Figure 2. X-Band ESR spectra of [(triphos)Rh{CH(COOMe)-CH_2(COOMe)}]$^+$ in CH_2Cl_2 at 100 K (a) and at 298 K (b).

three-line resolution in each perpendicular absorption is assigned to interaction with the basal phosphorus atoms ($A \cong 18$ G). The spectrum at 298 K consists of a doublet of doublets with $\langle g \rangle = 2.070$ ($\langle g_{calcd} \rangle = 2.072$). The large value of $\langle A_{P_{apical}} \rangle$ (234.7 G) is still present whereas the apparent coupling to only one basal phosphorus ($\langle A \rangle = 18$ G) is consistent with a remarkable distortion in the coordination polyhedron.[6]

One-electron reduction of the Rh(II) succinyl restores the starting cis hydride (alkene) 2. Reasonably, a Rh(I) succinyl complex forms which transforms to 2 via β-H elimination as soon as generated at the electrode surface.

In the attempt of understanding why oxidation of 2 induces olefin insertion, the following additional experimental pieces of information are noteworthy. (i) The related cis hydride(ethylene) complex [(triphos)RhH(C_2H_4)][7] (5) undergoes ethylene insertion across the Rh-H bond by reaction with either excess ethylene to form [(triphos)-Rh(C_2H_5)(C_2H_4)][7] or 1 atm of CO to give [(triphos)Rh-(C_2H_5)(CO)].[7] In contrast, ethylene insertion is not promoted by chemical or electrochemical oxidation. (ii) Compound 2 in THF solution is stable when treated with excess DMFU, ethylene, or CO even at reflux temperature. On the other hand, 2 (THF, room temperature) proves an efficient catalyst for the isomerization of the cis olefin dimethyl maleate (DMMA) to the trans isomer DMFU, thus indicating the occurrence of olefin insertion/β-H elimination. In the light of these results, it is evident that the CO_2Me substituents on the alkene play a key role in promoting the hydride (DMFU) → succinyl conversion. In particular, the ester C=O groups can electronically and coordinatively saturate rhodium during the oxidation process. Obviously, this is most important to stabilize both the dicationic (3 or 3a) and monocationic (4) species.

Registry No. 1, 100333-94-6; 2, 117469-71-3; 3, 117469-73-5; 3a, 117469-75-7; 4, 117469-74-6.

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(7) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Fujiwara, Y.; Jintoku, T.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* 1988, 299.

Stepwise Reaction of CS_2 with the Nickelacyclopentene Complexes $(R_3P)_2Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)$. Influence of the Ancillary Phosphine Ligands

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Summary: The reaction of the nickelacyclopentene complexes $(R_3P)_2Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)$ ($PR_3 = PMe_3$, **1a**; $(R_3P)_2 = Me_2PCH_2CH_2PMe_2$, dmpe, **1b**) with CS_2 follows a different course depending on the nature of phosphine coligands. Compound **1a** provides (3 equiv of CS_2, 20 °C) the known $Ni(C_2S_4PMe_3)PMe_3$ (**2**) and the dithiolactone $S{=}C(S)CH_2CMe_2\text{-}o\text{-}C_6H_4$ (**3**) through the intermediacy of the Ni(0) species $(Me_3P)_2Ni(S{=}C(S)CH_2CMe_2\text{-}o\text{-}C_6H_4)$ (**4a**) which contains **3** as an η^2-C=S ligand and can be isolated from **1a** and CS_2 (1 equiv, -90 °C). Complex **1b** reacts with CS_2 to provide first a 1,1-dithiolate derivative, $(dmpe)Ni(SSCCH_2CMe_2\text{-}o\text{-}C_6H_4)$ (**5**), and then the trithiocarbonate $(dmpe)Ni(S_2CS)$ (**6**) along with the thioketone $S{=}CCH_2CMe_2\text{-}o\text{-}C_6H_4$ (**7**). These two reactions can be respectively thought of as the insertion of CS_2 into both Ni-C bonds of **1b** and as the reductive disproportionation of two molecules of CS_2. In the latter process, the thiocarbonyl group becomes incorporated into the thioketone functionality of **7**.

The reactivity of transition-metal complexes toward small, unsaturated molecules continues to arouse much attention.[2] We have recently shown that the nickelacyclopentene complex $(Me_3P)_2Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)$ (**1a**) reacts with unsaturated C1 molecules such as CO, CO_2, and CH_2O, with formation of products resulting from insertion of the unsaturated molecule into either the nickel alkyl or the nickel aryl carbon bonds.[3] Only in the case of CO does reductive elimination (to Ni(0) and the corresponding ketone) follow insertion. In this paper we wish to present additional studies concerning the related reactions of **1a** and its dmpe analogue **1b**, $(dmpe)Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)$ (dmpe = $Me_2PCH_2CH_2PMe_2$), with CS_2. As shown in Scheme I, these correspond to a novel type of reactivity and have led to a variety of organic and inorganic species.[4]

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(1) (a) Universidad de Sevilla. (b) Universidad Complutense de Madrid.

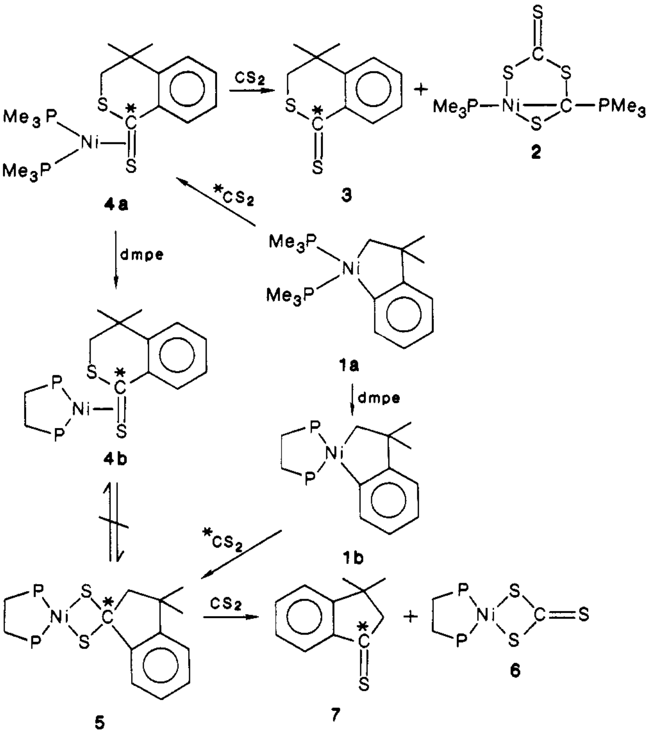
(2) See, for example: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(3) Carmona, E.; Palma, P.; Paneque, M.; Poveda, M. L.; Gutiérrez-Puebla, E.; Monge, A. *J. Am. Chem. Soc.* 1986, *108*, 6424.

(4) Satisfactory analytical data (C, H, S; Pascher, Bonn and Analytical Service, University of Sevilla) have been obtained for all new compounds (see Table IV, supplementary material).

0276-7333/88/2307-2577$01.50/0

Scheme I



The room-temperature addition of CS_2 (3–4 equiv) to a diethyl ether solution of **1a** produces a red-brown microcrystalline solid and a dark-red solution. Spectroscopic data for the former allows its identification as the complex $Ni(C_2S_4PMe_3)PMe_3$ (**2**) previously characterized by Ibers and co-workers,[5] while from the red solution dark red crystals of the dithiolactone **3** can be isolated in very high yields. Formation of **2**, a Ni(II) derivative containing a head-to-tail CS_2 dimer, suggests the intermediacy of a Ni(0) species, which could result from a reductive elimination reaction, following CS_2 insertion. To confirm this assumption and with the aim of isolating a nickeladithiolactone complex, $(Me_3P)_2\overline{Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4C(X)X)}$ (X = S), analogous to the CO_2 insertion product (X = O),[3] complex **1a** was reacted with 1 equiv of CS_2, at −90 °C. An amber, crystalline material, identified as the η^2-C=S dithiolactone species $(Me_3P)_2\overline{Ni(S{=}C(S)CH_2CMe_2\text{-}o\text{-}C_6H_4)}$ (**4a**) is instead obtained,[6] although, as anticipated, it reacts with excess of CS_2 with formation of **2** and **3**. It seems therefore likely that the reaction proceeds through the above-mentioned CS_2 insertion product which spontaneously undergoes reductive elimination with concomitant intramolecular C–S bond formation to yield the observed dithiolactone complex **4a**. The structure of this complex has been unequivocally established by an X-ray study, whose results are shown in Figure 1, as an ORTEP perspective view.[7] The triatomic NiCS linkage exhibits a bonding situation which is comparable with that found in η^2-thioketone[8,9] and -thioketene[10] complexes. For instance, the coordinated C–S bond length of 1.77 (1) Å in **4a** is essentially identical with the values of 1.769 (2) and 1.762 (4) Å, found respectively in molybdenum[8] and vanadium[9] thioketone compounds.

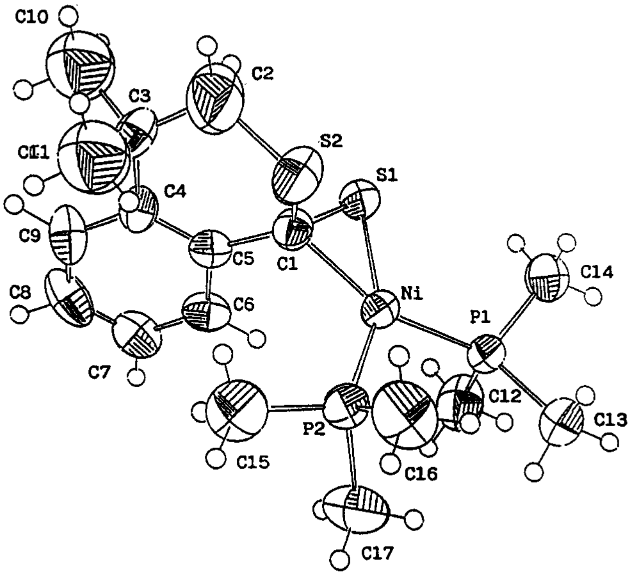


Figure 1. ORTEP diagram for **4a** and atom-labeling scheme. Important bond distances (Å) and angles (deg) are as follows: Ni–P1 = 2.180 (3), Ni–P2 = 2.146 (3), Ni–C1 = 1.939 (11), Ni–S1 = 2.129 (3), C1–S1 = 1.765 (11), C1–S2 = 1.784 (9); P1–Ni–P2 = 105.7 (1), C1–Ni–S1 = 51.1 (3), Ni–C1–S1 = 70.0 (4), Ni–C1–S2 = 110.6 (5), S1–C1–S2 = 116.5 (5).

While addition of dmpe to solutions of **4a** produces displacement of the coordinated PMe_3 ligands and formation of the related dmpe derivative $(dmpe)\overline{Ni(S{=}C(S)CH_2CMe_2\text{-}o\text{-}C_6H_4)}$ (**4b**), the reaction of the dmpe complex **1b** with CS_2 follows a different course to that described above for **1a**. Thus, **1b** slowly reacts with 1 equiv of CS_2, with formation of an orange crystalline species identified[11] as the 1,1-dithiolate $(dmpe)Ni(SS\overline{CCH_2CMe_2\text{-}o\text{-}C_6H_4})$ (**5**) which, in a formal sense, can be considered as the insertion product of CS_2 into both

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(5) Mason, M. G.; Swepston, P. N.; Ibers, J. A. *Inorg. Chem.* **1983**, *22*, 411.

(6) To a stirred solution of **1a** in Et_2O (0.34 g, ca. 1 mmol, 20 mL) cooled at −90 °C was added 1 mL of a 1 M CS_2 solution in toluene. The reaction mixture was allowed to warm to room temperature, and the solvent was removed under vacuum. The residue was extracted with 10 mL of a 1:1 Et_2O–hexanes mixture, filtered, concentrated, and cooled at −20 °C overnight. **4a** (0.33 g, 80% yield) were obtained in this way. Selected spectroscopic data for **4a**: ^1H NMR (200 MHz, CD_2Cl_2, 22 °C) δ 3.32 and 2.46 (d, diastereotopic CH_2 protons, $^2J_{HH}$ = 7.1 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 22 °C) δ −9.5 and −10.7 (b s, PMe_3 ligands); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22 °C) δ 16.5 (d, P_AMe_3, $^1J_{CP}$ = 24.3 Hz), 18.1 (d, P_BMe_3, $^1J_{CP}$ = 22.8 Hz), 30.8 (s, CMe_2), 35.3 (s, CMe_2), 45.8 (s, CH_2), 65.8 (s, >C=S), 123.8, 124.5, 126.6, 130.7 (s, CH Ar), 143.9, 149.5 (s, quaternary aromatic carbons).

(7) Crystal data for $\mathbf{4a}\cdot{}^1/_2Et_2O$ ($C_{17}H_{30}S_2P_2Ni\cdot{}^1/_2C_4H_{10}O$): M_r 464.5, monoclinic, space group $P2_1/n$; a = 19.847 (8) Å, b = 9.343 (2) Å, c = 13.939 (3) Å, β = 109.79 (3)°, V = 2432 (1) Å^3, Z = 4, D_{calcd} = 1.27 g/cm^3, μ(Mo Kα) = 11.01 cm^{-1}, T = 295 K, $F(000)$ = 972, R_F = 0.071 for 2765 observed reflections.

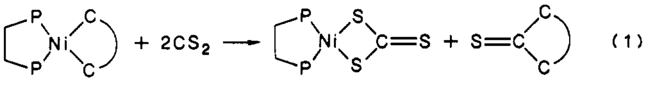
(8) Alper, H.; Silvawe, N. D.; Birnbaum, G.; Ahmed, F. *J. Am. Chem. Soc.* **1979**, *101*, 6582.

(9) Pasquali, M.; Leoni, P.; Floriani, C.; Chiesi-Villa, A.; Guastini, G. *Inorg. Chem.* **1983**, *22*, 841.

(10) Werner, H.; Kolb, O.; Schubert, U.; Ackermann, K. *Chem. Ber.* **1985**, *118*, 873.

(11) To a stirred solution of **1b** (0.34 g, ca. 1 mmol) in acetone (20 mL) 1 mL of a 1 M solution of CS_2 in toluene was added at room temperature, the reaction mixture was filtered, the solvent removed under vacuum, and the resulting solid extracted with 20 mL of acetone. The solution was filtered, concentrated, and cooled at −20 °C overnight to provide orange crystals of **5** in ca. 75% yield. Representative spectroscopic data for **5**: ^1H NMR (200 MHz, CD_2Cl_2, 22 °C) δ 1.33 (s, CMe_2), 1.40 (pseudoquartet, P–Me, $J_{HP_{app}}$ = 5.5 Hz), 1.70 (pseudodoublet, P–CH_2, $J_{HP_{app}}$ = 15.1 Hz), 2.50 (s, S_2CCH_2; $^{13}CS_2$-enriched sample; d, $^2J_{HC}$ = 4.5 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 22 °C) δ 42.9 (s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22 °C) δ 12.6 (pq, P–Me, $J_{CP_{app}}$ = 8.7 Hz), 27.4 (pt, P–CH_2, $J_{CP_{app}}$ = 23.9 Hz), 30.6 (s, CMe_2), 42.8 (s, CMe_2), 66.2 (s, S_2C<), 67.0 (s, CH_2; $^{13}CS_2$-enriched sample; d, $^1J_{CC}$ = 35.6 Hz), 121.4, 124.8, 126.7 (s, 1:1:2 intensity ratio, C–H Ar), 148.8 (s, C_{Ar}–CMe_2), 153.4 (s, C_{Ar}–CS_2; $^{13}CS_2$-enriched sample; d, $^1J_{CC}$ = 45.1 Hz). The formulation proposed for this complex has been confirmed by X-ray studies: Gutiérrez-Puebla, E., unpublished results. For related 1,1-dithiolates see ref 10 and: Alper, H.; Chan, A. S. K. *J. Am. Chem. Soc.* **1973**, *95*, 4905. Alper, H.; Chan, A. S. K. *Inorg. Chem.* **1974**, *13*, 232.

nickel–carbon bonds. If **1b** is reacted with an excess of CS_2 (ca. 3 equiv), the yellow, sparingly soluble trithiocarbonate (dmpe)Ni(S_2CS) (**6**) and the violet thioketone $S{=}\overline{CCH_2CMe_2\text{-}o\text{-}C_6H_4}$ (**7**) are instead obtained, as shown in eq 1. Note that, formally, this reaction corresponds to a



(1)

1b **6** **7**

reductive disproportionation of carbon disulfide ($2CS_2 + 2e \rightleftharpoons CS + CS_3^{2-}$), with the thiocarbonyl unit becoming incorporated into the thioketone functionality. Interestingly, the reaction takes place *without change* in the oxidation state of the metal center, the required two electrons being provided (always in a formal sense) by the organic ligand in complex **1b**.

As expected, compounds **6** and **7** are also formed when **5** is reacted with 1 equiv of CS_2 (Scheme I). Isotopic labeling studies, carried out with **5*** (ca. 50% enriched in $^{13}CS_2$) show that the carbon atom of the CS_3^{2-} ligand derives exclusively from the added CS_2. While more than one pathway can be envisaged for this reaction, an attractive proposal is to invoke the intermediacy of an elusive dithiirane,[12] $R_1R_2\overline{CSS}$,[13] which, by sulfur transfer to CS_2, would provide the observed "disproportionation" products **6** and **7**. Studies are under way to clarify these and other aspects of the CS_2 reactions herein reported.

Acknowledgment. Generous support (to E.C. and E.G.-P.) by the Comisiōn Asesora de Investigaciōn Cientifica y Tēcnica (CAICYT) is very gratefully acknowledged. J.C. acknowledges a research grant from the Ministerio de Educaciōn y Ciencia (MEC).

Supplementary Material Available: Tables of bond distances and angles, final fractional coordinates, and thermal parameters for **4a** (Tables I–III) and microanalytical data for compounds **3**–**7** (Table IV) (7 pages); a listing of structure factors (29 pages). Ordering information is given on any current masthead page.

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[12] Stable dithiiranes are apparently unknown. See Zoller, U. *Heterocyclic compounds*; Hassner, A., Ed.; Wiley: London, 1983; Vol. 42, p 608.

[13] Note that dithiiranes are formally the products of reductive elimination of 1,1-dithiolate liggands, or, conversely, that 1,1-dithiolate complexes are the products of oxidative addition of a dithiirane to a transition-metal center.

Activation of C–H Bond of Ethylene by Dinuclear Tetrahydride-Bridged Ruthenium Complex

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Summary: Tetrahydride complex (η^5-C_5Me_5)Ru(μ-H)$_4$Ru(η^5-C_5Me_5) (**1**) reacts with ethylene to give a novel dinuclear divinyl complex, (η^5-C_5Me_5)Ru($CH_2{=}CH_2$)($CH{=}CH_2$)$_2$Ru(η^5-C_5Me_5) (**2**), via activation of a vinylic C–H bond.

Transition-metal polyhydride complexes have been shown to be of importance as the precursors of the active species for the alkane C–H activation reaction.[1] While these exists a fair body of examples of C–H bond cleavage of both alkanes and arenes with low-valent complexes of late transition metals, there are only several reported examples of intermolecular activation of vinylic C–H bond of alkenes with metal polyhydride complexes.[2]

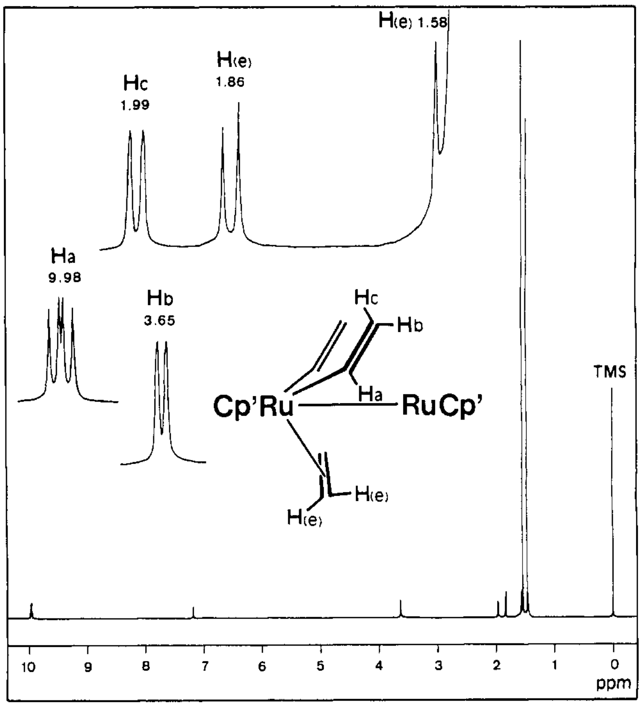
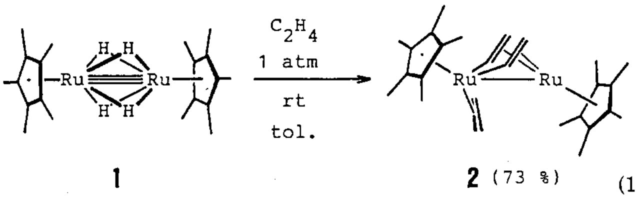


Figure 1. 500-MHz ^1H NMR spectrum of (η^5-C_5Me_5)Ru($CH_2{=}CH_2$)($CH{=}CH_2$)$_2$Ru(η^5-C_5Me_5) (**2**) in C_6D_6 at 25 °C.

Since we have reported the preparation of tetrahydride-bridged dinuclear ruthenium complex which causes a coordinatively highly unsaturated species under thermal conditions,[3] we have investigated the reaction of a number of simple olefins with the tetrahydridodiruthenium **1**. We report here a formation of a novel binuclear vinyl complex by the reaction of **1** with ethylene via a vinylic C–H activation reaction.

Treatment of the dinuclear tetrahydride-bridged complex (η^5-C_5Me_5)Ru(μ-H)$_4$Ru(η^5-C_5Me_5) (**1**) in toluene solution (20 °C) with an atmospheric pressure of ethylene for 1 day resulted in the formation of deep red powder, formulated as (η^5-C_5Me_5)Ru($CHCH_2$)$_2$(CH_2CH_2)Ru(η^5-C_5Me_5) (**2**) (eq 1). Crystallization from toluene–pentane



1 **2** (73 %) (1)

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[1] For example, see: (a) Shilov, A. E. *The Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Reidel Publishing Co.: Dordrecht, 1984. (b) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (c) Green, M. L. H.; O'Hare, D. *Pure Appl. Chem.* **1985**, *57*, 1987. (d) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41 and references cited therein.

[2] (a) Bhaduri, S.; Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Raithby, P. R.; Rehani, S.; Sheldrick, G. M.; Wong, K. *J. Chem. Soc., Dalton Trans.* **1979**, 562. (b) Keister, J. B.; Shapley, J. R. *J. Organomet. Chem.* **1975**, *85*, C29. (c) Fryzuk, M. D.; Jones, T.; Einstein, F. W. B. *Organometallics* **1984**, *3*, 185. (d) Faller, J. W.; Felkin, H. *Organometallics* **1985**, *4*, 1488. (e) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1986**, *108*, 7433, 7436. (f) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581.

[3] Suzuki, H.; Omori, H.; Lee, D. H.; Yoshida, Y.; Morooka, Y. *Organometallics*, in press.

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