receptor, as often illustrated by the formation of stable 1:1 complexes with catecholamines.[9-11] Thus the oxygen counterpart of L (i.e., 18-crown-6) would recognize dopamine as postulated in Figure 3, wherein the reversed roles of donor-acceptor by the macrocyclic receptor models are compared.

Surprisingly, we have found that the 1,2-dioxychelate is not essential for the interaction with L, as shown by the strong association of resorcinol (1,3-dihydroxybenzene, **9**) (see Table II). However, this is in line with a property of biological catechol receptors that can often recognize resorcinols, as illustrated by some commercial adrenergic drugs bearing the resorcinol function (e.g., metaproterenol). Our catechol receptor model L (as $3H^+$ species) further recognizes an adrenergic blocking drug, dichloroisoproterenol (**10**), most likely for its 1,2-dichlorobenzene part.

Still further, the catechol receptor model L was discovered to be a useful complexing agent with drugs and some functions of drugs or biochemical reagents: tropolone (**11**) (e.g., 4-isopropyltropolone is an inhibitor of tyrosine hydroxylase),[13,14] salicylic acid (**12**) (e.g., aspirin), *p*-aminosalicylic acid (**13**), and α-picolinic acid (**14**) (e.g., fusaric acid, i.e., 5-butylpicolinic acid, is an inhibitor of dopamine β-hydroxylase).[13] Biological activities (e.g., as catecholamine-related enzyme inhibitors), medicinal applications (e.g., drug carriers)[15] or analytical applications (e.g., biochemical analysis of catecholamines and their methoxy metabolites) of L and its various derivatives are now underway in our laboratory.

Registry No. 1, 120-80-9; **1**·L, 84775-03-1; **2**, 51-61-6; **2**·L, 84775-04-2; **3**, 59-92-7; **3**·L, 84775-05-3; **4**, 51-43-4; **4**·L, 84775-06-4; **5**, 121-33-5; **5**·L, 84775-07-5; **6**, 120-14-9; **6**·L, 84775-08-6; **7**, 93-07-2; **7**·L, 84775-09-7; **8**, 54-04-6; **8**·L, 84775-10-0; **9**, 108-46-3; **9**·L, 84775-11-1; **10**, 59-61-0; **10**·L, 84775-12-2; **11**, 533-75-5; **11**·L, 84775-13-3; **12**, 69-72-7; **12**·L, 84775-14-4; **13**, 65-49-6; **13**·L, 84775-15-5; **14**, 98-98-6; **14**·L, 84775-16-6; L, 296-35-5.

(13) Nagatsu, T. "Biochemistry of Catecholamines"; University of Tokyo Press: Tokyo, 1973.

(14) We have tested with colchicine, which has both the 1,2,3-trimethoxybenzene and tropolone parts. Because of the poor reversibility of the polarogram, we could not estimate the β_L value, although the interaction was certain.

(15) We have also found that L is a good carrier of penicillins at neutral pH, which will be reported elsewhere.

Communications to the Editor

Coordination Chemistry and Catalytic Properties of Hydrido(phosphine)ruthenate Complexes

Robert Wilczynski, William A. Fordyce, and Jack Halpern*

Department of Chemistry, The University of Chicago Chicago, Illinois 60637

Received October 18, 1982

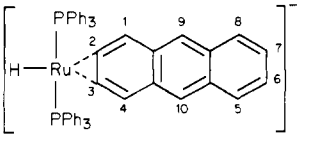
The recently synthesized anionic hydride complex $[RuH_2(PPh_3)_2(PPh_2C_6H_4)]^-$ (**1**)[1] has been reported to exhibit distinctive catalytic properties, including the ability to catalyze the selective hydrogenation of arenes, for example, of anthracene to 1,2,3,4-tetrahydroanthracene.[2] While the role of $[RuH_2(PPh_3)_2(PPh_2C_6H_4)]^-$ as the catalyst precursor was clearly demonstrated, neither the chemistry of the complex under the conditions of the catalytic reactions nor the mechanistic features of the reactions were elucidated. We report here the results of our preliminary studies directed at these themes. These studies encompass the synthesis and characterization of several new anionic ruthenium hydride complexes and the elucidation of their chemistry.

Reaction of $[RuH_2(PPh_3)_2(PPh_2C_6H_4)]^-$ with H_2. Formation of *fac*-$[RuH_3(PPh_3)_3]^-$ (2). $K[RuH_2(PPh_3)_2(PPh_2C_6H_4)]$, prepared as previously described,[1] reacted with H_2 (1 atm) in THF at 25 °C (eq 1) to form, after 24 h in ca. 85% yield, *fac*-$[RuH_3(PPh_3)_3]^-$, which was isolated as the yellow K^+ salt.[3,4] The ^1H NMR signal[3] at δ −9.53 due to the three Ru-bonded protons corresponded to a six-peak multiplet resembling that previously reported for *fac*-$[IrH_3(PPhEt_2)_3]$ and analyzed by computer simulation as an AA′A″XX′X″ pattern.[5]

$$[RuH_2(PPh_3)_2(PPh_2C_6H_4)]^- + H_2 \rightarrow \underset{\mathbf{2}}{fac\text{-}[RuH_3(PPh_3)_3]^-} \quad (1)$$

Reaction of *fac*-$[RuH_3(PPh_3)_3]^-$ with Anthracene. Formation of $[RuH(PPh_3)_2(anthracene)]^-$ (3). *fac*-$[RuH_3(PPh_3)_3]^-$ reacted with an excess of anthracene in THF to form, in quantitative yield (NMR), a new red complex, $[RuH(PPh_3)_2(anthracene)]^-$ (**3**), which was isolated as the K^+ salt.[6] The reaction (eq 2) went to completion in ca. 24 h at 65 °C. The ^1H NMR spectrum[6] of **3** resembles that previously reported for $[Fe(CO)_3(anthracene)]$[7] and is interpreted in terms of an analogous structure (**3**). A structurally related compound, $[IrH(P\text{-}i\text{-}Pr_3)_2(butadiene)]$,[8] has been characterized crystallographically.[9]

$$\underset{\mathbf{2}}{fac\text{-}[RuH_3(PPh_3)_3]^-} + 1.5\text{anthracene} \rightarrow \underset{\mathbf{3}}{[RuH(PPh_3)_2(anthracene)]^-} + 0.5(1,2,3,4\text{-tetrahydroanthracene}) + PPh_3 \quad (2)$$



3

Reaction 2 exhibited the same rate law as the isotopic exchange of **2** with D_2 (eq 3), i.e., $-d[\mathbf{2}]/dt = k_4[\mathbf{2}]$, where $k_4 = 7.6 \times 10^{-4}$ s^{-1} at 65 °C, independent of the H_2 (or anthracene) concentration. This implies that both reactions proceed through a common

(1) Pez, G. P.; Grey, R. A.; Corsi, J. *J. Am. Chem. Soc.* **1981**, *103*, 7528-7535.

(2) Grey, R. A.; Pez, G. P.; Wallo, A. *J. Am. Chem. Soc.* **1980**, *102*, 5948-5949.

(3) **2**: ^1H NMR (THF-d_8) δ −9.53 (m, 3 H), 6.70 (m, 18 H), 6.79 (m, 9 H), 7.15 (m, 18 H); $^{31}P\{^1H\}$ NMR (THF-d_8) δ 65.9 (relative to external 85% H_3PO_4; m, 3 P); IR (Nujol) 1857, and 1815 cm^{-1} (RuH); IR (THF) 1835 cm^{-1} (RuH).

(4) All the new complexes described in this communication are extremely air and water sensitive in both the solid state and solution. Compounds **5** and **6** thermally decompose in THF solution over a period of several hours.

(5) Mann, B. E.; Masters, C.; Shaw, B. L. *J. Inorg. Nucl. Chem.* **1971**, *33*, 2195-2204.

(6) **3**: ^1H NMR (THF-d_8) δ −14.1 (t, 1 H, RuH, J_{P-H} = 24 Hz), 2.43 (d, 2 H, $H_{1,4}$), 4.65 (br s, 2 H, $H_{2,3}$), 5.38 (s, 2 H, $H_{9,10}$), 6.52 (m, 4 H, $H_{5,6,7,8}$), 6.87-7.60 (m, 30 H, PPh_3 H); $^{31}P\{^1H\}$ NMR (THF-d_8) δ 69.8 (s, 2 P; splits into expected doublet upon selective decoupling from aromatic protons); IR (Nujol) 1850 cm^{-1} (m, br, RuH).

(7) Manuel, T. A. *Inorg. Chem.* **1964**, *3*, 1794-1796.

(8) Clerici, M. G.; Di Gioacchino, S.; Maspero, F.; Perrotti, M.; Zanobi, A. *J. Organomet. Chem.*, **1975**, *84*, 379-388.

(9) Del Piero, G.; Perego, G.; Cesari, M. *Gazz. Chim. Ital.* **1975**, *105*, 529-537.

0002-7863/83/1505-2066$01.50/0

$$fac\text{-}[RuH_3(PPh_3)_3]^- \xrightarrow{D_2} [RuHD_2(PPh_3)_3]^- \left(\xrightarrow{D_2} [RuD_3(PPh_3)_3]^-\right) \quad (3)$$

unimolecular rate-determining step, namely, the reductive elimination of H_2 to form the common intermediate $[RuH(PPh_3)_3]^-$ (**4**), an isomer of **1** (eq 4).

$$fac\text{-}[RuH_3(PPh_3)_3]^- \xrightarrow[-H_2]{k_4} [RuH(PPh_3)_3]^- \quad (4)$$

$$[RuH(PPh_3)_3]^- \xrightarrow[-PPh_3]{\text{anthracene}} [RuH(PPh_3)_2(\text{anthracene})]^- \quad (4a)$$

$$[RuH(PPh_3)_3]^- \xrightarrow{D_2} [RuHD_2(PPh_3)_3]^- \quad (4b)$$

4

Reaction of $[RuH(PPh_3)_2(anthracene)]^-$ with H_2. Formation of $[RuH_5(PPh_3)_2]^-$ (5). $[RuH(PPh_3)_2(anthracene)]^-$ reacted rapidly with H_2 in THF at 25 °C (eq 5) to yield $[RuH_5(PPh_3)_2]^-$

$$[RuH(PPh_3)_2(\text{anthracene})]^- + 4H_2 \rightarrow [RuH_5(PPh_3)_2]^- + \text{1,2,3,4-tetrahydroanthracene} \quad (5)$$

5

(**5**), which was isolated as the white K^+ salt.[10] The spectral data[10] are consistent with a pentagonal bipyramidal (or fluxional) structure for **5** analogous to that of the known compounds $[IrH_5(PR_3)_2]$ (R = Ph, Et, etc.).[11]

Reactions of $[RuH_5(PPh_3)_2]^-$. $[RuH_5(PPh_3)_2]^-$ reacted with a stoichiometric amount (1:2) of anthracene in THF (eq 6) to

$$[RuH_5(PPh_3)_2]^- + 2\text{anthracene} \rightarrow [RuH(PPh_3)_2(\text{anthracene})] + \text{1,2,3,4-tetrahydroanthracene} \quad (6)$$

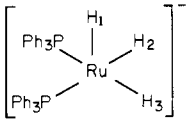
$$[RuH_5(PPh_3)_2]^- + \text{1-hexene} \rightarrow [RuH_3(PPh_3)_2]^- + \text{hexane} \quad (7)$$

6

$$[RuH_5(PPh_3)_2]^- + 5C_2H_4 \rightarrow [\overline{Ru(PPh_3)(PPh_2C_6H_4)}(C_2H_4)_2]^- + 3C_2H_6 \quad (8)$$

7

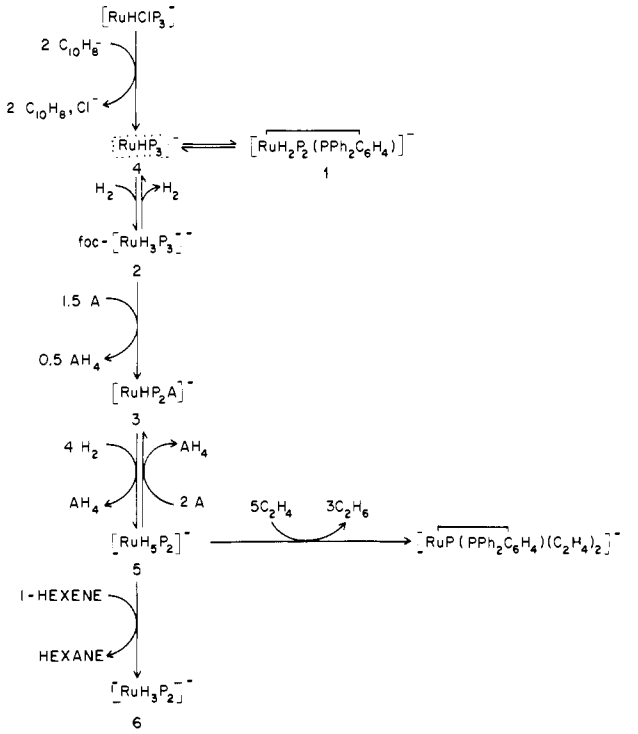
form $[RuH(PPh_3)_2(anthracene)]^-$ in quantitative yield (ca. 24 h at 25 °C, 0.5 h at 65 °C). The corresponding reaction with cyclohexadiene yielded the analogous diene adduct $[RuH(PPh_3)_2(cyclohexadiene)]^-$ together with cyclohexane and cyclohexene. Reaction of **5** with 1-hexene (eq 7) resulted in partial dehydrogenation and formation of $[RuH_3(PPh_3)_2]^-$, whose NMR spectrum is consistent with structure **6**.[12] Reaction of **5** with ethylene (eq 8) yielded a new compound whose IR and NMR spectra were consistent with the tentative formulation as the orthometalated complex $[\overline{Ru(PPh_3)(PPh_2C_6H_4)}(C_2H_4)_2]^-$ complex (**7**)[13] by comparison with the analogously prepared and structurally characterized compound $[\overline{Ir(PPh_3)(PPh_2C_6H_4)}(C_2H_4)_2]$.[8,14]



6

The chemistry of hydridoruthenate complexes that we have described is summarized in Scheme I and encompasses the synthesis and characterization of several new complexes. It is noteworthy that nearly every new anionic ruthenium complex that these studies have uncovered finds a parallel in a known (and, in most cases, structurally characterized) neutral iridium complex, $[\overline{IrH_2(PPh_3)_2(PPh_2C_6H_4)}]$,[15] *fac*-$[IrH_3(PEt_2Ph)_3]$,[5] $[IrH(P\text{-}i\text{-}Pr_3)_2(C_4H_6)]$,[8,9] $[IrH_5(PEt_2Ph)_2]$,[11] and $[\overline{Ir(PPh_3)_2(PPh_2C_6H_4)}(C_2H_4)_2]$[8,14] being direct analogues of **1**, **2**, **3**, **5**, and **7**, respectively. We also have noted limited parallels between the chemistry of such corresponding species.

Scheme I. Summary of Reaction Chemistry (P = triphenylphosphine, A = Anthracene, AH_4 = 1,2,3,4-Tetrahydroanthracene)



Catalytic Hydrogenation of Anthracene. We have confirmed that **1** serves as a catalyst or catalyst precursor for the hydrogenation of anthracene to 1,2,3,4-tetrahydroanthracene as previously reported.[2] Complexes **2**, **3**, and **5** also were found to serve as catalyst precursors for the hydrogenation of anthracene with rates that, in some cases, were initially higher than that obtained with **1** but ultimately leveled off at approximately the same rate, suggesting that they give rise to a common catalytic mechanism. In the light of the chemistry that we have described, it seems likely that, under the conditions of the reactions, the orthometalated precursor **1** is converted rapidly and irreversibly to other species (notably **3** and **5**) and so is not directly involved in the catalytic mechanism. It further seems likely that the species that are involved in the catalytic cycle contain only two phosphine ligands per Ru, as do the active catalyst precursors **3** and **5**.

The combination of reaction 5 and 6, as depicted by eq 9,

$$[RuHP_2(\text{anthracene})]^- \underset{\text{tetrahydroanthracene}\quad 2\text{anthracene}}{\overset{4H_2\quad \text{tetrahydroanthracene}}{\rightleftharpoons}} [RuH_5(PPh_3)_2]^- \quad (9)$$

corresponds to a catalytic cycle for the hydrogenation of anthracene and, thus, clearly constitutes one demonstrated mechanism for this reaction.

The determination of whether this is the only mechanism will require further kinetic studies, which now are in progress, on the overall catalytic reactions as well as on the several component steps

(10) **5**: ^1H NMR (THF-d_8) δ −7.64 (t, 5 H, $J_{P\text{-}H}$ = 15 Hz), 7.05 (br s, 18 H), 7.69 (br s, 12 H); $^{31}P\{^1H\}$ NMR (THF-d_8) δ 75.2 (s, 2 P; splits into a sextet upon selective decoupling from aromatic protons); IR (Nujol) 1750 cm^{-1} (s, br, RuH).

(11) Mann, B. E.; Masters, C.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1970**, 703.

(12) **6**: ^1H NMR (THF-d_8) δ −13.38 (tt, 1 H, H_1, $J_{P\text{-}H}$ = 21 Hz, $J_{H\text{-}H}$ = 7 Hz), −8.08 (m, 2 H, $H_{2,3}$), 6.96 (m, 18 H), 7.35 (m, 12 H); $^{31}P\{^1H\}$ NMR (THF-d_8) δ 62.6 (br s, 2 P).

(13) **7**: ^1H NMR (THF-d_8) δ 1.40 (br, 8 H, 2 C_2H_4), 6.38–7.54 (m, 29 H, PPh_3 H); $^{31}P\{^1H\}$ NMR (THF-d_8) δ −12.7 (d, 1 P, $PPh_2C_6H_4$, $J_{P\text{-}P}$ = 16 Hz), 55.6 (d, 1 P, PPh_3).

(14) Perego, G.; Del Piero, G.; Clerici, M. G.; Perrotti, E. *J. Organomet. Chem.* **1973**, *54*, C51–C52.

(15) Morandini, F.; Longato, B.; Bresadola, S. *J. Organomet. Chem.* **1977**, *132*, 291–299.

that we have identified. It also remains to be established to what extent the chemistry that we have identified is relevant to the catalysis by **1** of the hydrogenation of other (notably polar) substrates such as ketones, nitriles, and esters.[16]

Acknowledgment. This research was supported by a grant from the National Science Foundation.

Registry No. 1, 74981-90-1; **2**, 84800-50-0; **3**, 84774-77-6; **5**, 84751-07-5; **6**, 84751-08-6; **7**, 84751-09-7; [RuH(PPh$_3$)$_2$B] (B = cyclohexadiene), 84751-10-0; anthracene, 120-12-7.

(16) (a) Grey, R. A.; Pez, G. P.; Wallo, A.; Corsi, J. *J. Chem. Soc., Chem. Commun.* **1980**, 783-784. (b) Grey, R. A.; Pez, G. P.; Wallo, A. *J. Am. Chem. Soc.* **1981**, *103*, 7536-7542.

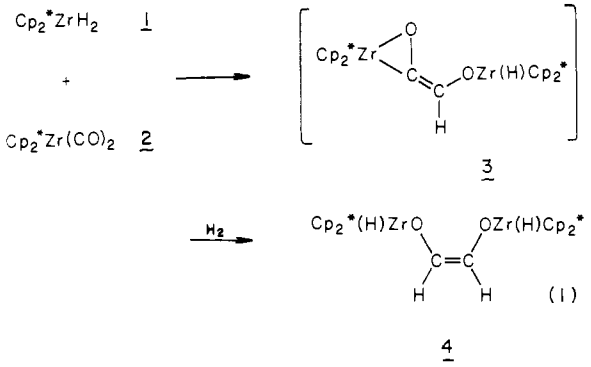
Synthesis and Structure of Ketene Complexes of Permethylzirconocene and Their Hydrogenation to Zirconium Enolate Hydrides

Eric J. Moore, Daniel A. Straus, Justine Armantrout, Bernard D. Santarsiero,[1] Robert H. Grubbs,* and John E. Bercaw*[2]

Contribution No. 6742 from the Laboratories of Chemistry California Institute of Technology Pasadena, California 91125

Received October 12, 1982

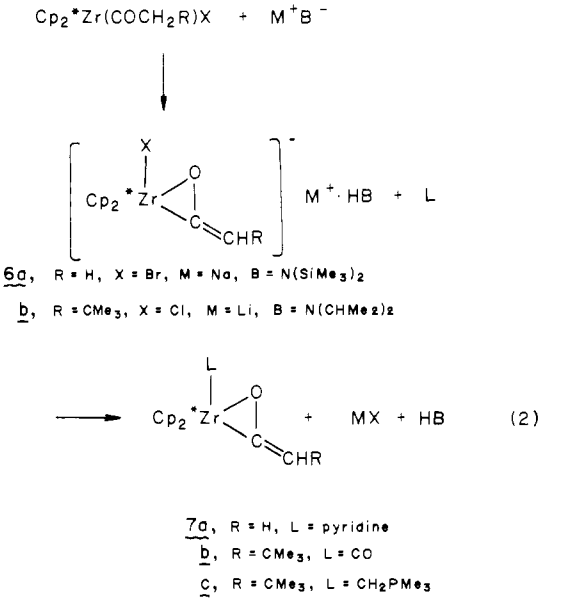
The reduction of carbon monoxide by Cp*$_2$ZrH$_2$ (**1**, Cp* = η^5-C$_5$Me$_5$) is complex and yields a variety of products depending on reaction conditions.[3] Whereas the mechanism leading to *trans*-(Cp*$_2$ZrH)$_2$(μ-OCH=CHO) from **1** and free CO is relatively well established, the steps leading to *cis*-(Cp*$_2$ZrH)$_2$(μ-OCH=CHO) (**4**) from **1**, Cp*$_2$Zr(CO)$_2$ (**2**), and H$_2$ are largely speculative. The favored scheme[3] involves initial attack of **1** at a carbonyl ligand of **2**[4] followed by carbene-carbonyl coupling affording coordinated "zirconoxy" ketene **3**, which undergoes hydrogenation to **4** (eq 1). The cis geometry of this enediolate



(1)

prod··ct was proposed to result from (i) the structure of **3** in which the bulky Cp*$_2$ZrO moieties are sterically constrained in a cis arrangement and (ii) its stereospecific hydrogenation to **4**.[3,5] Recently a general route to titanocene and zirconocene ketene complexes, dehydrohalogenation of haloacyl compounds, has been developed.[6] Application of this methodology to the permethylzirconocene system has led to isolation of monomeric, Lewis base adducts of Cp*$_2$Zr(C,O-η^2-R$_2$C=CO). We report the results of a structure determination for Cp*$_2$Zr(py)(C,O-η^2-H$_2$C=CO) (py = pyridine) and the stereochemistry of the hydrogenation of the *tert*-butyl ketene complex, which bears on the proposed CO reduction mechanism.

The requisite haloacyl compounds Cp*$_2$Zr(COCH$_3$)(Br) (**5a**)[7] and Cp*$_2$Zr(COCH$_2$CMe$_3$)(Cl) (**5b**)[8] were prepared by carbonylation of the corresponding haloalkyl complexes.[9,10] Deprotonation of **5a** with NaN(SiMe$_3$)$_2$ or **5b** with LiN(CHMe$_2$)$_2$ in toluene affords the soluble anionic halo ketene compounds **6a**[11] or **6b**.[12] The ^{1}H NMR parameters for **6a** and **6b** are similar to those reported for the analogous anionic complex (Cp$_2$Zr-(COCH$_2$)CH$_3$)Na$^+$·Et$_2$O (Cp = η^5-C$_5$H$_5$).[6] The ionic ligands of **6a** and **6b** are readily displaced by a variety of neutral donors to yield the neutral ketene complexes **7a**,[14] **7b**,[15] and **7c**[16] (eq 2).



(2)

(7) **5a:** analyzed as C$_{22}$H$_{33}$BrOZr (C, H, Br).

(8) **5b:** analyzed as C$_{26}$H$_{41}$ClOZr (C, H, Zr).

(9) Cp*$_2$Zr(CH$_3$)(Br) is prepared by treatment of Cp*$_2$ZrBr$_2$ with CH$_3$MgBr in toluene/Et$_2$O solution at 50 °C for 12 h (analyzed as C$_{21}$H$_{33}$BrZr (C, H, Br)).

(10) Cp*$_2$Zr(CH$_2$CMe$_3$)(Cl) was prepared by treatment of LiCH$_2$CMe$_3$ with Cp*$_2$ZrCl$_2$ in toluene at 25 °C for 12 h. Analyzed as C$_{25}$H$_{41}$ClZr (C, H, Zr).

(11) **6a:** ^{1}H NMR (benzene-d_6) δ 1.86 (s, C$_5$(CH$_3$)$_5$), 5.01 (s, =CH), 4.01 (s, =CH), 0.09 (s, Si(CH$_3$)$_3$); the NH was not located.

(12) **6b:** analyzed as C$_{32}$H$_{55}$ClLiNOZr (C, H, Zr); mol wt (see ref 13), 430 (mol wt calcd 561); ^{1}H NMR (benzene-d_6) δ 1.90 (s, C$_5$(CH$_3$)$_5$), 4.19 (s, CH), 2.43 (m, NCH), 1.40 (C(CH$_3$)$_3$), 0.83 (d, $^3J_{HH}$ = 6.6 Hz, C(CH$_3$)$_3$), the NH proton was not located; ^{13}C{^{1}H} NMR (benzene-d_6) δ 189.37 (COZr), 115.28 (*C*$_5$(CH$_3$)$_5$), 102.79 (=*C*HC(CH$_3$)$_3$), 45.68 (*C*H(CH$_3$)$_2$), 32.71 (*C*-(CH$_3$)$_3$), 32.59 (C(*C*H$_3$)$_3$), 22.88 (CH(*C*H$_3$)$_2$), 12.13 (C$_5$(*C*H$_3$)$_5$); IR (Njuol) ν(NH) 3250 cm^{-1}.

(13) Molecular weight analysis of **6b** and **7c** were determined via isothermal distillation using the Signer method. See: Signer, R. *Justus* Liebigs *Ann. Chem.* **1930**, *478*, 246. The molecular weight of **6b** was low for a monomeric complex and is probably due to labile ligand dissociation. No free diisopropylamine was observed in the ^{1}H NMR spectrum of **6b**.

(14) **7a:** ^{1}H NMR (THF-d_8) δ 1.60 (C$_5$(CH$_3$)$_5$), 9.26 (s, py), 8.43 (s, py), 7.91 (m, py), 7.56 (m, py), 4.57 (d, $^2J_{HH}$ = 1.6 Hz, CH), 3.51 (d, $^2J_{HH}$ = 1.6 Hz, CH); ^{13}C NMR (THF-d_8) δ 205.2 (t, $^2J_{CH}$ = 8 Hz, COZr), 153.0 (d, $^1J_{CH}$ = 182 Hz, py), 151.0 (d, $^1J_{CH}$ = 189 Hz, py), 139.1 (d, $^1J_{CH}$ = 166 Hz, py), 126.2 (d, $^1J_{CH}$ = 162 $^1J_{CH}$ py), 124.6 (d, $^1J_{CH}$ = 164 Hz, py), 115.1 (s, *C*$_5$(CH$_3$)$_5$), 72.8 (dd, $^1J_{CH}$ = 160.2 Hz, $^1J_{CH}$ = 148.4 Hz, CH$_2$), 11.67 (q, $^1J_{CH}$ = 125.0 Hz, C$_5$(*C*H$_3$)$_5$).

(15) **7b** could only be obtained as a dark green oil. Purity by ^{1}H NMR was 80%. ^{1}H NMR (benzene-d_6) important peak δ 4.49 (s, CH); ^{13}C{^{1}H} NMR (benzene-d_6) δ 228.0 (CO), 176.2 (COZr), 91.1 (CH(CMe$_3$)); IR (benzene) ν(CO) 1987 cm^{-1}.

(16) **7c:** analyzed as C$_{30}$H$_{51}$OPZr (C, H, P. Zr); mol wt (ref 13) 582 (mol wt calcd 550); important ^{1}H NMR (benzene-d_6) δ 4.22 (s, CH), 0.97 (d, $^2J_{PH}$ = 14 Hz, P(CH$_3$)$_3$), -0.43 (d, $^2J_{PH}$ = 13.2 Hz, ZrCH$_2$); ^{31}P{^{1}H} NMR (benzene-d_6, external H$_3$PO$_4$) δ 26.59 (P); ^{13}C{^{1}H} NMR (benzene-d_6) δ 186.85 (d, $^3J_{PC}$ = 7.8 Hz, COZr), 13.97 (d, $^1J_{PC}$ = 48.8 Hz, P(CH$_3$)$_3$).

(1) Myron A. Bantrell Fellow, 1981-1983.

(2) Camille and Henry Dreyfus Teacher-Scholar, 1977-1982.

(3) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121.

(4) Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 218.

(5) The reaction of asymmetric ketenes such as Me$_3$SiCH=C=O with (Cp*$_2$ZrN$_2$)$_2$N$_2$ gave only ketene-coupled metallacyclic products, whereas the reduction of such ketenes by **1** gives enolate hydrides, nonstereospecifically. Moore, E. J.; Bercaw, J. E., manuscript in preparation.

(6) (a) Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 5499. (b) Straus, D. A. Ph.D. Thesis, California Institute of Technology, 1983.

0002-7863/83/1505-2068$01.50/0