	96.0(3)	96.2(3)	S(1)−Rh(2)−C(28)	95.0(3)	96.3(3)
S(2)−Rh(1)−C(27)	174.4(3)	175.3(3)	S(2)−Rh(2)−C(28)	173.4(3)	171.4(3)
S(1)−Zr(1)−S(2)	82.19(7)	82.29(7)	G(1)−Zr(1)−G(2)[b]	126.86(15)	126.64(14)
S(1)−Zr(1)−G(1)[b]	109.27(13)	108.48(11)	S(2)−Zr(1)−G(1)[b]	109.96(12)	110.59(11)
S(1)−Zr(1)−G(2)[b]	111.14(11)	111.83(11)	S(2)−Zr(1)−G(2)[b]	108.41(11)	108.16(11)
Rh(1)−S(1)−Rh(2)	68.73(6)	68.41(6)	Rh(1)−S(2)−Rh(2)	68.66(6)	68.88(6)
Rh(1)−S(1)−Zr(1)	85.86(7)	84.03(6)	Rh(1)−S(2)−Zr(1)	85.23(7)	84.46(7)
Rh(2)−S(1)−Zr(1)	85.90(7)	87.46(7)	Rh(2)−S(2)−Zr(1)	84.41(7)	85.47(6)
Rh(1)−C(27)−O(1)	176.8(8)	177.0(8)	Rh(2)−C(28)−O(2)	176.4(8)	178.9(9)

[a] Values in the second column for each parameter are for the second crystallographically independent molecule. [b] G(1) and G(2) represent the centroids of the cyclopentadienyl ligands.

Table 3. Hydroformylation of 1-Octene Using the Complex $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (6) as Catalyst Precursor[a]

run	ligand	P/Rh	conversn[b] (%)	selectivity (%)[b]		% *n*
				aldehyde	isomerizn	
1	$P(OMe)_3$	2	79	95	5	76
2	$P(OMe)_3$	4	92	95	5	78
3	$P(OMe)_3$	6	80	98	2	82
4	$P(OPh)_3$	2	66	71	29	80
5	$P(OPh)_3$	4	99	81	19	81
6	$P(OPh)_3$	6	99	82	18	82
7	PPh_3	4	27	93	7	75
8	PPh_3	6	32	90	10	74

[a] Reaction conditions: 100 psi (CO/H_2, 1/1), 353 K, t = 8 h, 1-octene (10.2 mmol, 0.6 M), $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (0.017 mmol, 1 mM). [b] Determined by GC.

value 109.95(4)° in **6** and 109.73(4)° in **9**) are quite close to the ideal value for a tetrahedral geometry. The dihedral angles formed by the least-squares planes defined by the carbon atoms in the two Cp^{tt} rings are almost identical, 61.63(16)° in **6** and 62.1(2)° in **9**.

Without consideration of a potential Rh⋯Rh intermetallic interaction, the rhodium atoms exhibit square-planar geometries in both complexes, highly distorted in the case of **9**. The intermetallic Rh(1)⋯Rh(2) separation, 2.8397(7) Å in **6**, is considerably longer than that observed in **9**, 2.7404(6) Å, most likely due to the additional presence of the bridging diphosphine ligand. Despite this difference, both intermetallic distances are close to those reported in related complexes where the presence of an attractive intermetallic interaction has been suggested.[20] However, in both complexes the rhodium atoms are out of the least-squares planes calculated through the coordinated atoms (0.1087(4) Å in **6** and 0.5712(5) and 0.5644(5) Å in **9**) moving away from the other Rh center. These observations suggest the absence of an attractive intermetallic interaction and point toward the bridging system as the cause for the short Rh⋯Rh separations observed.

The Rh−S bond distances in **6** (2.3769(11) and 2.4096(11) Å) are significantly shorter than the values observed in **9** (mean value 2.429(1) Å), probably as a consequence of the better π-acceptor character of the carbonyl groups compared to that of the diphosphine. As observed for the Zr−S bond distances, the Rh−S bond lengths in **9** also show the asymmetry of the central $ZrRh_2S_2$ skeleton (see Table 2). The two Rh−P bonds in **9** (mean 2.252(1) Å) are shorter than the values found in the binuclear rhodium complex $[Rh_2Cl_2(CO)_2(dppm)_2]$ (2.3141(9), 2.3315(9) Å).[21]

Catalytic Activity. The complex $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**6**) in the presence of different P-donor ligands has been used as a catalyst precursor in toluene for the hydroformylation of oct-1-ene under mild conditions of temperature and pressure. The effect of the P/Rh ratio of different monodentate P-donor ligands in the hydroformylation reaction has been studied, and the data obtained from these experiments are presented in Table 3. It is remarkable that the hydrogenation product (octane) has only been observed in trace amounts (<1%), while 1-nonanal and 2-methyloctanal are exclusively obtained in these reactions; 2-ethylheptanal and 2-propylhexanal were not detected.

When $P(OMe)_3$ was used as modifying ligand (P/Rh = 2), a 79% conversion of 1-octene, at 100 psi and 353 K, was obtained in 8 h (entry 1). The aldehyde selectivity was 95% with a 76% regioselectivity for the linear aldehyde. Increasing the P/Rh ratio to 4 resulted in an increase of the conversion up to 92% with identical aldehyde selectivity and only slight improvement of the regioselectivity (entry 2). Higher P/Rh ratios provided higher regioslectivity (82%) but significantly lower conversion, despite a slight reduction of the isomerization activity (entry 3).

The catalytic system obtained using $P(OPh)_3$ as modifying ligand is much less selective in the hydroformylation of 1-octene, as a consequence of the high isomerization activity that produces internal *n*-octenes (mainly 2-octene isomers). It is noticeable that under the experimental conditions these internal olefins do not react, since neither 2-ethylheptanal nor 2-propylhexanal were detected by GC. Although a significant reduction of the isomerization activity has been observed as the ligand to metal ratio is increased, the optimal ratio found, P/Rh = 4, gave a 99% conversion in 8 h with a moderate aldehyde selectivity (81%) and 81% regioselectivity for the linear aldehyde (entry 5).

The combinations of the catalytic precursor **6** with other P-donor ligands, such as triphenyl- and trialkylphosphines, gave systems that are much less active for the hydroformylation of oct-1-ene under identical conditions. For example, when PPh_3 was used as the modifying ligand (P/Rh = 6), a 32% conversion of 1-octene was attained in 8 h. The aldehyde selectivity was 90% with a 74% regioselectivity for the linear aldehyde (entry 8).

Discussion

Synthesis of Trinuclear ZrM_2 Early−Late Heterobimetallic Complexes (M = Rh, Ir). The present study was aimed to prepare new complexes of zirconium and rhodium or iridium of the type early−late d^0−d^8, which could be useful for catalytic processes or reactivity studies. The search for an appropriate zirconium precursor led us to synthesize[15] the metallocene hydrosulfide complex $[Cp^{tt}_2Zr(SH)_2]$, with two bulky cyclopentadienyl rings. This compound shows a remarkable stability with respect to the elimination of H_2S when compared with the analogous compound $[Cp_2Zr(SH)_2]$, probably because of the steric shielding of the metal atom given by the bulky substituents on the cyclopentadienyl rings. Moreover, the deprotonation of the hydrosulfide groups in $[Cp^{tt}_2Zr(SH)_2]$ was accomplished by reaction with with *n*-BuLi at low temperature to give solutions that behave as a source of the zirconium−sulfido metallocene $[Cp^{tt}_2ZrS_2]^{2-}$ anion. This species is a rare example of a complex of the group 4 metals containing terminal sulfido ligands,[22] which was not isolated. Evidence of such an anion in these solutions comes from the isolation of the new trinuclear complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{ML_2\}_2]$, obtained through its reactions of metathesis with d^8-$[\{MClL_2\}_2]$ (M = Rh, Ir) metal

---

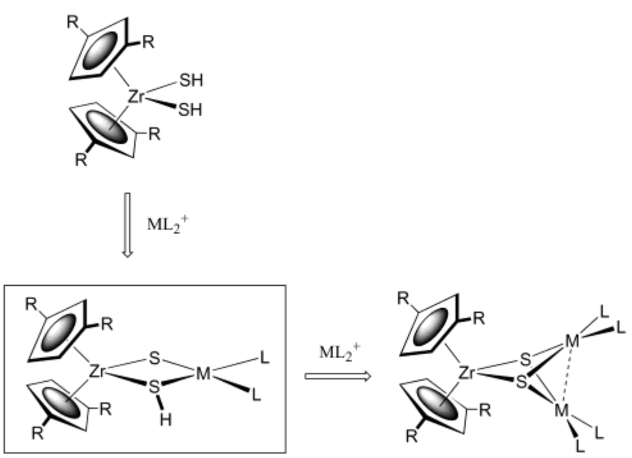
(19) Ashby, M. T.; Alguindigue, S. S.; Masood, A. K. *Inorg. Chim. Acta* **1998**, *270*, 227.

(20) Masdeu, A. M.; Ruiz, A.; Castillón, S.; Claver, C.; Hitchcock, P. B.; Chaloner, P. A.; Bó, C.; Poblet, J. M.; Sarsa, P. *J. Chem. Soc., Dalton Trans.* **1993**, 2689.

(21) Cowie, M.; Stephen, K. D. *Inorg. Chem.* **1980**, *19*, 2500.

(22) Firth, A. V.; Witt, E.; Stephan, D. W. *Organometallics* **1998**, *17*, 3716.

Scheme 3



chloride complexes. The heterobimetallic complexes result from the coordination of two d^8-ML_2 metal fragments to both sulfur atoms of the anionic metalla ligand to give a predictable triangular disposition of the metals. On the other hand, this result diverges from the deprotonation of $[Cp_2Ti(SH)_2]$ with strong bases[23] to give the dianion $[\{CpTi(S)\}_2(\mu\text{-}S)_2]^{2-}$ with elimination of cyclopentadiene. The latter provides a way to the complexes of the cores "$CpTiS_3M_3$" and "$Cp_2Ti_2S_4M_2$" but, in turn, makes inaccessible the related complexes $[Cp_2Ti(\mu_3\text{-}S)_2\{ML_2\}_2]$ through a similar route.

Alternative syntheses of the complexes $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{ML_2\}_2]$ are the additive-deprotonation reactions of $[Cp^{tt}{}_2Zr(SH)_2]$ with suitable rhodium and iridium complexes. These reactions are strongly sensitive to the ancillary ligands on the d^8-metal complexes used in the syntheses and to the solvent. As smaller and better π-acceptors the ancillary ligands give the cleanest reaction results, as exemplified by the multiple ways to prepare $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**6**) almost quantitatively. In contrast, the syntheses of the complexes with the bulkiest diolefin, cod, $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{M(cod)\}_2]$ (**3**, **4**), are frequently accompanied by the formation of the hydride clusters $[M_3(\mu\text{-}S)_2(\mu\text{-}H)(cod)_3]$ (M = Rh, Ir)[17,18] as well as free HCp^{tt} (NMR evidence), due to the transference of the sulfido ligands. Monitoring these reactions shows that the formation of the dinuclear intermediary species $[Cp^{tt}{}_2Zr(\mu_2\text{-}S)(\mu_2\text{-}SH)M(cod)]$ is faster than further additive deprotonation to give the ZrM_2 core (Scheme 3) in aprotic solvents. Thus, two such complexes, $[Cp^{tt}{}_2Zr(\mu_2\text{-}S)(\mu_2\text{-}SH)Rh(nbd)]$ and $[Cp^{tt}{}_2Zr(\mu_2\text{-}S)(\mu_2\text{-}SH)Rh(cod)]$, were detected by ^1H NMR in the early stages of the reactions of $[Cp^{tt}{}_2Zr(SH)_2]$ with $[Rh(acac)(nbd)]$ and with $[\{Rh(\mu\text{-}OMe)(cod)\}_2]$, respectively, in $CDCl_3$.[24] Since the dinuclear intermediate species from the first step accumulate and then evolve to the final products, the second step is slow in aprotic solvents. Therefore, we believe that the slowness of the second step along with the sensitivity of the intermediate species to the byproducts of these reactions (MeOH, Hacac, $HNEt_3^+$, and H_2O) are the source of the side reactions in aprotic solvents. In methanol, however, the reactions occur more quickly, with two opposite results shown by the quite clean synthesis of compound **3** from the reaction of $[Cp^{tt}{}_2Zr(SH)_2]$ with $[\{Rh(\mu\text{-}OH)(cod)\}_2]$ and the complete transfer of the sulfido groups in the reaction with the iridium complex in this solvent.

The influence of the solvent in the reactions leading to the early–late heterotrinuclear complexes becomes evident in the synthesis of the complex $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}_2]$ (**7**), which is isolated in 72% yield from the reaction of $[IrCl_2(CO)_2]^-$ with $[Cp^{tt}{}_2Zr(SH)_2]$ in dichloromethane/MeOH. A partial transfer of the sulfide ligands occurs in this mixture of solvents, since the anionic triiridium carbonyl complex $[Ir_3(\mu_3\text{-}S)_2(CO)_6]^-$[25] and the methoxo zirconium complexes $[Cp^{tt}{}_2Zr(OMe)_2]$ and $[Cp^{tt}{}_2ZrCl(OMe)]$[26] are detected in the solution remaining after crystallization by IR and ^1H NMR. However, in the absence of methanol the yield in **7** is considerably reduced (<20%), because an extensive formation of $[Ir_3(\mu_3\text{-}S)_2(CO)_6]^-$ occurs.

The additive deprotonation of $[Cp^{tt}{}_2Zr(SH)_2]$ with the complexes $[M(acac)L_2]$ gives acetylacetone (Hacac), which may interfere in the synthesis of ZrM_2 heterotrinuclear complexes. This is the case of the reaction of $[Cp^{tt}{}_2Zr(SH)_2]$ with $[Ir(acac)(cod)]$ to give $[Cp^{tt}(acac)Zr(\mu_3\text{-}S)_2\{Ir(cod)\}_2]$ (**5**), which involves the replacement of one cyclopentadienyl ring on the early metal by acetylacetonate. Moreover, this type of replacement has been found to occur in the reactions of $[Cp_2Ti(SH)_2]$ with $[M(acac)L_2]$ to give cleanly the diolefin complexes $[Cp(acac)Ti(\mu_3\text{-}S)_2\{M(diolefin)\}_2]$.[13] Although it might be thought that the replacement of Cp by acac occurs in an intermediate step, an independent experiment showed that $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{Ir(cod)\}_2]$ (**4**) reacts cleanly with Hacac to give **5**.

A further example of the replacement of one cyclopentadienyl ring by acac in $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}_2]$ (**7**) was observed on monitoring the reaction of $[Cp^{tt}{}_2Zr(SH)_2]$ with $[Ir(acac)(CO)_2]$ by IR in dichloromethane. The complex $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}_2]$ (**7**) is formed in the early stages of the reaction, and then $[Cp^{tt}(acac)Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}_2]$ (**8**) results from the reaction of **7** with the acetylacetone present in the reaction medium. Finally, the reaction is further complicated by the transfer of sulfido ligands to give $[Ir_3(\mu_3\text{-}S)_2(CO)_6]^-$, which become predominant at extended reaction times.

Restricted Rotation in Trinuclear ZrM_2 Early–Late Heterobimetallic Complexes (M = Rh, Ir). The introduction of sterically demanding substituents in metallocene complexes results in significant barriers to rotation about the metal–cyclopentadienyl bond.[27] The bulky substituents in bent metallocenes with a wedge-like structure exhibit a strong preference to occupy sites in the open part of the wedge, but repulsions between the substituents on different rings cause the rings to adopt a mutually staggered conformation.[28] The disposition of the *tert*-butyl groups found in the solid state for

---

[23] Lundmark, P. J.; Kubas, G. L.; Scott, B. L. *Organometallics* **1996**, *15*, 3631.

[24] Both intermediates show equivalent Cp^{tt} ligands and an SH signal at δ 2.20 (nbd) and 2.62 (cod) in the ^1H NMR spectrum. ^1H NMR: $[Cp^{tt}{}_2Zr(\mu_2\text{-}S)(\mu_2\text{-}SH)Rh(nbd)]$, δ 5.75, 5.58, and 5.25 (2H each, H_2, H_4, and H_5), 1.24 and 1.16 (s, 18H each, *t*-Bu); $[Cp^{tt}{}_2Zr(\mu_2\text{-}S)(\mu_2\text{-}SH)Rh(cod)]$, δ 5.77, 5.61, 5.47 (t, 2H each, H_2, H_4, and H_5), 1.27 and 1.19 (s, 18H each, *t*-Bu).

[25] Pergola, R. D.; Garlaschelli, L.; Martinengo, L.; Demartin, F.; Manassero, M.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1986**, 2463.

[26] Hernandez-Gruel, M. A. F.; et al. Unpublished results.

[27] Hughes, R. P.; Lomprey, J. R.; Rheingold, A. L.; Haggerty, B. S.; Yap, G. P. A. *J. Organomet. Chem.* **1996**, *517*, 89.

[28] (a) Howie, R. A.; McQuillan, G. P.; Thompson, Q. W.; Lock, G. A. *J. Organomet. Chem.* **1986**, *303*, 213. (b) Howie, R. A.; McQuillan, G. P.; Thompson, Q. W. *J. Organomet. Chem.* **1984**, *268*, 149.

mononuclear bent-metallocene complexes containing Cp^{tt} ligands ranges from the nearly eclipsed conformation in $[Cp^{tt}_2TiCl_2]$[29] (torsion angle between the Cp^{tt} rings $C_2-G(1)-G(2)-C_2' = -34.8(3)°$) to the partially staggered conformation found in $[Cp^{tt}_2ZrI_2]$[30] (−119.27°). An intermediate situation has been found in the complex $[Cp^{tt}_2Zr(SH)(OSO_2CF_3)]$ with a torsion angle between the Cp^{tt} rings of 52.4(5)°.[15]

The diolefin complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{M(\text{diolefin})\}_2]$ exist in solution as two rotamers arising from the hindered rotation of the cyclopentadienyl rings about the Cp^{tt}(centroid)−Zr axis. In contrast, the carbonyl compounds $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{M(CO)_2\}_2]$ (**6**, **7**) show no restriction to the rotation of the Cp^{tt} rings. Therefore, the steric demand of the ancillary ligands (L) on the ML_2 fragments determines whether the Cp^{tt} ligands can rotate freely, undergo a restricted rotation, or do not rotate at all. An associated fact is that the steric demand of the ancillary diolefin ligands also strongly influences the ratio of both rotamers, Thus, while the eclipsed rotamer prevails in the complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(nbd)\}_2]$ (**1**) and $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(tfbb)\}_2]$ (**2**), the predominance of the staggered rotamer is evident for the complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{M(cod)\}_2]$ (**4**). This observation is again in agreement with the greater bulkiness of the 1,5-cyclooctadiene ligands and reflects the fact that the main contribution to the energetic barrier associated with the rotation of the Cp^{tt} ligands is the steric demand of the ancillary ligands on the d^8 metal centers. The constancy in the ratio of rotamers for compounds **1** and **2**, independent of the synthetic method, strongly suggests that both rotamers interconvert in solution, as was confirmed experimentally for **1**. In addition, we have found that the temperature has little effect on the ratio of rotamers, since the proportion of the staggered rotamer in **1** increases from 38 to 41% in the range 273−328 K in $CDCl_3$.

The preference for the staggered conformation observed for cod complexes **3** and **4** and the lack of interconversion with the eclipsed isomer indicates that the rotational barrier in these compounds is exceedingly high, and then the rotation of the Cp^{tt} ligands is frozen. Thus, although rotational barriers associated with the rotation of (η^5-cyclopentadienyl)metal complexes have generally been found to be less than 13 kcal mol^{-1},[31] the significant steric hindrance produced by a single Rh(cod) fragment in the ELHB complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{ML_2\}_2]$ results in the larger rotational barrier of 17.2 kcal mol^{-1} found for the trimetallic complex $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}\{Rh(cod)\}]$, which exists as two interconverting rotamers in solution.[16]

The replacement of two carbonyl ligands in $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**6**) by P-donor ligands is enough to cause a restricted rotation of the Cp^{tt} ligands in the complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)(P(OR)_3)\}_2]$ (**11**, **12**) independent of the cone angle of the phosphite ligands (R = Me, 107°; R = Ph, 128°).[32] In sharp contrast, the related complexes containing a bridging dppm ligand, $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{M(CO)\}_2(\mu\text{-dppm})]$ (**9**, **10**), show a free rotation of the Cp^{tt} ligands.

To ascertain which factors affect the rotation of the Cp^{tt} ligands in the heterotrinuclear complexes, we should note the steric influence of the X groups on the narrow ("back") portion of the zirconocene wedge in bent metallocenes $[Cp_2MX_2]$. It has been shown that the conformation of the Cp^{tt} and Cp′ ligands (Cp′ = 1,3-bis(trimethylsilyl)cyclopentadienyl) in uranocene complexes $[Cp_2UX_2]$ is directly related to the size of the X ligands.[33] The complexes show an idealized C_{2v} structure (eclipsed conformation) for X = F, Cl, Br and a C_2 structure (partially staggered conformation) with larger ligands such as as I and Me. In addition, this steric influence is also transferred to the back of the metallocene clamshell in such a way that, the larger the size of the X ligand, the smaller the angle between the idealized planes of both Cp ligands. This effect can be observed in the zirconium chemistry on comparing the complexes $[Cp^{tt}_2ZrCl_2]$[34] and $[Cp^{tt}_2ZrI_2]$,[30] with angles of 58.9(1) and 53.04°, respectively.

As far as the $ZrRh_2$ complexes are concerned, the angle between the idealized planes of both Cp^{tt} ligands in the complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**6**) and $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}\{Rh(cod)\}]$ are 61.63(16) and 53.8(4)°, respectively. The angle of 62.1(2)° observed in the complex $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)\}_2(\mu\text{-dppm})]$ (**9**), similar to that of the carbonyl complex, is large enough to allow the free rotation of the Cp^{tt} ligands. An additional difference with the related phosphite complexes **11** and **12** is the bridging coordination mode of the dppm ligand. This produces an important contraction of the Rh−Rh separation along with a very distorted coordination environment around the rhodium atoms with small P−Rh−S angles and prevents the rotation about the Rh−P bonds. These factors working together result in a reduction of the steric encumbrance of the dinuclear subunit "$Rh_2(\mu\text{-}S)_2(\mu\text{-dppm})(CO)_2$" in the complexes **9** and **10** with reference to "$Rh_2(\mu\text{-}S)_2(CO)_2(P(OR)_3)_2$" in the complexes **11** and **12**, which seems to be enough to allow the free rotation of the Cp^{tt} rings.

Replacement Reactions and Catalytic Activity. The ZrM_2 triangular core in the heterotrinuclear carbonyl clusters $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{M(CO)_2\}_2]$ (**6**, **7**; M = Rh, Ir) is maintained in the replacement reactions of carbonyl by P-donor ligands. The outcome of these reactions depends on the character of the P-donor ligands, as exemplified by the reactions with dppm, $P(OMe)_3$, and $P(OPh)_3$. Thus, the replacement reactions with the short-bite bidentate dppm ligand are stereoselective and the products $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{M(CO)\}_2(\mu\text{-dppm})]$ (**9**, **10**) are cleanly obtained as a single isomer. In contrast, the disubstituted complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)(P(OR)_3)\}_2]$ (**11**, **12**) are obtained as a cis/trans mixture of isomers, as a result of the unselective replacement of the carbonyl ligands. The lack of stereoselectivity in the substitution process has also been observed in the tetracarbonyl complexes $[Cp(acac)Ti(\mu_3\text{-}S)_2\{M(CO)_2\}_2]$[13] and $[\{M(\mu_2\text{-}SR)(CO)_2\}_2]$ (M = Rh, Ir),[35] which contain two sym-

---

[29] Urazowski, I. F.; Ponomaryov, V. I.; Ellert, O. G.; Nifant'ev, I. E.; Lemenovskii, D. A. *J. Organomet. Chem.* **1988**, *356*, 181.

[30] King, W. A.; Di Bella, S.; Gulino, A.; Lanza, G.; Fragalà, I. L.; Stern, C. L.; Marks, T. *J. Am. Chem. Soc.* **1999**, *121*, 355.

[31] (a) Winter, C. H.; Zhou, X.-X.; Heeg, M. J. *Inorg. Chem.* **1992**, *31*, 1808. (b) Winter, C. H.; Dobbs, D. A.; Zhou, X.-X. *J. Organomet. Chem.* **1991**, *403*, 145. (c) Okuda, J. *J. Organomet. Chem.* **1990**, *397*, C37.

[32] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

[33] Lukens, W. W., Jr.; Beshouri, S. M.; Blosch, L. L.; Stuart, A. L.; Andersen, R. A. *Organometallics* **1999**, *18*, 1235.

[34] Chirik, P. J.; Day, M. W.; Bercaw, J. E. *Organometallics* **1999**, *18*, 1873.

metrically arranged sulfido and thiolate bridging ligands, respectively.

In view of the interest in the development of a new heterobimetallic catalyst that might lead to increased catalytic activity with enhanced chemo- and regioselectivity in the hydroformylation of alkenes, we have studied the catalytic activity of the cluster $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**6**). Interestingly, certain early−late heterobimetallic systems have been shown to be efficient hydroformylation catalysts.[5] In fact, we have recently shown that the tetranuclear early−late heterobimetallic complexes $[CpTi(\mu_3\text{-}S)_3\{Rh(diolefin)\}_3]$ in the presence of P-donor ligands are active precursors in the hydroformylation of hex-1-ene and styrene.[5a]

The compound $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**6**) in combination with monodentate P-donor ligands provides catalytic systems which are active in the hydroformylation of oct-1-ene under mild conditions of pressure and temperature. The catalytic systems obtained with the phosphite ligands $P(OR)_3$ are much more active than the corresponding systems with triphenylphosphine (Table 3). In addition, the system formed with $P(OMe)_3$ is much more selective than the system obtained with $P(OPh)_3$, giving an aldehyde selectivity of 95% with a regioslectivity close to 80% with the optimal ligand to metal ratio. The investigation of the solutions obtained after the hydroformylation reactions with the precursor **6** shows no evidence of the complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)(P(OR)_3)\}_2]$ (**11**, **12**), which indicates that the heterotrinuclear complexes are not maintained as such; most probably, they break down to active monomeric rhodium species. This behavior is opposite to that observed in the hydroformylation of hex-1-ene using the catalyst precursor $[CpTi(\mu_3\text{-}S)_3\{Rh(diolefin)\}_3]$, in which PPh_3 gave results superior to those for the $P(OR)_3$ ligands. High-pressure NMR spectroscopic studies have shown that under hydroformylation conditions the 62-electron clusters $[CpTi(\mu_3\text{-}S)_3Rh_3(\mu\text{-}CO)(CO)_4(PPh_3)_2]$ and $[CpTi(\mu\text{-}S)_3Rh_3(\mu\text{-}CO)(CO)_3(PPh_3)_3]$ are formed. Interestingly, the resting state of the precursor after the catalysis is the heterotetranuclear compound $[CpTi(\mu_3\text{-}S)_3\{Rh(CO)(PPh_3)\}_3]$, obtained by decarbonylation of the latter, which indicated an outstanding stability of the heterotetranuclear framework.[5a]

Concluding Remarks

The zirconium bis(hydrosulfido) complex $[Cp^{tt}_2Zr(SH)_2]$, containing the bulky Cp^{tt} ligands, is a precursor for the synthesis of d^0-d^8 early−late heterotrinuclear clusters with the cores $ZrRh_2$ and $ZrIr_2$. The controlled synthesis of these compounds can be accomplished through additive-deprotonation reactions involving rhodium and iridium complexes. The clusters possess a predictable triangular structure, which have no precedent in the related titanium chemistry. Some of the compounds exist in solution as two rotamers, as a consequence of the hindered rotation of the Cp^{tt} ligands. It is noteworthy that this phenomenon is affected by the steric demand of the ancillary ligands bonded to the d^8 metal fragments, which is transmitted to the metallocene moiety through the modification of the angle between the idealized planes of both cyclopentadienyl ligands.

Experimental Section

General Methods. All manipulations were performed under a dry argon atmosphere using Schlenk-tube techniques. Solvents were dried by standard methods and distilled under argon immediately prior to use. The complex $[Cp^{tt}_2Zr(SH)_2]$ was prepared as described previously.[15] Standard literature procedures were used to prepare the mononuclear complexes [M(acac)(diolef)] (M = Rh, diolef = nbd, tfbb;[36] M = Ir, diolef = cod[37]), $[Rh(acac)(CO)_2]$,[38] and $(PPh_3Bz)[MCl_2(CO)_2]$ (M = Rh, Ir).[39] The compounds $[\{Rh(\mu\text{-}Cl)(nbd)\}_2]$,[40] $[\{Rh(\mu\text{-}OH)(cod)\}_2]$,[41] and $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$[42] were prepared according to previously reported methods, and 1-octene was purchased from Aldrich and was distilled prior to use. In several cases (complexes **4**, **10**, and **11**) we encountered difficulty (as have other investigators)[43] in obtaining satisfactory elemental analyses on zirconium complexes, due presumably to incomplete combustion of the samples.

Scientific Equipment. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on Varian Gemini 300 spectrometers operating at 300.08, 121.47, and 75.46 MHz, respectively. Chemical shifts are reported in parts per million and referenced to Me_4Si using the signal of the deuterated solvent (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P) as external references, respectively. Assignments in complex NMR spectra were done by simulation with the program gNMR, version 3.6 (Cherwell Scientific Publishing Limited) for Macintosh. The initial choices of chemical shifts and coupling constants were optimized by successive iterations following a standard least-squares procedure; a numerical assignment of the experimental frequencies was used. IR spectra were recorded on a Nicolet-IR 550 spectrometer (4000−400 cm^{-1}). Elemental C, H, and N analyses were performed on a Perkin-Elmer 240-C microanalyzer. Molecular weights were determined with a Knauer osmometer using chloroform solutions of the complexes. Mass spectra were recorded on a VG Autospec double-focusing mass spectrometer operating in the FAB^+ mode. Ions were produced with the standard Cs^+ gun at ca. 30 kV; 3-nitrobenzyl alcohol (NBA) was used as the matrix. Hydroformylation experiments were carried out in a stainless steel magnetically stirred autoclave (100 mL) equipped with a thermocouple and an external heating mantle. Syngas ($CO/H_2 = 1$) was supplied at constant pressure from a ballast. The drop-in pressure in the ballast was monitored using a pressure transducer.

Standard Hydroformylation Experiment. In a typical run, a solution of the catalyst precursor $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**6**; 0.017 mmol) containing the phosphine or phosphite ligand (0.20−0.60 mmol), 1-octene (10.2 mmol), and toluene (15.4 mL) was transferred from a Schlenk tube under argon to the autoclave by using a stainless steel cannula. The autoclave was purged with syngas three times at 120 psi and then pressurized at 50 psi and heated to 80 °C. When the thermal equilibrium was reached, the pressure was adjusted to 100 psi and the mixture stirred for 8 h with a continuous

---

(35) (a) Poilblanc, R. *Inorg. Chim. Acta* **1982**, *62*, 75. (b) Bonnet, J. J.; Thorez, A.; Maisonnat, A.; Galy, J.; Poilblanc, R. *J. Am. Chem. Soc.* **1979**, *101*, 5940. (c) Bonnet, J. J.; Kalck, P.; Poilblanc, R. *Inorg. Chem.* **1977**, *16*, 1514.

(36) Bonati, F.; Wilkinson, G. *J. Chem. Soc.* **1964**, 3156.

(37) Robinson, S. R.; Shaw, B. L. *J. Chem. Soc.* **1965**, 4997.

(38) Varshavskii, Y. S.; Cherkasova, T. G. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1967**, *12*, 899.

(39) (a) Vallarino, L. M..*Inorg. Chem.* **1965**, *4*, 161. (b) Foster, D. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 433.

(40) Abel, E. W.; Bennet, M. A.; Wilkinson, G. J. *J. Chem. Soc.* **1959**, 3178.

(41) (a) Usón, R.; Oro, L. A.; Cabeza, J. A. *Inorg. Synth.* **1985**, *23*, 126. (b) Selent, D.; Ramm, M. *J. Organomet. Chem.* **1995**, *485*, 135.

(42) Powell, J.; Shaw, B. L. *J. Chem. Soc.* **1968**, 212.

(43) Carney, M. J.; Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1992**, *11*, 761.

supply of syngas at constant pressure. After the reaction time, the autoclave was cooled to room temperature and depressurized. The reaction mixture was analyzed by gas chromatography with a Hewlett-Packard 5890 instrument equipped with a capillary column (HP, ULTRA 1, 25 m × 0.32 mm × 0.17 μm) and a flame-ionization detector. The products were quantified by the internal standard method using anisole.

Synthesis of the Complexes. [Cp^{tt}$_2$Zr(μ_3-S)$_2${Rh(nbd)}$_2$] (1). Method A. To a finely divided solid mixture of [Cp^{tt}$_2$Zr(SH)$_2$] (0.100 g, 0.195 mmol) and [Rh(acac)(nbd)] (0.115 g, 0.390 mmol) was added 10 mL of methanol at room temperature. The suspension, which turned from yellow to brick orange within 1 min, was stirred for 30 min. The brick orange solid was filtered, washed with methanol (5 mL), and vacuum-dried. Yield: 0.148 g (84%).

Method B. [Cp^{tt}$_2$Zr(SH)$_2$] (0.100 g, 0.195 mmol) was reacted with triethylamine (60 μL, 0.432 mmol) and [{Rh(μ-Cl)(nbd)}$_2$] (0.090 g, 0.195 mmol) in dichloromethane (10 mL) for 30 min to give a brown cloudy solution. The solvent was removed under vacuum and the residue washed with methanol (10 mL) and diethyl ether (5 mL). The crude product was extracted with dichloromethane (20 mL) and then filtered to give a clear brown-red solution. Addition of *n*-hexane (50 mL) and concentration of the solution to ca. 15 mL afforded the compound as an orange-brown solid, which was filtered, washed with *n*-hexane (10 mL), and dried under vacuum. Yield: 0.105 g (60%).

Method C. A pale yellow solution of [Cp^{tt}$_2$Zr(SH)$_2$] (0.100 g, 0.195 mmol) in diethyl ether (10 mL) was reacted with *n*-butyllithium (156 μL, 2.5 mol L^{-1}, 0.39 mmol) at −50 °C. Then, solid [{Rh(μ-Cl)(nbd)}$_2$] (0.090 g, 0.195 mmol) was added to this solution and the temperature was raised to −0 °C for 1 h. The resulting brown-red suspension was evaporated to dryness. Recrystallization of the residue from dichloromethane/*n*-hexane following the procedure described above gave the compound in 62% yield (0.109 g). Anal. Calcd for $C_{40}H_{58}S_2Rh_2Zr$: C, 53.38; H, 6.49; S, 7.12. Found. C, 53.32; H, 6.78; S, 7.11. MS (FAB$^+$, CH_2Cl_2, *m/z*): 898 (M$^+$, 37%), 806 (M$^+$ − nbd, 14%), 721 (M$^+$ − Cp^{tt}, 100%). Molecular weight: found 902 (calcd 900). ^{1}H NMR (CDCl$_3$, 293 K): rotamer **1a** (60%), δ 6.67 (t, 2.4 Hz, 2H, H$_2$), 5.71 (d, 2.4 Hz, 4H, H$_4$ and H$_5$) (Cp^{tt}), 4.26−3.68 (m, 12H, =CH and CH), 1.43−1.33 (m, 4H, >CH$_2$) (nbd), 1.31 (s, 36H, *t*-Bu); rotamer **1b** (40%), δ 7.36 (d, 2.6 Hz, 2H, H$_4$ and H$_5$), 5.59 (t, 2.6 Hz, 1H, H$_2$) (Cp^{tt}), 6.61 (t, 2.6 Hz, 1H, H$_2$), 5.72 (d, 2.6 Hz, 2H, H$_4$ and H$_5$) (Cp^{tt}), 4.26−3.68 (m, 12H, =CH and CH), 1.43−1.33 (m, 4H, >CH$_2$) (nbd), 1.32 and 1.24 (s, 18H each, *t*-Bu). ^{13}C{^{1}H} NMR (CDCl$_3$, 293 K): rotamer **1a**, δ 146.2 (C$_1$ and C$_3$), 117.7 (C$_2$), 107.7 (C$_4$ and C$_5$) (Cp^{tt}), 62.8 (d, J_{Rh-C} = 6.5 Hz, >CH$_2$), 57.8 and 51.5 (br d, J_{Rh-C} = 9.2 Hz, =CH), 51.2 and 50.2 (br, CH) (nbd), 34.1 (*C*Me$_3$), 32.6 (C*Me*$_3$); rotamer **1b**, δ 148.6 (C$_1$ and C$_3$), 139.6 (C$_1$ and C$_3$), 121.6 (C$_2$), 117.3 (C$_4$ and C$_5$), 110.0 (C$_2$), 104.1 (C$_4$ and C$_5$) (Cp^{tt}), 63.0 and 62.7 (d, J_{Rh-C} = 6.5 Hz, >CH$_2$), 56.7 and 52.5 (br d, J_{Rh-C} = 9.2 Hz, =*C*H), 49.2 (br, CH) (nbd), 34.3 and 33.7 (*C*Me$_3$), 32.9 and 31.9 (*C*Me$_3$).

[Cp^{tt}$_2$Zr(μ_3-S)$_2${Rh(tfbb)}$_2$] (2). To a finely divided solid mixture of [Cp^{tt}$_2$Zr(SH)$_2$] (0.100 g, 0.195 mmol) and [Rh(acac)(tfbb)] (0.167 g, 0.390 mmol) was added 10 mL of methanol at room temperature. The yellow suspension, which turned progressively dark orange, was stirred for 1 h and then filtered to give a brick orange powder, which was washed with methanol (5 mL) and dried under vacuum. Yield: 0.212 g (93%). Anal. Calcd for $C_{50}H_{54}F_8S_2Rh_2Zr$: C, 51.41; H, 4.66; S, 5.49. Found: C, 51.17; H, 4.66; S, 5.47. MS (FAB$^+$, CH_2Cl_2, *m/z*): 1166 (M$^+$, 43%), 989 (M$^+$ − Cp^{tt}, 100%), 940 (M$^+$ − tfbb, 21%), 714 (M$^+$ − 2tfbb, 11%). ^{1}H NMR (CDCl$_3$, 293 K): rotamer **2a** (55%), δ 6.91 (t, 2.4 Hz, 2H, H$_2$), 5.92 (d, 2.4 Hz, 4H, H$_4$ and H$_5$) (Cp^{tt}), 5.66 and 5.50 (m, 2H each, CH), 4.03−3.80 (m, 8H, =CH) (tfbb), 1.34 (s, 36H, *t*-Bu); rotamer **2b** (45%), δ 7.48 (d, 2.4 Hz, 2H, H$_4$ and H$_5$), 5.76 (t, 2.4 Hz, 1H, H$_2$) (Cp^{tt}), 6.85 (t, 2.4 Hz, 1H, H$_2$), 5.92 (d, 2.4 Hz, 2H, H$_4$ and H$_5$) (Cp^{tt}), 5.82, 5.64, 5.47, and 5.45 (m, 1H each, CH), 4.03−3.80 (m, 8H, =CH) (tfbb), 1.35 and 1.21 (s, 18H each, *t*-Bu). ^{13}C{^{1}H} NMR (CDCl$_3$, 293 K): rotamer **2a**, δ 147.4 (C$_1$ and C$_3$), 118.2 (C$_2$), 109.0 (C$_4$ and C$_5$) (Cp^{tt}), 57.0 and 53.9 (d, J_{Rh-C} = 9.7 Hz) (=CH region, tfbb), 34.3 (*C*Me$_3$), 32.5 (C*Me*$_3$); rotamer **2b**, δ 149.8 (C$_1$ and C$_3$), 141.0 (C$_1$ and C$_3$), 122.3 (C$_2$), 118.2 (C$_4$ and C$_5$), 110.7 (C$_2$), 105.5 (C$_4$ and C$_5$) (Cp^{tt}), 57.2, 56.0, 54.3, and 53.5 (d, J_{Rh-C} = 9.9 Hz) (=CH region, tfbb), 33.9 and 34.5 (*C*Me$_3$), 32.9 and 31.8 (C*Me*$_3$).

[Cp^{tt}$_2$Zr(μ_3-S)$_2${Rh(cod)}$_2$] (3). Method A. A pale yellow solution of [Cp^{tt}$_2$Zr(SH)$_2$] (0.056 g, 0.11 mmol) in diethyl ether (10 mL) was reacted with *n*-butyllithium (130 μL, 1.68 mol L^{-1}, 0.22 mmol) at −60 °C. Then, solid [{Rh(μ-Cl)(cod)}$_2$] (0.054 g, 0.11 mmol) was added to this solution and the temperature was raised to room temperature for 2 h. The resulting dark brown suspension was evaporated to dryness, and the residue was washed with methanol (3 × 10 mL) to give a black-brown crystalline solid, which was dried under vacuum. Yield: 0.083 g (81%).

Method B. To a finely divided solid mixture of [Cp^{tt}$_2$Zr(SH)$_2$] (0.100 g, 0.195 mmol) and [{Rh(μ-OH)(cod)}$_2$] (0.089 g, 0.195 mmol) was added 10 mL of methanol at room temperature to give a light brown suspension, which was stirred for 30 min. The brown solid was filtered, washed with methanol (5 mL), and dried under vacuum. Yield: 0.157 g (86%). Anal. Calcd for $C_{42}H_{66}S_2Rh_2Zr$: C, 54.12; H, 7.14; S, 6.88. Found: C, 53.82; H, 8.02; S, 7.07. MS (FAB$^+$, CH_2Cl_2, *m/z*): 930 (M$^+$, 32%), 822 (M$^+$ − cod, 25%), 753 (M$^+$ − Cp^{tt}, 100%), 714 (M$^+$ − 2cod, 21%). ^{1}H NMR (CDCl$_3$, 293 K): rotamer **3b**, δ 7.32 (d, 2.6 Hz, 2H, H$_4$ and H$_5$), 5.70 (t, 2.6 Hz, 1H, H$_2$) (Cp^{tt}), 6.48 (t, 2.6 Hz, 1H, H$_2$), 5.89 (d, 2.6 Hz, 2H, H$_4$ and H$_5$) (Cp^{tt}), 4.42 (br m, 6H, =CH), 4.29 (br m, 2H, =CH), 2.7−1.7 (m, 16H, >CH$_2$) (cod), 1.32 and 1.26 (s, 18H each, *t*-Bu). ^{13}C{^{1}H} NMR (CDCl$_3$, 293 K): δ 148.4 (C$_1$ and C$_3$), 139.9 (C$_1$ and C$_3$), 121.0 (C$_2$), 117.0 (C$_4$ and C$_5$), 111.0 (C$_2$), 105.5 (C$_4$ and C$_5$) (Cp^{tt}), 79.4, 79.2, 78.2, and 78.1 (d, J_{Rh-C} = 11.5 Hz, =CH, cod), 34.5 and 33.7 (*C*Me$_3$), 33.0 and 32.0 (C*Me*$_3$), 31.6, 31.0, and 30.9 (>CH$_2$, cod).

A mixture of the staggered (**3b**) and eclipsed (**3a**) rotamers in a 85/15 molar ratio was observed on monitoring the reaction of method B in CDCl$_3$ by ^{1}H NMR: rotamer **3a**, δ 6.63 (t, 2.4 Hz, 2H, H$_2$), 5.86 (d, 2.4 Hz, 4H, H$_4$ and H$_5$), 1.32 (s, 36H, *t*-Bu).

[Cp^{tt}$_2$Zr(μ_3-S)$_2${Ir(cod)}$_2$] (4). A solution of [Cp^{tt}$_2$Zr(SH)$_2$] (0.056 g, 0.11 mmol) in diethyl ether (10 mL) at −60 °C was treated with *n*-butyllithium (0.134 mL, 1.68 mol L^{-1}, 0.225 mmol). Then, solid [{Ir(μ-Cl)(cod)}$_2$] (0.074 g, 0.11 mmol) was added to this solution and the temperature was raised to −20 °C for 1 h. The resulting black-green suspension was evaporated to dryness. The residue was washed with 6 mL of diethyl ether/methanol (1/1) and then with methanol (3 × 5 mL) to give a black-green solid, which was dried under vacuum. Yield: 0.062 g (51%). Satisfactory elemental analyses could not be obtained for this compound, although it was characterized by spectroscopic methods as follows. MS (FAB$^+$, CH_2Cl_2, *m/z*): 1110 (M$^+$, 28%), 933 (M$^+$ − Cp^{tt}, 100%). ^{1}H NMR (CDCl$_3$, 293 K): rotamer **4a** (20%), δ 6.37 (t, 2.7 Hz, 2H, H$_2$), 6.00 (d, 2.7 Hz, H$_4$ and H$_5$), 3.97 (m, 8H, =CH cod), 2.45−2.30, 1.90−1.80, and 1.72 (m, 6H each, >CH$_2$ cod), 1.32 (s, 36H, *t*-Bu); rotamer **4b** (80%), δ 7.15 (d, 2.4 Hz, 2H, H$_4$ and H$_5$), 5.78 (t, 2.4 Hz, 1H, H$_2$) (Cp^{tt}), 6.25 (t, 2.4 Hz, 1H, H$_2$), 6.04 (d, 2.4 Hz, 2H, H$_4$ and H$_5$) (Cp^{tt}), 3.93−3.85 (m, 8H, =CH cod), 2.45−2.30, 1.90−1.80, and 1.74 (m, 6H each, >CH$_2$ cod), 1.32 and 1.26 (s, 18H each, *t*-Bu). ^{13}C{^{1}H} NMR (CDCl$_3$, 293 K): rotamer **4b**, δ 149.9 (C$_1$ and C$_3$), 141.3 (C$_1$ and C$_3$), 120.1, 119.9 (C$_2$, C$_4$ and C$_5$), 112.5 (C$_2$), 107.3 (C$_4$ and C$_5$) (Cp^{tt}), 64,7, 63.8, 62.6, and 60.5 (=CH, cod), 34.8 and 34.0 (*C*Me$_3$), 33.0 and 31.9 (C*Me*$_3$), 32.6, 31.7, and 31.3 (>CH$_2$, cod).

[Cp^{tt}(acac)Zr(μ_3-S)$_2${Ir(cod)}$_2$] (5). To a yellow solution of [Ir(acac)(cod)] (0.400 g, 1.001 mmol) in diethyl ether (40 mL) was added solid [Cp^{tt}$_2$Zr(SH)$_2$] (0.256 g, 0.500 mmol). The mixture was refluxed to give a greenish blue solution in 1 h. The solvent was removed under vacuum, and the residue was washed with methanol (2 × 5 mL) at −78 °C. The crude product was extracted with *n*-pentane (40 mL) and then filtered to give a dark blue solution. Evaporation to dryness under reduced pressure gave the compound as a dark blue powder. Yield: 0.284 g (55%). Anal. Calcd for $C_{34}H_{52}O_2S_2Ir_2Zr$: C, 39.55; H, 5.08; S, 6.21. Found: C, 39.38; H, 5.13; S, 6.19. MS (FAB$^+$, CH_2Cl_2, *m*/*z*): 1032 (M$^+$, 100%), 924 (M$^+$ − cod, 20%), 855 (M$^+$ − Cp^{tt}, 67%), 747 (M$^+$ − cod − Cp^{tt}, 32%). ^{1}H NMR ($CDCl_3$, 293 K): δ 7.02 (d, 2.7 Hz, 2H, H_4 and H_5, Cp^{tt}), 5.81 (s, 1H, CH, acac), 5.47 (t, 2.7 Hz, 1H, H_2, Cp^{tt}), 3.96 (br m, 8H, =CH), 2.21 (m, 4H, >CH_2) (cod), 2.00 (s, 6H, CH_3, acac), 1.83 (m, 8H, >CH_2), 1.57 (m, 4H, >CH_2) (cod), 1.16 (s, 18H, *t*-Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 190.5 (*C*O, acac), 144.7 (C_1 and C_3), 108.5 (C_4 and C_5), 107.9 (C_2) (Cp^{tt}), 105.1 (CH, acac), 65.0 and 62.8 (=CH, cod), 33.0 (*C*Me$_3$), 32.9 and 31.5 (>CH_2, cod), 31.1 (C*Me*$_3$), 26.0 (CH_3, acac).

[Cp$^{tt}{}_2$Zr(μ_3-S)$_2$\{Rh(CO)$_2$\}$_2$] (6). Method A. Carbon monoxide was bubbled through a deep red solution of [Cp$^{tt}{}_2$Zr(μ_3-S)$_2$\{Rh(nbd)\}$_2$] (0.140 g, 0.156 mmol) in benzene (10 mL) at room temperature for 15 min to give a dark green solution. Then, *n*-hexane (20 mL) was added and the bubbling was continued for 15 min more to give an emerald green suspension, which was kept overnight at 7 °C under a CO atmosphere. The suspension was quickly filtered, washed with *n*-hexane (2 × 10 mL), and dried under vacuum. Yield: 0.098 g (76%).

Method B. [Rh(acac)(CO)$_2$] (0.504 g, 1.953 mmol) was added to a yellow solution of [Cp$^{tt}{}_2$Zr(SH)$_2$] (0.500 g, 0.977 mmol) in diethyl ether (20 mL). The solution immediately turned dark green and a solid crystallized out while the mixture was stirred for 10 min at room temperature. Filtration of the resulting suspension gave the compound as an emerald green microcrystalline powder after washing with *n*-hexane (2 × 10 mL) and drying in vacuo. Yield: 0.753 g (93%).

Method C. Triethylamine (60 μL, 0.432 mmol) and [\{Rh(μ-Cl)(CO)$_2$\}$_2$] (0.076 g, 0.196 mmol) were rapidly and succesively added to a vigorously stirred solution of [Cp$^{tt}{}_2$Zr(SH)$_2$] (0.100 g, 0.195 mmol) in dichloromethane (5 mL) at room temperature. The yellow solution turned emerald green immediately, and a green solid started to precipitate. The reaction mixture was stirred for 5 min, and then 10 mL of methanol was added. After the mixture was stirred for 5 min more, the solid was collected by filtration, washed with 10 mL of methanol, and dried under vacuum. Yield: 0.153 g (95%).

Method D. [Cp$^{tt}{}_2$Zr(SH)$_2$] (0.100 g, 0.195 mmol), triethylamine (60 μL, 0.432 mmol), and (PPh$_3$Bz)[RhCl$_2$(CO)$_2$] (0.228 g, 0.391 mmol) were reacted in dichloromethane (5 mL), following the procedure described in method C, to give a green suspension. Workup as above gave the compound in 92% yield (0.148 g). Anal. Calcd for $C_{30}H_{42}O_4S_2Rh_2Zr$: C, 43.53; H, 5.11; S, 7.75. Found: C, 43.60; H, 5.12; S, 7.82. MS (FAB+, CH_2Cl_2, *m*/*z*): 826 (M$^+$, 29%), 770 (M$^+$ − 2CO, 39%), 742 (M$^+$ − 3CO, 34%), 714 (M$^+$ − 4CO, 100%). ^{1}H NMR ($CDCl_3$, 293 K): δ 6.56 (t, 2.6 Hz, 2H, H_2), 6.03 (d, 2.6 Hz, 4H, H_4 and H_5), 1.31 (s, 36H, *t*-Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 185.3 (d, J_{Rh-C} = 73 Hz, *C*O), 148.6 (C_1 and C_3), 121.3 (C_2), 109.0 (C_4 and C_5), 34.6 (*C*Me$_3$), 32.3 (C*Me*$_3$). IR (CH_2Cl_2, cm^{-1}): ν(CO) 2066 (s), 2041 (s), 1994 (s).

[Cp$^{tt}{}_2$Zr(μ_3-S)$_2$\{Ir(CO)$_2$\}$_2$] (7). Triethylamine (290 μL, 2.086 mmol) and finely divided (PPh$_3$Bz)[IrCl$_2$(CO)$_2$] (1.315 g, 1.955 mmol) were quickly and successively added to a well-stirred yellow solution of [Cp$^{tt}{}_2$Zr(SH)$_2$] (0.500 g, 0.977 mmol) in 35 mL of dichloromethane/methanol (1/6) at room temperature. The solution became immediately dark green, and a apple green microcrystalline solid started to precipitate. After the mixture was stirred for 5 min, the solid was filtered, washed with methanol (2 × 10 mL) and diethyl ether (2 × 10 mL), and dried under vacuum. Yield: 0.708 g (72%). Anal. Calcd for $C_{30}H_{42}O_4S_2Ir_2Zr$: C, 35.80; H, 4.21; S, 6.37. Found: C, 35.37; H, 4.11; S, 6.38. MS (FAB+, CH_2Cl_2, *m*/*z*): 1006 (M$^+$, 93%), 829 (M$^+$ − Cp^{tt}, 100%). ^{1}H NMR ($CDCl_3$, 293 K): δ 6.74 (t, 2.6 Hz, 2H, H_2), 6.24 (d, 2.6 Hz, 4H, H_4 and H_5), 1.31 (s, 36H, *t*-Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 174.7 (*C*O), 150.0 (C_1 and C_3), 127.5 (C_2), 111.0 (C_4 and C_5), 35.1 (*C*Me$_3$), 32.1 (C*Me*$_3$). IR (CH_2Cl_2, cm^{-1}): ν(CO) 2056 (s), 2027 (s), 1979 (s).

[Cp^{tt}(acac)Zr(μ_3-S)$_2$\{Ir(CO)$_2$\}$_2$] (8). Carbon monoxide was bubbled through a solution of [Cp^{tt}(acac)Zr(μ_3-S)$_2$\{Ir(cod)\}$_2$] (**6**; 0.200 g, 0.194 mmol) in *n*-pentane (20 mL) to give a golden brown suspension in 20 min. The suspension was cooled to −78 °C and then filtered to gave a golden microcrystalline solid that was washed with *n*-pentane at low temperature and dried under vacuum. Yield: 0.157 g (87%). Anal. Calcd for $C_{22}H_{28}O_6S_2Ir_2Zr$: C, 28.47; H, 3.04; S, 6.91. Found: C, 28.35; H, 3.14; S, 6.83. ^{1}H NMR ($CDCl_3$, 293 K): δ 6.96 (d, 2.5 Hz, 2H, H_4 and H_5, Cp^{tt}), 6.01 (s, 1H, CH, acac), 5.87 (t, 2.5 Hz, 1H, H_2, Cp^{tt}), 2.09 (s, 6H, CH_3, acac), 1.23 (s, 18H, *t*-Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 191.9 (*C*O, acac), 174.3 (Ir−*C*O), 147.0 (C_1 and C_3), 112.3 (C_4 and C_5), 110.7 (C_2) (Cp^{tt}), 107.4 (CH, acac), 33.4 (*C*Me$_3$), 30.9 (C*Me*$_3$), 26.0 (CH_3, acac). IR (CH_2Cl_2, cm^{-1}): ν(CO) 2058 (s), 2033 (s), 1983 (s).

[Cp$^{tt}{}_2$Zr(μ_3-S)$_2$\{Rh(CO)\}$_2$(μ-dppm)] (9). A solid mixture of [Cp$^{tt}{}_2$Zr(μ_3-S)$_2$\{Rh(CO)$_2$\}$_2$] (0.19 g, 0.23 mmol) and dppm (0.088 g, 0.23 mmol) was dissolved in dichloromethane (5 mL) to give a dark green solution with evolution of carbon monoxide. The reaction mixture was stirred for 10 min at room temperature, and then *n*-hexane (15 mL) was added. Concentration of the solution under vacuum to ca. 5 mL gave the compound as a greenish black microcrystalline solid, which was filtered, washed with 2 × 5 mL of *n*-hexane, and dried under vaccum. Yield: 0.253 g (95%). Anal. Calcd for $C_{53}H_{64}O_2P_2S_2Rh_2Zr$: C, 55.06; H, 5.58; S, 5.55. Found: C, 54.68; H, 5.62; S, 5.47. MS (FAB$^+$, CH_2Cl_2, *m*/*z*): 1154 (M$^+$, 15%), 1126 (M$^+$ − CO, 6%), 1098 (M$^+$ − 2CO, 100%). ^{1}H NMR (C_6D_6, 293 K): δ 7.70−6.50 (m, 20H, dppm), 6.19, 5.62, and 5.48 (br, 2H each, H_2, H_4 and H_5, Cp^{tt}), 4.64 and 2.54 (br m, 1H each, >CH_2 dppm), 1.64 and 1.15 (br, 18H each, *t*-Bu). $^{13}C\{^1H\}$ NMR (C_6D_6, 293 K): δ 193.8 (br d, $J_{Rh-C} = 88$ Hz, Rh-*C*O), 144.6 and 144.0 (br, C_1 and C_3, Cp^{tt}), 137.2 and 135.4 (d, $J_{P-C} = 45$ Hz, C_{ipso}), 133.9 (m), 132.1 (m), 129.7 (s), 129.4 (s), 128.7 (m), 127.8 (m) (dppm), 118.2, 106.5, and 106.1 (br, C_2, C_4 and C_5, Cp^{tt}), 34.4 and 33.5 (br s, *C*Me$_3$), 32.9 and 32.4 (br s, C*Me*$_3$), 28.1 (t, $J_{P-C} = 34$ Hz, >CH_2 dppm). $^{31}P\{^1H\}$ NMR (C_6D_6, 293 K): δ 24.9 (br d, $J_{Rh-P} = 169$ Hz). This signal results in a AA′XX′ spin system (A = ^{31}P and X = ^{103}Rh) centered at δ 24.7 ppm at 213 K, which has been successfully simulated with the parameters $^1J_{Rh-P} = 171$ Hz, $^2J_{P-P} = 35$ Hz, and $^3J_{Rh-P} = -1.7$ Hz. IR (CH_2Cl_2, cm^{-1}): ν(CO) 1962 (s), 1933 (s).

[Cp$^{tt}{}_2$Zr(μ_3-S)$_2$\{Ir(CO)\}$_2$(μ-dppm)] (10). To a suspension of [Cp$^{tt}{}_2$Zr(μ_3-S)$_2$\{Ir(CO)$_2$\}$_2$] (0.061 g, 0.061 mmol) in dichloromethane (7 mL) was slowly added a solution of dppm (0.023 g, 0.061 mmol) in dichloromethane (7 mL) to give a brown-yellow solution upon evolution of carbon monoxide. After 30 min, the solvent was removed under vacuum and the residue extracted with *n*-hexane (30 mL) and then filtered. Cooling of the solution to −40 °C gave the compound as orange crystals, which were collected by filtration at low temperature. Yield: 0.057 g (70%). Anal. Calcd for $C_{53}H_{64}O_2P_2S_2Ir_2Zr$: C, 47.69; H, 4.83; S, 4.80. Found: C, 44.09; H, 4.29. MS (FAB$^+$, CH_2Cl_2, *m*/*z*, %): 1333 (M$^+$, 76%), 1278 (M$^+$− 2CO, 62%), 1157 (M$^+$ − Cp^{tt}, 100%). ^{1}H NMR ($CDCl_3$, 293 K): δ 7.58 (m, 4H), 7.38 (m, 4H), 7.20 (m, 12H) (dppm), 5.72 (m, 4H), 5.22 (t, 2H) (Cp^{tt}), 3.45 (m, 2H, >CH_2 dppm), 1.29 and 0.99 (s, 18H each, *t*-Bu). ^{31}P NMR ($CDCl_3$, 293 K): δ 11.4 (s). IR (CH_2Cl_2, cm^{-1}): ν(CO) 1965 (s), 1925 (s).

[Cp$^{tt}{}_2$Zr(μ_3-S)$_2$\{Rh(CO)(P(OMe)$_3$)\}$_2$] (11). To a solution of [Cp$^{tt}{}_2$Zr(μ_3-S)$_2$\{Rh(CO)$_2$\}$_2$] (0.100 g, 0.121 mmol) in toluene (5 mL) was slowly added a solution of P(OMe)$_3$ (28.6 μL, 0.242 mmol) in toluene (4 mL) to give a green solution upon evolution of carbon monoxide. The solvent was removed under vacuum and the residue dissolved in *n*-hexane (3 mL). Stirring of the solution gave the compound as an apple green microcrystalline solid, which was filtered, washed with *n*-hexane, and dried

Table 4. Crystal Data and Data Collection and Refinement Details for Complexes 6 and 9

	6	**9**
empirical formula	$C_{30}H_{42}O_4Rh_2S_2Zr{\cdot}H_2O$	$C_{53}H_{64}O_2P_2Rh_2S_2Zr{\cdot}CH_2Cl_2$
fw	845.81	1241.07
cryst size, mm	0.252 × 0.116 × 0.064	0.36 × 0.20 × 0.20
cryst syst	monoclinic	triclinic
space group	$P2/n$ (No. 13)	$P\bar{1}$ (No. 2)
a, Å	12.6643(12)	11.1621(5)
b, Å	9.4235(9)	22.1108(11)
c, Å	13.4335(13)	22.1713(11)
α, deg	90	87.408(1)
β, deg	95.247(2)	88.050(1)
γ, deg	90	84.023(1)
V, Å^3	1596.5(3)	5434.3(5)
Z	2	4
D_{calcd}, g cm^{-3}	1.760	1.517
μ, mm^{-1}	1.509	1.061
no. of measd rflns	10 461 ($2.1 \leq \theta \leq 28.5°$)	44 437 ($2.6 \leq \theta \leq 30.1°$)
no. of unique rflns	3696 ($R_{int} = 0.0302$)	18 474 ($R_{int} = 0.0698$)
min, max transmissn factor	0.737, 0.910	0.7012, 0.8158
no. of data/restraints/params	3328/0/193	12 892/0/1188
GOF (all data)^a	1.098	1.061
R1(F) ($F^2 \geq 2\sigma(F^2)$)^b	0.0431	0.0711
wR2(F^2) (all data)^c	0.1154	0.1435

[a] GOF = $(\sum[w(F_o^2 - F_c^2)^2]/(n - p))^{1/2}$, where n and p are the number of data and parameters. [b] R1(F) = $\sum||F_o| - |F_c||/\sum|F_o|$. [c] wR2($F^2$) = $(\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2])^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ and $P = [\max(0, F_o^2) + 2F_c^2]/3$.

under vaccum. Yield: 0.086 g (70%). Anal. Calcd for $C_{34}H_{60}O_8P_2S_2Rh_2Zr$: C, 40.04; H, 5.93; S, 6.29. Found: C, 38.28; H, 4.79. MS (FAB$^+$, CH_2Cl_2, *m/z*): 1019 (M$^+$, 22%), 962 (M$^+$ − 2CO, 15%), 838 (M$^+$ − 2CO − P(OMe)$_3$, 90%). IR (toluene, cm^{-1}): ν(CO) 1978 (m), 1963 (s, br). ^{31}P{^{1}H} NMR (C_6D_6, 293 K): rotamer *trans*-**11a**, δ 139.7 (AA′XX′ spin system, $^1J_{Rh-P} = 273$ Hz, $^3J_{P-P} = 3$ Hz, $^2J_{Rh-P} = -1.3$ Hz, $^1J_{Rh-Rh} = 17$ Hz); rotamer *cis*-**11a**, δ 140.2 (d, $^1J_{Rh-P} = 272$ Hz); rotamers *trans*-**11b** and *cis*-**11b**, δ 140.3 (d, $^1J_{Rh-P} = 272$ Hz), 139.5 (d, $^1J_{Rh-P} = 270$ Hz), 139.4 (d, $^1J_{Rh-P} = 272$), 138.2 (d, $^1J_{Rh-P} = 271$ Hz).

[Cp$^{tt}_2$Zr(μ_3-S)$_2${Rh(CO)(P(OPh)$_3$)}$_2$] (12). To a solution of [Cp$^{tt}_2$Zr(μ_3-S)$_2${Rh(CO)$_2$}$_2$] (0.048 g, 0.058 mmol) in toluene (5 mL) was slowly added a solution of P(OPh)$_3$ (31 μL, 0.116 mmol) in toluene (4 mL) to give a green solution upon evolution of carbon monoxide. Workup as above gave the compound as an apple green microcrystalline solid that was filtered, washed with *n*-hexane, and dried under vaccum. Yield: 0.052 g (64%). Anal. Calcd for $C_{64}H_{72}O_8P_2S_2Rh_2Zr$: C, 55.21; H, 5.21; S, 4.61. Found: C, 55.02; H, 5.43; S, 4.42. MS (FAB$^+$, CH_2Cl_2, *m/z*): 1390 (M$^+$, 27%), 1024 (M$^+$ − 2CO − P(OPh)$_3$, 94%), 931 (M$^+$ − 2CO − P(OPh)$_3$ − OPh, 100%). IR (toluene, cm^{-1}): ν(CO) 1995 (s, br), 1981 (m, br). ^{31}P{^{1}H} NMR (C_6D_6, 293 K): rotamer *trans*-**12a**, δ 118.6 (AA′XX′ spin system, $^1J_{Rh-P} = 296$ Hz, $^3J_{P-P} = 3$ Hz, $^2J_{Rh-P} = -1.5$ Hz, $^1J_{Rh-Rh} = 21$ Hz); rotamer *trans*-**12b**, δ 119.36 and 119.28 ppm (ABXY, spin system, $^1J_{Rh-P} = 296$ Hz, $^3J_{P-P} = 8$ Hz, $^2J_{Rh-P} = -8.4$ Hz, $^1J_{Rh-Rh} = 24$ Hz).

Structural Determination of Complexes 6 and 9. Single crystals for the X-ray diffraction studies were grown by slow diffusion of *n*-hexane into concentrated solutions of the complexes in dichloromethane (−20 °C) (**9**) or dichloromethane/acetonitrile (**6**) in the freezer. A summary of crystal data, data collection, and refinement parameters for the structural analysis is given in Table 4. Green (**6**) and black crystals (**9**) were glued to glass fibers and mounted on Bruker SMART APEX and Bruker AXS-SMART diffractometers, respectively. Both instruments were equipped with CCD area detectors, and data were collected using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) and low-temperature equipment (100 K for **6** and 150 K for **9**). Cell constants for **6** were obtained from the least-squares refinement of three-dimensional centroids of 3383 reflections in the range $4.6 \leq 2\theta \leq 56.4°$ and from 150 reflections in the region $4.6 \leq 2\theta \leq 38°$ for **9**. Data were measured through the use of CCD recording of ω rotation frames (0.3° each). All data were corrected for Lorentz and polarization effects. Absorption correction for **6** was applied by using the SADABS routine[44] and the DIFABS strategy[45] for **9**. Both were integrated with the Bruker SAINT program.[46]

Structures were solved by Patterson (**6**) or direct methods (**9**). Both structures were completed by subsequent difference Fourier techniques and refined by full-matrix least squares on F^2 (SHELXL-97)[47] with initial isotropic thermal parameters. One solvate water molecule per dinuclear complex was observed in **6**. Two crystallographically independent molecules and two solvent molecules (CH_2Cl_2) were detected for **9**. Anisotropic thermal parameters were used in the last cycles of refinement for all non-hydrogen atoms in **6**, except for the oxygen of the water molecule and for all non-hydrogen atoms in **9**, except carbon atoms involved in a disordered phenyl group and those atoms of the solvent molecule. A model of rotational disorder based on two alternative positions was assumed for the disordered phenyl group of **9**. Two "CCl_2" moieties with complementary occupancy factors (0.54(1) and 0.46(1)) were also included to account for the disordered solvent molecule. Hydrogen atoms were included in calculated positions in both **6** and **9** and refined with positional and thermal parameters riding on carbon atoms. Atomic scattering factors were used as implemented in SHELXL-97.[47]

Acknowledgment. We wish to thank the Dirección General de Enseñanza Superior (DGES) and Diputación General de Aragón (DGA) for financial support (Projects PB88-0641 and P051/2000, respectively). Fellowships from the Ministerio de Educación y Cultura (M.A.F.H.-G.), Diputación General de Aragón (I.T.D.), and Programa CYTED (A.B.R.) are gratefully acknowledged.

Supporting Information Available: Tables of X-ray crystallographic data for complexes **6** and **9**; these data are also available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0209576

---

[44] Blessing, R. H. *Acta Crystallogr., Sect, A* **1995**, *51*, 33.

[45] Walker, N.; Stuart, D. *Acta Crystallogr., Sect, A* **1983**, *39*, 158.

[46] SAINT+, version 6.01; Bruker AXS, Inc., Madison, WI, 2000, and SAINT, version 4.0.

[47] Sheldrick, G. M. SHELXL-97: Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.