Selective dehydrogenation of alcohols and diols catalyzed by a dihydrido iridium PCP pincer complex

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Abstract: The PCP pincer complex, $IrH_2\{C_6H_3-2,6-(CH_2P-t-Bu_2)_2\}$ (1) catalyzes the transfer dehydrogenation of primary and secondary alcohols. Dehydrogenation occurs across the C—O bond rather than the C—C bonds and the corresponding aldehydes or ketones are obtained as the sole products arising from the dehydrogenation reactions. Methanol is an exception to this pattern of reactivity and undergoes only stoichiometric dehydrogenation with 1 to give the carbonyl complex, $Ir(CO)\{C_6H_3-2,6-(CH_2P-t-Bu_2)_2\}$ (2). The products are obtained in nearly quantitative yields when the reactions are carried out in toluene solutions. Under the same conditions, 2,5-hexanediol is converted to the annulated product, 3-methyl-2-cyclopenten-1-one which has been isolated in 91% yield in a preparative scale reaction.

Key words: alcohol, dehydrogenation, ketones, iridium pincer complex, annulation.

Résumé : Le complexe PCP en forme de pince, $IrH_2[C_6H_3-2,6-(CH_2P-t-Bu_2)_2]$ (1) catalyse la réaction de déshydrogénation par transfert des alcools primaires et secondaires. La déshydrogénation se fait à travers la liaison C—O plutôt qu'à travers les liaisons C—C et on n'obtient que les aldéhydes et les cétones comme seuls produits de ces réactions de déshydrogénation. Le méthanol est une exception à ce mode de réactivité et il ne subit qu'une déshydrogénation stoechiométrique avec 1 pour conduire à la formation d'un complexe de carbonyle, $Ir(CO){C_6H_3-2,6-(CH_2P-t-Bu_2)_2}$ (2). Lorsqu'on effectue les réactions en solution dans le toluène, les produits sont obtenus en rendements pratiquement quantitatifs. Dans les mêmes conditions, l'hexane-2,5-diol est transformé en produit cyclique, la 3-méthylcyclopent-2én-1-one qui a été isolée avec un rendement de 91% au cours d'une réaction à l'échelle préparative.

Mots clés : alcool; déshydrogénation, cétones, complexe de l'iridium en forme de pince, annellation.

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Introduction

Ketones and aldehydes are most commonly prepared through the oxidation of alcohols (1). The large scale commercial production of acetone and 2-butanone is accomplished through aerobic dehydrogenation of alcohols using heterogenous catalysts such as copper chromite and silver (2). The high (>250°C) temperatures that are required for these processes, however, limits their application to production of only the simplest ketones. A remarkable homogeneous catalyst for the aerobic oxidation of alcohols has been discovered by James and co-workers (3) that operates at ambient temperature but proceeds at unpractical (1.5 turn-

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This paper is dedicated to Professor Brian James on the occasion of his 65th birthday, in recognition of his inspirational pioneering spirit.

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overs/day) rates. Stoichiometric methods have been developed for the selective oxidation of alcohols to a variety of sensitive ketones and aldehvdes. However, there are increasing environmental concerns about the highly toxic reagents employed in methods such as Moffatt (DMSO, DCC, and phosphoric acid), and Swern (oxalyl chloride) oxidations (1). Alternatively, the conversion of alcohols to ketones and aldehydes can be accomplished under mild conditions through transfer dehydrogenation. Oppenaurer oxidation, in which hydrogen is transferred from an alcohol to a ketone acceptor in the presence of a base (most commonly aluminum tert-butoxide in nearly stoichiometric amounts), has been widely employed in organic synthesis (1, 4). Several transition-metal complexes have been shown to catalyze the transfer of hydrogen from alcohols to olefins (5), acetylenes (6), or aldehydes and ketones (7, 8) acceptors. Other complexes have been found to catalyze "acceptor-less" dehydrogenation of alcohols (9, 10). Catalytic hydrogen transfer systems have been utilized in organic synthesis for the reduction of oxo-steriods to hydroxy-steriods (8) and its mircroreverse (10). More recently, enantioselective versions of this reaction have been developed for asymmetric synthesis (8d-f).

The iridium PCP pincer complex $IrH_2\{C_6H_3-2,6-(CH_2P-t-Bu_2)_2\}$ (1) has been found to be an efficient and robust catalyst for the transfer dehydrogenation of alkanes (11, 12),

Table 1. Crystallographic	data for	$Ir(CO) \{C_6H_3-2, 6-(CH_2P-t-$
$Bu_2)_2$ (2).		

Formula	$C_{25}H_{43}OIrP_2$
Formula weight	613.73
T (K)	293(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
Crystal dimensions (mm)	$0.4 \times 0.4 \times 0.3$
<i>a</i> (Å)	15.443(4)
<i>b</i> (Å)	11.619(3)
c (Å)	30.608(8)
α (deg)	90
β (deg)	93.22
γ (deg)	90
V (Å ³)	5483(3)
Ζ	8
$\mu (cm^{-1})$	49.99
Transmission coeff. min, max	0.389, 1.000
λ (Å) (Mo K α radiation)	0.71073
2θ range (deg)	3–45
Independent reflections	7143
Unique data with $I >> 2((I)$	5290
Parameter refined	526
Goodness-of-fit ^a	0.986
ρ calcd. (g cm ⁻³)	1.487
Scan type	ω
R^b (%)	3.78
$R_{\rm w}^{\rm c}$ (%)	8.87

^{*a*}GOF = $[w\sigma(|F_{o}| - |F_{c}|)^{2}/(N_{o} - N_{v})]^{1/2}$.

 ${}^{b}R = \sigma |(F_{\rm o}| - |F_{\rm c}|/\sigma|F_{\rm o}|.$

 ${}^{c}R_{w} = [w\sigma(|F_{o}| - |F_{c}|)^{2}/\sigma wF_{o}^{2}]^{1/2}.$

ethers (13), alkyl arenes (13), and amines (14). Thus it was of interest to examine the reactivity of 1 towards alcohols. We have found that 1 catalyzes the selective transfer dehydrogenation of primary and secondary alcohols to aldehydes and ketones in very high yields. We have also found that 1 catalyzes the unusual dehydrogenation and (or) annulation of 2,5-hexanediol to 3-methyl-cyclopenten-1-one. The results of these studies are reported herein.

Experimental

All manipulations were carried out using standard Schlenk and glovebox techniques under purified argon. Solvents were degassed and dried using standard procedures. The alcohols were purchased from Aldrich Chemicals Co. and used without further purification. The complex $IrH_2\{C_6H_3-2,6-(CH_2P-t-Bu_2)_2\}$ (1) was synthesized by the literature methods (12). The ¹H NMR spectra were recorded on a Varian Unity Inova 400 spectrometer. Chemical shifts are reported in ppm down field of TMS using the solvent as internal standard (CDCl₃, 7.26 or cyclohexane- d_{12} , 1.38). ¹³C and ³¹P NMR spectra were recorded with complete proton decoupling and are reported in ppm down field of TMS with solvent as internal standard (CDCl₃, 77.0 or cyclohexane- d_{12} , 26.43) and external 85% H₃PO₄, respectively. Infrared spectra were recorded in a PerkinElmer Paragon FT IR spectrometer as Nujol mulls in NaCl plates. Gas chromatographic analyses were performed with a Hewlett-Packard 5890 instrument with a HP 5980A flame ionization detector and HP-1 capillary column (25.0 m). Gas chromatographic– mass spectral analyses were carried out using a HP 5890 Series II instrument with an 5971A mass selective detector and HP-1 capillary column (25.0 m).

Catalytic reactions

Solutions of the substrates (0.26 mmol), tbe (0.20 mL, 1.53 mmol), and 4 mL of toluene were charged with 1 (22 mg, 0.037 mmol) in sealed Schlenk tubes in a Vacuum Atmospheres glovebox under argon. The tubes were then fully immersed in a constant temperature bath at 200°C for the prescribed reaction times. After this time the tubes are allowed to cool down to room temperature. The products were identified by GC–MS analysis upon comparison to purchased samples of the authentic compounds. Product yields were calculated from the ratio of the integrated intensities of signals produced by the products and those of the toluene solvent after weighting the data by a predetermined relative molar response factor.

The attempted acceptor-less dehydrogenation reactions were carried out with mesitylene solutions of the substrates (0.26 mmol) and **1** (22 mg, 0.037 mmol) that were refluxed while passing a stream of argon above the condensor. Gas chromatographic analysis of the reaction mixtures following 72 h of rigorous reflux showed no traces of dehydrogenated products.

Preparative scale synthesis of 3-methyl-2-cyclopenten-1one

A solution of the 2.5-hexanediol (1.0 mL, 81 mmol), the (2.2 mL, 17 mmol), and 4 mL of toluene was charged with 1 (100 mg, 0.17 mmol) in a sealed Schlenk tube in a Vacuum Atmospheres glovebox under argon. The tube was then fully immersed in a constant temperature bath at 200°C for 78 h. After this time, the reaction mixture was cooled to room temperature and concentrated to ~1.4 mL. The product was then separated by column chromatography (Davisil (100-200 mesh silica gel) by eluting first with pentane and then with acetone. The product fraction was collected and concentrated under vacuum. The isolated product (yield: 0.73 mL, 91%) was identified as 3-methyl-2-cyclopenten-1-one by MS and NMR (¹H and ¹³C) analysis upon comparison to an authentic sample. MS (m/z): $[M]^+$ 96, $[M-CH_3]^+$ 81. ¹H NMR (400.00 MHz, CDCl₃) δ: 5.91 (m, 1H, HC-2), 2.55 (m, 2H, H_2 C-5), 2.38 (m, 2H, H_2 C-4), 2.10 (s, 3H, CH_3). ¹³C NMR (100.60 MHz, CDCl₃) δ: 210.15 (s, C=O), 178.82 (s, C-3), 130.62 (s, C-2), 35.66 (s, C-5), 32.97 (s, C-4), 19.30 $(s, CH_3).$

Synthesis of $Ir(CO)\{C_6H_3-2, 6-(CH_2P-t-Bu_2)_2\}$ (2)

A pentane (5 mL) solution of **1** (20 mg, 0.034 mmol) was treated with *tert*-butylethylene (66 μ L, 0.51 mmol) under 1 atm (1 atm = 101.325 kPa) of argon at 25°C. After 1 h of reaction, the resulting red-purple solution was treated with degassed methanol (0.1 mL, 5.6 mmol). Removal of the solvent in vacuo yields **2** as a deep yellow-orange solid. Yield: 19 mg, 90%. ¹H NMR (400.00 MHz, cyclohexane- d_{12}) &: 6.93 (d, $J_{\text{HH}} = 7.3$ Hz, 2H, *m*-H), 6.67 (t, $J_{\text{HH}} = 7.3$ Hz, 1H, *p*-H), 3.42 (vt, $J_{\text{HH}} = 3.0$ Hz, 4H, CH₂), 1.28 (vt, $J_{\text{PH}} =$



Table 2. Dehydrogenation of alcohols using $IrH_2\{C_6H_3-2,6-(CH_2P-t-Bu_2)_2\}$ (1).^{*a*}

"Reaction conditions: alcohol (0.26 mmol), the (1.53 mmol), 4 mL of benzene, and 1 (22 mg, 0.037 mmol) at 200 $^\circ$ C for 18 h.

^bYields based on GC analysis.

Traces of aldehyde were detected in the starting material; as a result, the performance of the catalyst was considerably reduced.

7.3 Hz, 36H, C(CH₃)₃). ¹³C NMR (100.60 MHz, cyclohexane- d_{12}) & 197.6 (s, Ir-C-O), 168.8 (s, C-1), 155.3 (vt, $J_{PC} =$ 12.0 Hz, o-C), 125.9 (s, p-C), 120.3 (vt, $J_{PC} =$ 9.1 Hz, m-C), 39.6 (vt, $J_{PC} =$ 13.9 Hz, CH₂P), 36.5 (vt, $J_{PC} =$ 10.7 Hz, C(CH₃)₃), 30.1 (s, C(CH₃)₃). ³¹P NMR (161.90 MHz, cyclohexane- d_{12}) & 82.8 (s). IR (KBr) (cm⁻¹): v_{IrCO} = 1913 (s). Anal. calcd. for C₂₅H₄₃OP₂Ir (613.77) (%): C 48.92, H 7.06; found: C 48.96, H 7.01.

Molecular structure determination of (2)

Yellow-orange crystals of **2** that were suitable for X-ray diffraction were obtained from slow evaporation of a pentane solution of the complex. Centering and data collection were performed with a Nicolet P3 diffractometer, graphite monochromator ($\lambda = 0.71073$ Å, Mo K α) at room temperature using a crystal that was mounted on a glass fiber with epoxy. The unit cell was determined from the angular

Fig. 1. Thermal ellipsoid (50% probablity) drawing of $Ir(CO){C_6H_3-2,6-(CH_2P-t-Bu_2)_2}$ (2). Hydrogen atoms have been omitted for clarity.



coordinates of 25 reflections with 2θ values between 15 and 30° . The diffractometer autoindexing routine found a monoclinic unit cell, which was confirmed by axial photographs.

Three check reflections, monitored every 100 reflections, showed no significant decay. The data were processed using SHELXTL program package (15), and an absorption correction was applied based upon y-scans of five reflections. Since the unit cell is triclinic, the space group P2(1)/n was assumed. The iridium was located by Patterson methods and the remainder of the structure was easily developed via a few cycles of least-squares refinement and difference Fourier maps. The unit cell was found to contain two symmetryindependent molecules of 2. Hydrogen atoms were input at calculated positions, and allowed to ride on the atoms to which they are attached. Two group of thermal parameters were refined for hydrogen atoms, one each for methylene and methyl protons. The final cycle of refinement was carried out on all non-zero data using SHELXL-97 (6) and anisotropic thermal parameters for all non-hydrogen atoms. Crystal data and relevant information are summarized in Table 1.

Results

The catalytic activity of 1 was initially screened using solutions consisting of the saturated alcohol, and the hydrogen acceptor, *tert*-butylethylene (tbe). The orange solutions were sealed in tubes under argon and fully immersed in an oil bath at 200°C for 18 h. The solutions became red upon heating and gradually change color to vellow-orange during the reaction period. Gas chromatographic analysis of the reaction mixtures showed the substrates were converted to the corresponding dehydrogenated compounds with greater than 99% selectivity. However, only ≈1% yields were obtained in preliminary experiments with the neat reaction mixture even upon longer reaction times and increased catalyst loadings. This finding was not unanticipated as dehydrogenation reactions catalyzed by 1 have generally been found to be inhibited at low concentrations of the unsaturated products (11-14, 16). Apparently deactivation of the active catalyst through a coordinative interaction with the carbonyl groups prevents the occurrence of the slower process of catalytic dehydrogenation of aliphatic groups. In support of this hypothesis, 2-hexanone was found to be unreactive with 1 under the conditions employed for the dehydrogenation of the alcohols.

To obtain high yields, it was necessary to dilute the reaction mixtures. A similar strategy has been used to achieve high yields in the catalytic dehydrogenation of secondary amines to imines by 1 (14). Table 2 summarizes the results of the dehydrogenation experiments in which toluene solutions of the alcohols, 1, and the were heated for 3 days at 200° C. The products were characterized by GC–MS analysis of the reaction mixtures. Excellent selectivities and yields were uniformly obtained without regio-restriction on the alcohol functionality. No traces of dehydrogenationated products were detected in acceptor-less experiments in which mesitylene solutions of alcohols and 1 were refluxed while passing a stream of argon above the condensor.

The dehydrogenation of 2,5-hexanediol produced an unexpected result. A single product arises upon heating dilute toluene solutions of the diol, 1, and the for 3 days at 200°C. MS and NMR analysis showed the product to be the cyclic ketone, 3-methyl-2-cyclopenten-1-one. This product can be understood to arise upon dehydrogenation across both of the C-O bonds to produce the hexadione followed by an internal aldol reaction and subsequent dehydrogenation as in the final step of a Robinson annulation reaction (17). We are unaware of any previous reports of the catalytic dehydrogenation of diols resulting in the formation of cyclic unsaturated ketones. To probe the possible synthetic utility of this type of reaction, the dehydrogenation of 2,5hexanediol was carried out on a preparative scale. Starting with 1.00 mL (81 mmol) of the diol, we were able to isolate 0.73 mL (74 mmol, 91% yield) of 3-methyl-2-cyclopenten-1-one upon work-up using silica gel column chromatography.

does The pincer complex not catalyze the dehydrogenation of methanol to formaldehyde but instead undergoes a stoichiometric reaction with methanol to yield the carbonyl compound $Ir(CO)\{C_6H_3-2,6-(CH_2P-t-Bu_2)_2\}$ (2). The presence of the carbonyl ligand of 2 is clearly indicated by the observation of a signal at 198.23 ppm in its ¹³C NMR spectrum and strong absorption at 1911.8 cm⁻¹ in the IR spectrum of the complex. Although carbonyl complexes commonly result upon the reaction of late transition-metal complexes with alcohols (for example see ref. 18; 19) it is surprising to find this partitioning in the reactivity of 1. A dichotomy was previously observed similar for [Ru₂Cl₃(PMePh₂)₆]Cl which reacts with KOH in isopropanol

Molecule 1		Molecule 2	
Bond lengths			
Ir(1)— $C(1A)$	2.102(8)	Ir(2)—C(1B)	2.090(9)
Ir(1)—C(25A)	1.873(10)	Ir(2)—C(25B)	1.852(12)
Ir(1)— $P(1A)$	2.298(2)	Ir(2)—P(1B)	2.304(2)
Ir(1)— $P(2A)$	2.291(2)	Ir(2)—P(2B)	2.298(2)
C(25A)—O(1A)	1.167(10)	C(25B)—O(1B)	1.127(12)
Bond angles			
C(1A)-Ir(1)-P(2A)	81.800(2)	C(1B)-Ir(2)-P(2B)	82.300(3)
C(1A)-Ir(1)-P(1A)	82.900(2)	C(1B)-Ir(2)-P(1B)	82.400(3)
P(2A)-Ir(1)-P(1A)	164.510(8)	P(2B)-Ir(2)-P(1B)	163.080(9)
C(25A)-Ir(1)-C(1A)	178.100(3)	C(25B)-Ir(2)-C(1B)	179.400(4)
C(25A)-Ir(1)-P(2A)	97.700(3)	C(25B)-Ir(2)-P(2B)	98.300(3)
C(25A)-Ir(1)-P(1A)	97.700(3)	C(25B)-Ir(2)-P(1B)	97.100(3)
O(1A)-C(25A)-Ir(1)	176.800(8)	O(1B)-C(25B)-Ir(2)	175.600(12)

Table 3. Selected bond distances (Å) and angles (°) for $Ir(CO)\{C_6H_3-2,6-(CH_2P-t-Bu_2)_2\}$ (2).

solution to give $[cis-Ru_2Cl_3(PMePh_2)_4]$ but yields $RuH_2(CO)(PMePh_2)_3$ when the reaction is carried out in ethanol (19).

The molecular structure of **2** was determined through a single crystal X-ray diffraction study.² The structure consists of two molecules of **2** in the asymmetric unit. A thermal ellipsoid drawing of one of the molecules with atomic number scheme of the obtained structure is presented in Fig. 1. Selected bond angles and distances are listed in Table 3.

A distorted square-planar coordination geometry can be recognized about the iridium consisting of the tridentate PCP pincer and carbonyl ligands. While the vector between the metalated carbon in the aromatic ring and the carbonyl ligand O(1A)-C(25A)-Ir(1) is a nearly ideal 176.800(8)°, the vector between the two phosphorus atoms (P(2A)-Ir(1)-P(1A), 164.510(8)°), is much more distorted due to the geometric constraints imposed upon establishing the chelating interaction of the PCP ligand. The Ir-P and Ir-metalated C distances are comparable to those observed in similar PCP pincer complexes (12, 20, 21).

Discussion

A plausible mechanism for the catalytic reaction is depicted in Scheme 1.

Alcohols apparently undergo O-H oxidative addition with the 14-electron complex arising upon dehydrogention of **1** by the to give intermediate alkoxy hydride complexes. In support of this hypothesis, the dehydrogenation of **1** in the presence of water produces the analogous hydroxy hydride complex IrH(OH)({C₆H₃-2,6-(CH₂P-*t*-Bu₂)₂}, that has been characterized spectroscopically and through a single crystal X-ray structure determination (22). The pincer alkoxide complexes would be expected to undergo the C-H β -elimination reaction that have generally been observed for metal alkoxide complexes (23) to produce η^2 -aldehyde or ketone



complexes. Dissociation of the dehydrogenated product then regenerates 1 and completes the catalytic sequence.

The alternate reaction pathway observed in the case of methanol can be rationalized in terms of the differing reactives of formyl and acyl complexes. As illustrated in Scheme 2, such intermediates could quite plausibly result from C-H oxidative addition of aldehydes in either: (*i*) an intermolecular process involving the 14-electron intermediate in the catalytic sequence; (*ii*) or an intramolecular process involving a 16-electron η^2 -aldehyde species arising upon reductive elimination of H₂ from the 18-electron, η^2 -aldehyde, dihydride intermediate in the catalytic sequence. Hydride elimination from a formyl ligand to generate a hydrido carbonyl complex is well known to be much more facile than the corresponding alkyl deinsertion from an acyl

²Copies of material on deposit (tables of crystal data, thermal parameters, bond distances, bond angles, and atomic coordinates for $Ir(CO)\{C_6H_3-2,6-(CH_2P-t-Bu_2)_2\})$ may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically). Some of this material has also been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Scheme 2.



intermediate (24). Thus while all aldehydes are likely to undergo C-H oxidative addition in this catalytic system, subsequent deinsertion to form a carbonyl is competitive with the mircoreverse, reductive elimination of aldehyde only in the case of the formyl intermediate.

Conclusions

In summary, the PCP pincer complex **1** catalyzes the highly selective dehydrogenation of a variety of primary and secondary alcohols to aldehydes and ketones, respectively. The problem of product inhibition of the catalyst is eliminated by carrying out the dehydrogenation reactions in dilute solutions and dehydrogenated products have been uniformly obtained in nearly quantititative yields. The unusual dehydrogenation and (or) annulation of 2,5-hexanediol to 3-methyl-2-cyclopenten-1-one has been carried out on the preparative scale suggesting that the catalytic conversion of diols to cyclic enones could be utilized in organic synthesis.

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References

- M.B. Smith and J. March. Advanced organic chemistry. Reactions, mechanisms, and structure. 5th ed. John Wiley and Sons, New York. 2001. Chap. 19. pp. 1514–1517.
- (a) S. Sifniades. In Ullmann's encyclopedia of industrial chemistry. 5th ed. Vol. A 1. Edited by W. Gerhartz, Y.S. Yamamoto, F.T. Campbell, R. Pfefferkorn, and J.F. Rounsaville. VCH Verlagsgesellschaft, Weinheim, Germany. 1985. pp. 84–85; (b) W. Neier. In Ullmann's encyclopedia of industrial chemistry. 5th ed. Vol. A 4. Edited by W. Gerhartz, Y.S. Yamamoto, F.T. Campbell, R. Pfefferkorn, and J.F. Rounsaville. VCH Verlagsgesellschaft, Weinheim, Germany. 1985. p. 477.
- 3. S.Y.S. Cheng, N. Rajpakse, S. J. Rettig, and B.R. James. J. Chem. Soc. Chem. Commun. 2669 (1994).
- (a) C. Djerassi. Org. React. (N.Y.), 6, 207, (1951); (b) K.G. Akamanchi and B.A. Chaudhari. Tetrahedron Lett. 38, 6925 (1997).
- (a) J. Trocha-Grimshaw and H.B. Henbest. Chem. Commun. 544, (1967); (b) Y. Sasson and J. Blum. Tetrahedron Lett. 2167 (1971); (c) Y. Sasson and G.L. Rempel. Can. J. Chem. 52, 3825 (1974); (d) H. Imai, T. Nishiguchi, and K. Fukizumi. J. Org. Chem. 39, 1622 (1974); (e) Y. Sasson and J. Blum. J. Org. Chem. 40, 1887 (1975); (f) A.S. Goldman and J. Halpern. J. Organomet. Chem. 382, 237 (1990).
- (a) J. Trocha-Grimshaw and H.B. Henbest. J. Chem. Soc. Chem. Commun. 757 (1968); (b) R. Zanella, F. Canziani, R. Ros, and M. Graziani. J. Organomet. Chem. 67, 449 (1975).

- (a) H.B. Henbest and T.R.B. Mitchell. J. Chem. Soc. C, 785 (1970); (b) V.Z. Sharf, K. Freidlin, V.N. Krutii, and G.T. Prokopenko. Kinet. Catal. 14, 518 (1973); (c) M. Gullotti, R. Ugo, and S. Colonna. J. Chem. Soc. Chem. Commun. 2652 (1971); (d) R.A.W. Johnston, A.W. Wilby, and J.D. Entwistle. Chem. Rev. 85, 129 (1985); (e) R. Noyori and H. Takaya. Acc. Chem. Res. 23, 345 (1990); (f) J.E. Bäckvall, R.L. Choudhury, and U. Karlsson. J. Chem. Soc. Chem. Commun. 473 (1991).
- (a) Y.M.Y. Haddad, H.B. Henbest, J. Husbands, and T.R.B. Mitchell. Proc. Chem. Soc. London, 361 (1964); (b) P.A. Browne and D.N. Kirk. J. Chem. Soc. C, 1653 (1969); (c) J.C. Orr, M. Mersereau, and A. Sanford. J. Chem. Soc. Chem. Commun. 162 (1970); (d) G. Zassinovich, G. Mestroni, and S. Gladiali. Chem. Rev. 92, 1051 (1992); (e) R. Noyori and S. Hashiguchi. Acc. Chem. Res. 30, 97 (1997); (f) D.A. Alonso, D. Guijarro, P. Pinho, O. Temme, and P.G. Andersson. J. Org. Chem. 63, 2749 (1998), and refs. therein.
- (a) H.B. Charman. J. Chem. Soc. B, 584 (1970); (b) A. Dobson and S.D. Robinson. Inorg. Chem. 16, 137, 1977; (c) S. Shinoda, T. Kojima, and Y. Saito. J. Mol. Catal. 18, 99 (1983).
- 10. Y. Lin, D. Ma., and X. Lu. Tetrahedron Lett. 28, 3115 (1987).
- (a) M. Gupta, C. Hagen, W.C. Kaska, R. Flesher, and C.M. Jensen, J. Chem. Soc. Chem. Commun. 2083 (1996); (b) W. Xu, G.P. Rosini, M. Gupta, C.M. Jensen, W.C. Kaska, K. Krough-Jespersen, and A.S. Goldman. J. Chem. Soc. Chem. Commun. 2273 (1997); (c) F. Liu, E.B. Pak, B. Singh, C.M. Jensen, and A.S. Goldman. J. Am. Chem. Soc. 121, 4086 (1999).
- M. Gupta, C. Hagen, W.C. Kaska, R. Cramer, and C.M. Jensen. J. Am. Chem. Soc. **119**, 840 (1997).
- M. Gupta, W.C. Kaska, and C.M. Jensen. J. Chem. Soc. Chem. Commun. 461 (1997).

- D. Morales-Morales, W. Chen, and C.M. Jensen. Paper INOR 0572 presented at the 218th American Chemical Society National Meeting, New Orleans, Louisiana. 1999.
- G.M. Sheldrick. SHELXL-97. Program for crystal structure refinement. University of Göttingen, Germany. 1997.
- 16. C.M. Jensen. J. Chem. Soc. Chem. Commun. 2443 (1999).
- 17. E.M. Jung. Tetrahedron, 32, 3 (1976).
- (a) J. Chatt, B.L. Shaw, and A.E. Field. J. Chem. Soc. 3466 (1964); (b) J.A. Osborn, F.H. Jardine, J.F. Young, and G. Wilkinson. J. Chem. Soc. A, 1711 (1966); (c) M.S. Lupin and B.L. Shaw. J. Chem. Soc. A, 741 (1968).
- R.H. Crabtree and A.J. Pearman. J. Organomet. Chem. 157, 335 (1978).
- S. Nemeh, C.M. Jensen, E. Binamira-Soriaga, and W.C. Kaska. Organometallics, 2, 1442 (1983).
- 21. D.W. Lee, W.C. Kaska, and C.M. Jensen. Organometallics, 17, 1 (1998).
- 22. D. Morales-Morales, D.W. Lee, Z. Wang, and C.M. Jensen. Organometallics, **21**, 1144 (2001).
- 23. (a) M.A. Bennett, G.B. Robertson, P.O. Whimp, and T. Yoshida. J. Am. Chem. Soc. 95, 3028 (1973); (b) D.P. Arnold, M.A. Bennett, M.S. Bilton, and G.B. Robertson. J. Chem. Soc. Chem. Commun. 111 (1982); (c) H.E. Bryndza, S.A. Kretchmar, and T.H. Tulip. J. Chem. Soc. Chem. Commun. 977 (1985); (d) H.E. Bryndza, J.C. Calabrese, M. Marsi, D.C. Roe, W. Tam, and J.E. Bercaw. J. Am. Chem. Soc. 108, 4805 (1986); (e) O. Blum and D. Milstein. J. Am. Chem. Soc. 117, 4582 (1995).
- R.H. Crabtree. The organometallic chemistry of the transition metals. 3rd ed. John Wiley and Sons, New York. 2001. Chap. 12. p. 342.