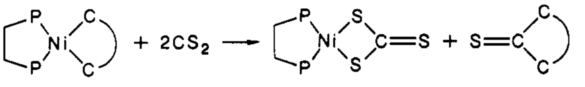
nickel–carbon bonds. If **1b** is reacted with an excess of CS_2 (ca. 3 equiv), the yellow, sparingly soluble trithiocarbonate (dmpe)Ni(S_2CS) (**6**) and the violet thioketone $S{=}\overline{CCH_2CMe_2\text{-}o\text{-}C_6H}_4$ (**7**) are instead obtained, as shown in eq 1. Note that, formally, this 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]

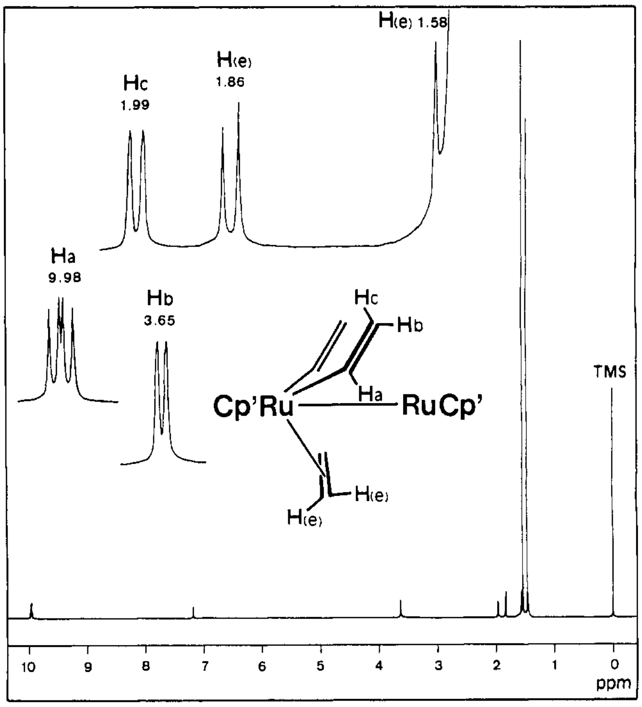
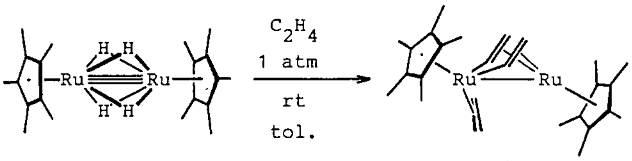


Figure 1. 500-MHz ^1H NMR spectrum of (η^5-C_5Me_5)Ru($CH_2{=}CH_2$)($CH{=}CH_2$)$_2$Ru(η^5-C_5Me_5) (**2**) in C_6D_6 at 25 °C.

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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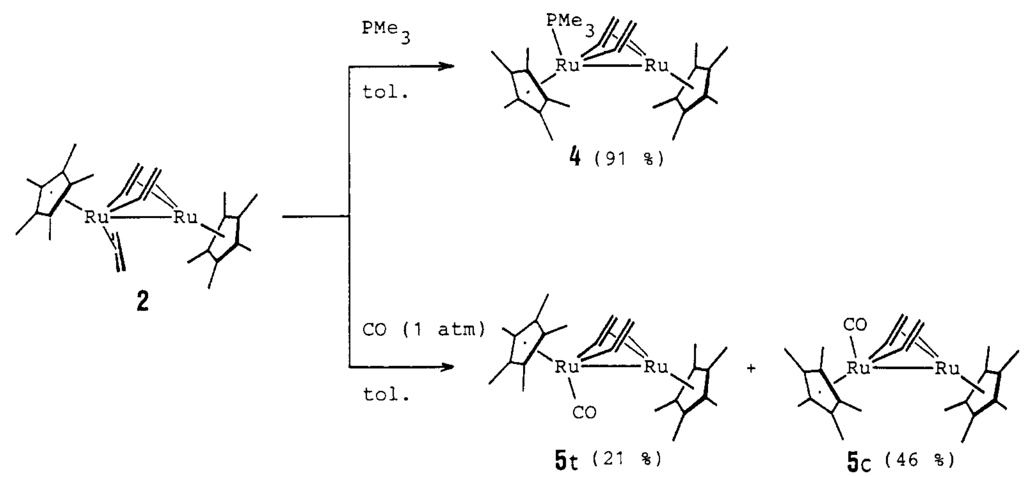
Scheme I



afforded analytically pure **2** as deep red plates in a 73% yield based on the tetrahydride **1**. The complex has been characterized by ^{1}H and ^{13}C NMR, FD mass spectrometry, infrared spectroscopy, and elemental analysis.[4]

The ^{1}H NMR spectrum of **2** revealed the coordination of an ethylene molecule and two magnetically equivalent vinyl groups (Figure 1). Characteristic resonances for the bridging vinyl ligands were observed at δ 1.99, 3.65, and 9.98 as an ABX pattern. The ethylene protons were observed as two nonequivalent doublets at δ 1.58 and 1.86. The ^{13}C resonance signals for the vinyl groups are observed at δ 188.5 (J_{CH} = 157 Hz) and 54.5 (J_{CH} = 146 and 160 Hz), and these values lie well within those for the bi- or trinuclear vinyl complexes of middle and late transition metals.[5] The signal for the coordinated ethylene appeared at δ 48.9 (J_{CH} = 151 and 157 Hz). A molecular structure determination of **2** by X-ray diffraction study showed that two C_5Me_5 ligands occupied the trans positions with respect to Ru–Ru bond (Figure 2).[6]

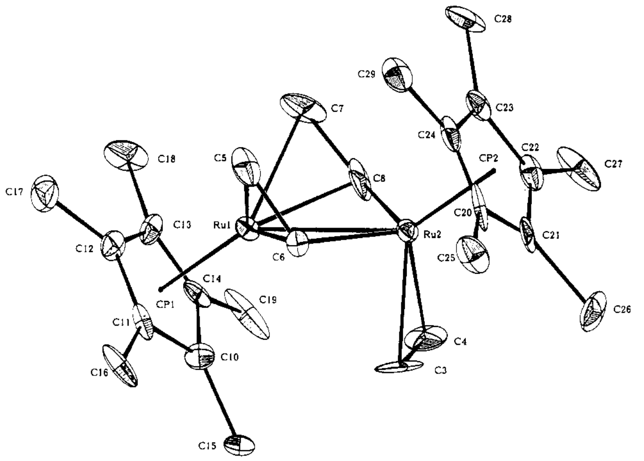


Figure 2. Molecular structure of $(\eta^5\text{-}C_5Me_5)Ru(CH_2{=}CH_2)(CH{=}CH_2)_2Ru(\eta^5\text{-}C_5Me_5)$ (**2**). CP indicates the centroid of a C_5Me_5 ring.

The reaction of tetradeuteride complex $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}D)_4Ru(\eta^5\text{-}C_5Me_5)$ (**1**-d_4) with an atmospheric pressure of ethylene in toluene afforded **2** and ethane. It is noteworthy that the isotopomers of ethane detected in this reaction were C_2H_6 and C_2H_5D[7] and that the formation of $C_2H_4D_2$ was not observed at all. This strongly suggests that the initial step of C–H activation of ethylene is the dissociation of H_2 from **1** to form a coordinatively unsaturated intermediate, $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_2Ru(\eta^5\text{-}C_5Me_5)$.

When the reaction of **1** with ethylene in toluene-d_8 was monitored by means of ^{1}H and ^{13}C NMR spectroscopy, resonance signals due to hydridovinylruthenium complex $(\eta^5\text{-}C_5Me_5)Ru(C_2H_4)(\mu\text{-}H)(CHCH_2)Ru(\eta^5\text{-}C_5Me_5)$ (**3**) were observed after the solution was left standing for 0.5 h at −78 °C.[8] When the reaction mixture is warmed to room temperature, a progressive increase in the intensity of resonance signals of **2** and a significant decrease in the intensity of **3** were observed. After 1 h at room temperature, **3** was completely converted to the vinyl complex **2**.

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[4] **2**: IR (KBr) 3046, 2965, 2934, 2896, 1447, 1374, 1235, 1175, 1022, 776, 485 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.49 (s, 15 H), 1.57 (s, 15 H), 1.58 (d, J = 11.0 Hz, 2 H), 1.86 (d, J = 11.0 Hz, 2 H), 1.99 (dd, J_{AC} = 9.2 Hz and J_{BC} = 1.2 Hz, 2 H, $RuCH_A{=}CH_BH_C$), 3.65 (dd, J_{AB} = 6.7 Hz and J_{BC} = 1.2 Hz, 2 H, $RuCH_A{=}CH_BH_C$), 9.98 (dd, J_{AB} = 6.7 Hz and J_{AC} = 9.2 Hz, 2 H, $RuCH_A{=}CH_BH_C$); ^{13}C NMR (C_6D_6) δ 9.7 (q, J_{CH} = 126.1 Hz, $C_5\mathit{Me}_5$), 10.3 (q, J_{CH} = 126.8 Hz, $C_5\mathit{Me}_5$), 48.9 (dd, J_{CH} = 157.0 and 151.2 Hz, $\mathit{C}H_2\mathit{C}H_2$), 54.5 (dd, J_{CH} = 146.1 and 160.1 Hz, $RuCH{=}\mathit{C}H_2$), 91.1 (s, C_5Me_5), 95.4 (s, C_5Me_5), 188.5 (d, J_{CH} = 156.9 Hz, $Ru\mathit{C}H{=}CH_2$); mp 159 °C dec. Anal. Calcd for $C_{26}H_{40}Ru_2$: C, 56.29; H, 7.27. Found: C, 56.02; H, 7.33. Field-desorption mass spectrum was recorded on a Hitachi M-80 high-resolution mass spectrometer, and intensities of the obtained isotopic peaks for $C_{26}H_{40}Ru_2$ agreed with the calculated values within the experimental error. The mass spectral data are available in the supplementary material.

[5] (a) Ting, C.; Messerle, L. *J. Am. Chem. Soc.* **1987**, *109*, 6506. (b) Gerlach, R. F.; Duffy, N. D.; Curtis, M. D. *Organometallics* **1983**, *2*, 1172. (c) Beck, J. A.; Knox, S. A. R.; Riding, G. H.; Taylor, G. M.; Winter, M. J. *J. Organomet. Chem.* **1980**, *202*, C49. (d) Ahmed, K. J.; Chisholm, M. H.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 989. (e) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1984**, *106*, 644. (f) King, R. B.; Treichel, P. M.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961**, *83*, 3600. (g) Dyke, A. F.; Knox, S. A. R.; Morris, M. J.; Naish, P. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1417. (h) Liu, J.-C.; Boyar, E.; Deeming, A. J.; Donovan-Mtunzi, S. *J. Chem. Soc., Chem. Commun.* **1984**, 1182. (i) Fryzuk, M. D.; Jones, T.; Einstein, F. W. B. *Organometallics* **1984**, *3*, 185.

[6] The divinyl complex **2** crystallized from toluene–pentane in the triclinic system, space group $P\bar{1}$, with a = 11.316 (6) Å, b = 14.343 (8) Å, c = 8.412 (5) Å, α = 94.93 (5)°, β = 117.03 (4)°, γ = 94.49 (5)°, and Z = 2. Intensity data were collected at 25 °C on a Rigaku AFC-5 diffractometer with graphite-monochromated Mo Kα radiation in the $2° < 2\theta < 60°$ range. The intensities of the collected data were somewhat weak, and the quality of the data was not sufficiently good because the shape of the crystal was a thin plate. The structure was solved by Patterson method and refined by a full-matrix least-squares technique. The current R value is 0.128 for 3820 independent reflections with $F_o > 5\sigma(F_o)$.

[7] The values of 2.2–2.8 for the molar ratio of isotopomers, C_2H_6/C_2H_5D, were obtained by means of FD-mass spectrometry.

[8] **3**: ^{1}H NMR (tol-d_8–THF-d_8, −78 °C) δ −16.37 (s, 1 H, Ru–H), 0.69 (m, 2 H, CH_2CH_2), 0.99 (m, 2 H, CH_2CH_2), 1.52 (s, 15 H), 1.75 (s, 15 H), 3.89 (d, J_{AB} = 8.4 Hz, $RuCH_A{=}CH_BH_C$), 7.36 (dd, J_{AB} = 8.4 Hz and J_{AC} = 12.0 Hz, $RuCH_A{=}CH_BH_C$); H_C obscured by resonance of C_5Me_5 at 1.75 ppm; ^{13}C NMR (tol-d_8–THF-d_8, −78 °C) δ 9.7 (q, J_{CH} = 127.2 Hz, $C_5\mathit{Me}_5$), 10.4 (q, J_{CH} = 125.2 Hz, $C_5\mathit{Me}_5$), 34.2 (t, J_{CH} = 155.0 Hz, $\mathit{C}H_2CH_2$), 34.5 (t, J_{CH} = 161.2 Hz, $CH_2\mathit{C}H_2$), 53.5 (dd, J_{CH} = 154.0 and 153.0 Hz, $RuCH{=}\mathit{C}H_2$), 93.0 (s, C_5Me_5), 95.0 (s, C_5Me_5), 189.4 (d, J_{CH} = 140.0 Hz, $Ru\mathit{C}H{=}CH_2$).

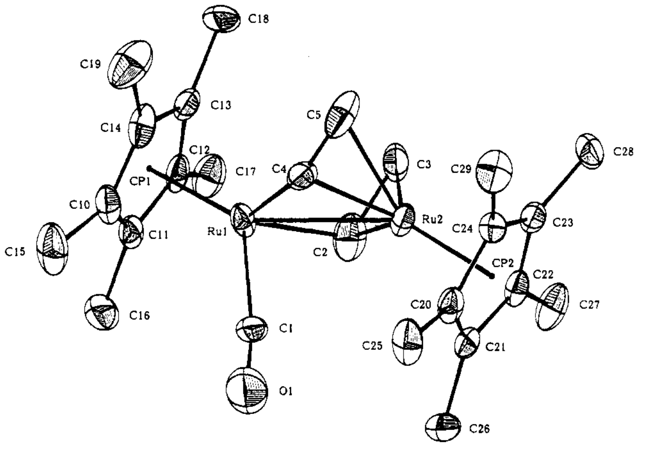

Figure 3. Molecular structure of *trans*-(η^5-C_5Me_5)Ru(CO)($CH{=}CH_2)_2$Ru(η^5-C_5Me_5) (**5t**). CP indicates the centroid of a C_5Me_5 ring.

Stirring the solution of **2** in pentane under an atmosphere of hydrogen (1 atm) for 20 h afforded the tetrahydride complex **1** and ethane. No C_2- and C_4-hydrocarbons other than ethane were detected in the volatiles by mass spectrometry.

Evidence of ligand exchange reaction between the coordinated and free ethylene molecules could not be obtained in the magnetization transfer experiment of **2** in the presence of ca. 10-fold excess amount of ethylene in C_6D_6 at 25 °C. However, the ethylene ligand in **2** was smoothly replaced by trimethylphosphine or carbon monoxide (Scheme I).

Treatment of **2** in toluene with 1.2 equiv of trimethylphosphine for 2 h at 50 °C leads to (η^5-C_5Me_5)Ru($CHCH_2)_2$(PMe_3)Ru(η^5-C_5Me_5) (**4**) in 91% yield with inversion of the stereochemistry at one of the ruthenium centers.[9] Preliminary results of the X-ray diffraction study of complex **4** show the cis configuration of the C_5Me_5 ligands with respect to the Ru–Ru bond.

Reaction of **2** with carbon monoxide (1 atm) in toluene afforded *trans*-(η^5-C_5Me_5)Ru($CHCH_2)_2$(CO)Ru(η^5-C_5Me_5) (**5t**) and its cis isomer **5c** in the 21 and 46% yields, respectively, after purification by column chromatography on Al_2O_3 (Merck Art. 1097).[10] A single-crystal X-ray investigation of **5t** confirmed the proposed structure (Figure 3).[11] A further reactivity study of **2** and a mechanistic study pertaining to the formation of **2** will be reported in due course.

Acknowledgment. Support from the Ministry of Education, Science and Culture of the Japanese Government (No. 63550618) is gratefully acknowledged.

Supplementary Material Available: Tables of mass spectral data, atomic parameters, and bond distances and angles for compounds **2** and **5t** (36 pages); listings of calculated and observed structure factors for compounds **2** and **5t** (49 pages). Ordering information is given on any current masthead page.

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[9] **4**: IR (KBr) 2942, 2896, 2863, 1475, 1417, 1376, 1275, 1259, 1027, 942, 925, 844, 482 cm^{-1}; ^1H NMR (C_6D_6) δ 0.86 (d, J_{PH} = 8.0 Hz, 9 H, P*Me*$_3$), 1.74 (s, 15 H), 1.76 (s, 15 H), 2.03 (dd, J_{AC} = 10.8 Hz and J_{PC} = 2.7 Hz, 2 H, $RuCH_A{=}CH_BH_C$), 3.49 (dd, J_{AB} = 6.8 Hz and J_{PB} = 6.7 Hz, 2 H, $RuCH_A{=}CH_BH_C$), 9.31 (ddd, J_{AB} = 6.8 Hz, J_{AC} = 10.8 Hz and J_{PA} = 4.0 Hz, 2 H, $RuCH_A{=}CH_BH_C$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 10.7 (s, C_5*Me*$_5$), 10.9 (s, C_5*Me*$_5$), 23.0 (d, J_{CP} = 5.2 Hz, P*Me*$_3$), 54.4 (d, J_{CP} = 13.0 Hz, RuCH=*C*H$_2$), 90.1 (s, *C*$_5$Me$_5$), 95.8 (d, J_{CP} = 2.3 Hz, *C*$_5$Me$_5$), 174.2 (d, J_{CP} = 5.2 Hz); $^{31}P\{^1H\}$ NMR (C_6D_6, external PPh_3) δ 11.0; mp 178 °C dec. Anal. Calcd for $C_{27}H_{45}PRu_2$: C, 53.81; H, 7.53. Found: C, 53.48; H, 7.91.

[10] **5t**: IR (KBr) 2949, 2941, 1921, 1223, 1022, 904, 759, 479 cm^{-1}; ^1H NMR (C_6D_6) δ 1.62 (s, 15 H), 1.74 (s, 15 H), 1.93 (dd, J_{AC} = 9.4 Hz and J_{BC} = 1.6 Hz, 2 H, $RuCH_A{=}CH_BH_C$), 3.55 (dd, J_{AB} = 6.3 Hz and J_{BC} = 1.6 Hz, 2 H, $RuCH_A{=}CH_BH_C$), 9.50 (dd, J_{AB} = 6.3 Hz and J_{AC} = 9.4 Hz, 2 H, $RuCH_A{=}CH_BH_C$); ^{13}C NMR (C_6D_6) δ 9.6 (q, J_{CH} = 127.2 Hz, C_5*Me*$_5$), 11.1 (q, J_{CH} = 127.0 Hz, C_5*Me*$_5$), 50.0 (dd, J_{CH} = 159.1 and 147.8 Hz, RuCH=*C*H$_2$), 92.1 (s, *C*$_5$Me$_5$), 98.9 (s, *C*$_5$Me$_5$), 177.3 (d, J_{CH} = 162.0 Hz, Ru*C*H=CH$_2$), 202.9 (s, *C*O); mp 172.0 °C dec. Anal. Calcd for $C_{25}H_{36}ORu_2$: C, 54.13; H, 6.54. Found: C, 54.17; H, 6.71. **5c**: IR (KBr) 2941, 2891, 1926, 1237, 1021, 914, 767, 479 cm^{-1}; ^1H NMR (C_6D_6) δ 1.60 (s, 15 H), 1.68 (s, 15 H), 2.22 (d, J_{AC} = 9.2 Hz, 2 H, $RuCH_A{=}CH_BH_C$), 3.58 (d, J_{AB} = 6.4 Hz, 2 H, $RuCH_A{=}CH_BH_C$), 9.04 (dd, J_{AB} = 6.4 Hz and J_{AC} = 9.2 Hz, 2 H, $RuCH_A{=}CH_BH_C$); ^{13}C NMR (C_6D_6) δ 10.1 (q, J_{CH} = 127.0 Hz, C_5*Me*$_5$), 10.3 (q, J_{CH} = 127.2 Hz, C_5*Me*$_5$), 56.0 (dd, J_{CH} = 143.1 and 160.9 Hz, RuCH=*C*H$_2$), 91.4 (s, *C*$_5$Me$_5$), 98.9 (s, *C*$_5$Me$_5$), 176.6 (d, J_{CH} = 152.2 Hz, Ru*C*H=CH$_2$), 207.4 (s, CO); mp 225.0 °C dec. Anal. Calcd for $C_{25}H_{36}ORu_2$: C, 54.13; H, 6.54. Found: C, 53.74; H, 6.60.

[11] Complex **5t** crystallized from toluene–pentane in the monoclinic system, space group $P2_1/n$, with a = 14.668 (5) Å, b = 16.644 (3) Å, c = 10.087 (4) Å, β = 106.24 (3)°, and Z = 4. Data were collected at 25 °C on a Rigaku AFC-5 diffractometer with graphite-monochromated Mo Kα radiation in the 2° < 2θ < 60° range. The structure was solved by Patterson method and refined by a full-matrix least-squares techniques. The current R value is 0.112 for 4853 independent reflections with $F_o > 5\sigma(F_o)$, and the accuracy of the carbon positions is somewhat low because the intensity data are dominated by the heavy-atom contributions.

Diastereotopic Group Selectivity in the Deprotonation of (η-Arene)$Cr(CO)_3$ Complexes

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Summary: Highly diastereospecific syntheses (de ≥ 94%) of (η-arene)$Cr(CO)_3$ complexes are effected via the group-selective deprotonation of complexes bearing a chiral benzylic directing group. The major diastereomers prepared by this technique are the opposite of those formed in face-selective diastereospecific complexation reactions.

The appeal of transition-metal π-arene reagents in organic synthesis stems from the diverse modifications of arene chemistry exhibited in the metal complexes.[1] Applications of (η-arene)$Cr(CO)_3$ reagents to synthetic problems have included the selective nucleophilic aromatic substitution of arene molecules (deoxyfrenolicin),[1b,2a] regiocontrolled spirocyclization reactions (acorenone-b),[1b,2b] the preparation of highly substituted cyclohexadienone and dihydronaphthalene molecules (daunomycinone and rabelomycin),[2c,d] and the regiospecific substitution of tetralin derivatives at benzylic sites (hydroxycalamene toxins).[2e,f] Recent studies have also demonstrated the potential utility

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[1] (a) Semmelhack, M. F.; Clark, G. R.; Garcia, J. L.; Harrison, J. J.; Trebtaranonth, Y.; Wulff, W.; Yamashita, A. *Tetrahedron*, **1981**, *37*, 3957. (b) Semmelhack, M. F. *Pure Appl. Chem.*, **1981**, *53*, 2379. (c) Uemura, M.; Take, K.; Isobe, K.; Minami, T.; Hoyashi, T. *Tetrahedron* **1985**, *41*, 5771. (d) Kundig, E. P. *Pure Appl. Chem.*, **1985**, *57*, 1855.

[2] (a) Semmelhack, M. F.; Bisaha, J.; Czarny, M. *J. Am. Chem. Soc.*, **1979**, *101*, 768. (b) Semmelhack, M. F.; Yamashita, A. *J. Am. Chem. Soc.*, **1980**, *102*, 5926. (c) Uemura, M.; Take, K.; Hayashi, T. *J. Chem. Soc., Chem. Commun.*, 1983, 858. (d) Kundig, E. P.; Desobry, V.; Simmons, D. P. *J. Am. Chem. Soc.*, **1983**, *105*, 6962. (e) Uemura, M.; Isobe, K.; Hayashi, Y. *Tetrahedron Lett.*, **1985**, *26*, 767. (f) Uemura, M.; Isobe, K.; Hayashi, Y. *Chem. Lett.*, **1985**, 91.

0276-7333/88/2307-2581$01.50/0