*Journal of Organometallic Chemistry*, 420 (1991) 237–252
Elsevier Sequoia S.A., Lausanne
JOM 22137

# Ketone, aldehyde and aldimine complexes of cyclopentadienylruthenium organometallic Lewis acids

J.W. Faller *, Y. Ma, C.J. Smart and M.J. DiVerdi
*Department of Chemistry, Yale University, New Haven, CT 06511 (USA)*

(Received February 27th, 1991)

**Abstract**

The interaction of aldehydes, ketones, and amines with the organometallic Lewis acids $[CpRuL_1L_2]^+$, where $L_1 = CO$ or $PPh_3$ and $L_2 = PPh_3$, have been investigated, A series of Lewis acid-base adducts has been synthesized and characterized. Stable $[CpRuL_1L_2(\eta^1\text{-HN=CHPh})]^+$ complexes were isolated in high yield as the $SbF_6^-$ or $PF_6^-$ salts. X-Ray crystallographic analysis confirmed the $\eta^1$-binding mode of the imine in $[CpRu(PPh_3)_2(HN=CHPh)]PF_6$ and the aldehyde carbonyl in $[CpRu(PPh_3)(CO)(\text{cinnamaldehyde})]PF_6$. The effects of conformational isomerism in these systems have been investigated.

## Introduction

The use of organometallic Lewis acids to enhance the electrophilicity of aldehydes and ketones has recently attracted increased attention [1]. Workers have focused on the stereochemical control that is possible in important organic transformations as a consequence of the reactivity of the intermediate coordination compounds [2]. During our study of stereoselective organic reactions mediated by transition metal Lewis acid complexes with ketones and aldehydes, we became interested in the possible utility of transition-metal imine complexes in stereocontrolled synthesis. Previously reported syntheses using conventional Lewis acids suggested the potential importance of more elaborate organometallic Lewis acids in the synthesis of nitrogen-containing natural products, e.g., alkaloids [3], amino acids [4] and $\beta$-lactams [5].

The complexation of N-protio imines is of particular concern because their subsequent reactions often lead to products with a simple amino group which are sometimes more desirable than substituted ones. Schiff reported numerous metal complexes of salicylaldimines as early as 1869 [6] and Schiff base ligands have subsequently played an important role in the development of modern coordination chemistry. Nevertheless, as in the case of Schiff's original reports, and in the vast majority of other work up to the present, a second donor was required in the Schiff base ligand, so that stabilized chelates could be formed. *ortho*-Hydroxyl groups

[7–9], as in salicylaldimines; di-imines from 1,2- or 1,3-diones [10]; and direct *ortho*-metallation of phenyl groups on the imine [11] have been effective in providing the required stabilization via the chelate effect. Reviews of this type of Schiff base complex have appeared [8,9]. Reports of imine complexes without a second donor to provide chelation are much less common, and of these, only a few rare cases have been reported in which nonchelated N-protio complexes were successfully prepared [12]. In the following work, we will discuss high-yield preparations and the characterization of ruthenium N-protio aldimine complexes, as well as some other related Lewis acid-base adducts with the general formula of $[CpRuL_1L_2(base)]^+$ where $L_1$ = phosphine and $L_2$ = phosphine or carbonyl.

## Experimental section

All manipulations during the preparations were performed in an inert atmosphere of dry nitrogen, using standard Schlenk techniques. Proton NMR spectra were recorded at 250 MHz and 500 MHz on Bruker WM-250 and AM-500 spectrometers, respectively, or at 490 MHz on a Yale-built 490 MHz spectrometer. IR spectra were recorded on a Nicolet 5SX FTIR. Solvents and reagents were used as received without further purification, except for $CH_2Cl_2$, which was distilled from $CaH_2$. $CpRu(PPh_3)(CO)(I)$, $CpRu(PPh_3)(CO)(Cl)$, and $CpRu(PPh_3)_2(Cl)$ were prepared according to published methods [13,14]. *Note that in the abstraction of halide by silver ion, only a small excess of $AgSbF_6$ can be tolerated.*

*Preparation of $[CpRu(PPh_3)(CO)(\eta^1\text{-}Me_2C{=}O)]SbF_6$, 1*

$AgSbF_6$ (0.621 g, 1.81 mmol) was added to a solution of $CpRu(PPh_3)(CO)I$ (1.01 g, 1.73 mmol) in 10 mL of acetone. A light yellow precipitate formed immediately and the color of the solution changed from orange to yellow. After 30 min of stirring in the dark, the mixture was centrifuged and the supernatant was separated from the AgI precipitate by decantation. A bright yellow crystalline precipitate was obtained by adding 30 mL of diethyl ether slowly to the supernatant. The solid was washed with diethyl ether and dried *in vacuo* for 24 h. This yielded **1** (1.25 g, 1.66 mmol, 96%) as yellow, air-stable crystals. IR ($CH_2Cl_2$): $\nu$(C≡O) 1977s and $\nu$(C=O) 1657w $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 25 °C, 500 MHz): $\delta$ 2.08 (s, 6H, $CH_3COCH_3$); 5.11 (s, 5H, HCp); 7.2–7.7 (m, 15H). Anal. Found: C, 43.05; H, 3.52. $C_{27}H_{26}F_6O_2PRuSb$ calcd.: C, 43.17; H, 3.49%.

*Preparation of $[CpRu(PPh_3)(CO)(\eta^1\text{-}PhCHO)]SbF_6$, 2*

A flask was charged with an excess of benzaldehyde (1.00 mL, 9.05 mmol), compound **1** (0.521 g, 0.693 mmol) and 5 mL of $CH_2Cl_2$. The solid dissolved rapidly and the mixture was allowed to stir for 10 min and the volatiles were removed on a rotary evaporator at room temperature. The oily solid residue was redissolved in 5 mL of $CH_2Cl_2$ and the solution was treated slowly with 25 mL of diethyl ether to give a bright yellow crystalline solid. The solid was washed with diethyl ether and dried *in vacuo* for 24 h. This yielded **2** (0.499 g, 0.625 mmol, 90%) as yellow, air-stable crystals. IR ($CH_2Cl_2$): $\nu$(C≡O) 1983s and $\nu$(C=O) 1624m $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 25 °C, 500 MHz): $\delta$ 5.19 (s, 5H, HCp); 7.2–7.7 (m, 20H); 9.64 (br, 1H, HCO). Anal. Found: C, 46.42; H, 3.36. $C_{31}H_{26}F_6O_2PRuSb$ calcd.: C,

46.64; H, 3.28%. Compound **2** can also be obtained with a comparable yield from the iodide following the procedure for the preparation of compound **1**.

*Preparation of [CpRu(PPh$_3$)(CO)($\eta^1$-PhCH=CHCHO)]SbF$_6$, 3*

Following the procedure for **1**, and using CpRu(PPh$_3$)(CO)Cl (0.030 g, 0.062 mmol) in 2 mL of $CH_2Cl_2$, the addition of $AgSbF_6$ (0.026 g, 0.074 mmol) caused an immediate precipitate of AgCl. Centrifugation and addition of hexane to the yellow supernatant gave a yellow precipitate of **3** (0.041 g, 0.050 mmol, 81%). IR ($CH_2Cl_2$): $\nu$(C≡O) 1982s and $\nu$(C=O) 1605w cm$^{-1}$. $^1$H NMR ($CDCl_3$, 250 MHz): $\delta$ 5.13 (s, 5H, HCp); 6.37 (dd, 8.4, 16.0 Hz, 1H, HC=C); 7.2–7.6 (m, 20H); 7.65 (d, 16.0 Hz, 1H, HC=C); 9.08 (d, 8.4 Hz, 1H, HC=O). X-ray crystallography showed that **3'**, the $PF_6^-$ analogue, contained no solvent of crystallization and that the cinnamaldehyde was $\eta^1$-bound, *vide infra*.

*Preparation of [CpRu(PPh$_3$)(CO)($\eta^1$-MeN=CHPh)]SbF$_6$, 4*

Five equivalents of benzylidenemethylamine were added dropwise while stirring to a solution of **2** (0.205 g, 0.257 mmol) in 2 mL of $CHCl_3$. A slight lightening in the color of the solution was noted upon addition of the Schiff base. Within 20 min of stirring, yellow crystalline needles began to form and the mixture was stirred for an additional 30 min. The suspension was stored at −20 °C overnight to allow development of larger crystals. The supernatant was decanted and the crystals were washed with cold $CHCl_3$ before being dried *in vacuo* for 24 h. This gave **4** (0.198 g, 0.244 mmol, 95%) as yellow, air-stable needles. IR ($CH_2Cl_2$): $\nu$(C≡O) 1984s and $\nu$(C=N) 1630w cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$, 25 °C, 500 MHz): $\delta$ 3.52 (d, 3H, HC=NMe); 5.22 (s, 5H, HCp); 7.2–7.7 (m, 20H); 8.38 (m, 1H, HC=NMe). Anal. Found: C, 47.20; H, 3.62; N, 1.71. $C_{32}H_{31}NF_6OPRuSb$ calcd.: C, 47.37; H, 3.60; N, 1.73%.

*Preparation of [CpRu(PPh$_3$)(CO)(NH$_3$)]SbF$_6$, 5*

A solution of compound **2** (0.523 g, 0.696 mmol) in 10 mL of $CH_2Cl_2$ was purged with a stream of ammonia for 5 min. A slight decoloration was noticed during the ammonia purge and the solution was allowed to stand for 10 min. Solvent was then removed under reduced pressure. The light yellow crystalline residue was washed with cold $CHCl_3$ and dried *in vacuo* for 24 h. This yielded **5** (0.501 g, 0.692 mmol, 99.5%) as light-yellow, air-stable crystals. IR ($CH_2Cl_2$): $\nu$(C≡O) 1972s cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$, 25 °C, 500 MHz): $\delta$ 2.00 (br, 3H, $NH_3$); 5.13 (s, 5H, HCp); 7.2–7.7 (m, 15H). Anal. Found: C, 40.56; H, 3.30; N, 1.93. $C_{24}H_{23}NF_6OPRuSb$ calcd.: C, 40.64; H, 3.27; N, 1.96%.

*Preparation of [CpRu(PPh$_3$)(CO)($\eta^1$-HN=CHPh)]SbF$_6$, 6*

A solution of compound **5** (0.0880 g, 0.124 mmol) in 20 mL of dry methanol was treated with 0.36 mL of 0.70 *M* NaOMe solution. Immediately after the addition of sodium methoxide, ten equivalents of benzaldehyde (0.200 mL, 2 mmol) were added to the reaction mixture. After 1 h of stirring under an atmosphere of nitrogen, the reaction had undergone complete conversion as determined by $^1$H NMR. At this juncture, an excess of $NaSbF_6$ (20 eq.) was added and the mixture agitated until the salt dissolved. The solvent was removed under reduced pressure, the residue was extracted with 20 mL of methylene chloride in three portions, and

the combined extracts were concentrated to 2 mL. Diethyl ether (15 mL) was added *slowly* to the dark yellow concentrate and a yellow crystalline solid precipitated. After being stored at −20 °C for 12 h, the supernatant was decanted and the solid was washed with diethyl ether and then dried *in vacuo* for 24 h. This yielded **6** (0.0854 g, 0.107 mmol, 86%) as dark yellow, air-stable crystals: IR ($CH_2Cl_2$): $\nu$(N–H) 3250m, $\nu$(C≡O) 1968s and $\nu$(C=N) 1618w $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 25 °C, 500 MHz): $\delta$ 5.24 (s, 5H, HCp); 7.2–7.7 (m, 20H); 7.56 (d, $J$ = 21.4 Hz, 1H′, HN=CH′); 10.07 (d, $J$ = 21.4 Hz, 1H, HN=CH′). Anal. Found: C, 46.61; H, 3.45; N, 1.71. $C_{31}H_{27}NF_6OPRuSb$ calcd.: C, 46.70; H, 3.41; N, 1.76%.

*Attempted preparation of a benzaldehyde complex from $CpRu(PPh_3)_2Cl$*

A 25 mL flask was purged with nitrogen and charged with $CpRu(PPh_3)_2Cl$ (0.055 g, 0.075 mmol) and 15 mL of $CH_2Cl_2$. To this solution was added benzaldehyde (0.02 mL, 0.20 mmol) and $AgPF_6$ (0.020 g, 0.079 mmol). Within a few minutes a white precipitate had formed, and the color lightened from orange to yellow. The proton NMR at this point showed formation of a new cyclopentadienyl-containing species with a Cp resonance at $\delta$ 4.96. No resonances in the spectrum were assignable to a coordinated aldehyde molecule, however. We were unable to isolate this compound; attempts to precipitate the material by addition of the $CH_2Cl_2$ solution to pentane led only to the formation of an oil which decomposed rapidly.

*Preparation of $[CpRu(PPh_3)_2(HN{=}CHPh)]PF_6$, 7*

A 50 mL three-necked round-bottom flask was charged with dry nitrogen, $CpRu(PPh_3)_2Cl$ (0.048 g, 0.066 mmol), $NH_4PF_6$ (0.1095 g, 0.672 mmol), and 20 mL of methanol. The mixture was slowly heated to the reflux point under an atmosphere of nitrogen. Before the solvent began to reflux, benzaldehyde (0.070 mL, 0.667 mmol) was added to the mixture via syringe. After heating under reflux for 30 min, the reaction appeared to be > 90% complete by $^1H$ NMR. After 1 h total reflux time, the reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The crude product was separated from the inorganic salts by extraction of the residue with $CH_2Cl_2$, followed by filtration of this extract into a large volume of cyclohexane. Immediately, a flocculent, light yellow precipitate formed. This was separated from the supernatant by centrifugation; the supernatant was decanted, and the precipitate was washed with diethyl ether and dried *in vacuo*. This gave **7** (0.060 g, 0.063 mmol, 96%) as yellow, air-stable crystals. $^1H$ NMR ($CDCl_3$): $\delta$ 4.55 (s, 5H); 7.10–7.95 (m, 35H); 8.62 (br d, $J$ = 22.0 Hz, 1H); 9.28 (br d, $J$ = 22.0 Hz, 1H). $^{31}P$ NMR ($CDCl_3$): $\delta$ 42.50 (s); −143.43 (septet, $J$ = 700 Hz). Recrystallization from methylene chloride and ether gave **7′**, which contained no solvent. Anal. Found: C, 61.06; H, 4.53; N, 1.46. $C_{48}H_{42}NF_6P_3Ru$ calcd.: C, 61.28; H, 4.50; N, 1.49%. Recrystallization from methylene chloride and pentane gave crystals, **7″** which contained both methylene chloride and pentane (*vide infra*).

*Preparation of $[CpRu(PPh_3)_2(NH_3)]PF_6$, 8*

A 250 mL, round-bottom flask was charged with dry nitrogen, $CpRu(PPh_3)_2Cl$ (0.124 g, 0.171 mmol), $NH_4PF_6$ (0.250 g, 1.53 mmol), and methanol (100 mL). The flask was fitted with a water-cooled reflux condenser, and the contents were

heated to reflux. After 2 h of heating under reflux, the solvent was removed under reduced pressure, and the residue was extracted with a small volume of methylene chloride. This extract was filtered into excess pentane, immediately giving a light yellow voluminous precipitate, which was isolated by centrifugation and decantation of the supernatant to yield **8** (0.115 g, 0.135 mmol, 79%). M.p. 150–153 °C. IR ($CH_2Cl_2$): $\nu$(N–H) 3358 $cm^{-1}$. $^1H$ NMR (490 MHz, 30 °C, $CDCl_3$): $\delta$ 7.37–6.98 (m, 30H); 4.36 (s, 5H, Cp); 2.43 (br s, 3H, $NH_3$). Anal. Found: C, 57.55; H, 4.38; N, 1.79. $C_{41}H_{38}NF_6P_3Ru$ calcd.: C, 57.75; H, 4.49; N, 1.64%.

*X-Ray crystallographic analysis of* $[CpRu(PPh_3)_2(HN{=}CHPh)]PF_6$, *7'*

Diffraction measurements for **7** using a crystal which measured 0.19 × 0.19 × 0.17 mm were carried out using an Enraf–Nonius CAD-4 fully automated diffractometer using graphite monochromated Mo-$K_\alpha$ radiation. The crystallographic data are summarized in Table 1 *. From the systematic absences of $0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; and $hk0$, $h = 2n + 1$, the space group was determined to be *Pbca*. The structure was solved using the Patterson heavy-atom method, which revealed the location of the ruthenium atom. The coordinates of the remaining non-hydrogen atoms were located in subsequent difference Fourier synthesis. Owing to the low absorption coefficient, no absorption correction was applied. Calculations were performed using the TEXSAN Structure Analysis Package of Molecular Structure Corporation. Anisotropic refinement of all atoms with inclusion of hydrogen atoms in calculated positions resulted in convergence of $R$ to 0.040. However, large thermal parameters ($B_{eq} \sim 9$) for some of the carbons in the benzylidene fragment suggested that there might be a disorder in the benzylideneamine ligand. The largest peak in the difference Fourier map was found in the vicinity of the imine nitrogen indicative of a rotational disorder about the Ru–N bond. Other difference Fourier peaks in the vicinity of the phenyl suggested this as well. The relatively large Ru–N–C angle allows the phenyls of both conformers to overlap extensively; whereas the carbon attached to nitrogen (C6A) was displaced sufficiently that it could be refined easily. In order to estimate the occupancy of the conformers, constrained refinement of populations of C6 and C6A yielded an occupancy of 79:21. Rigid group refinement of the position, orientation and isotropic temperature factors for the major phenyl (C7–C12) and a benzylidene (C6A–C12A) indicated that the conformer had the synperiplanar arrangement of Cp–Ru relative to N=C about the Ru–N bond. The minor conformer corresponded to the antiperiplanar arrangement. Anisotropic refinement of non hydrogen atoms (except for isotropic refinement of C6 and N atoms and the rigid groups), and inclusion of calculated hydrogen atoms with $B$'s 30% greater than the atoms to which they were attached converged to $R = 0.043$ and $R_w = 0.043$. The structure of the cation is shown in Fig. 1. Positional parameters, bond distances and bond angles are given in Tables 2, 3, and 4 *. The minor conformer of the imine ligand showed substantial distortions. The structure of **7''** (*vide infra*) showed no evidence for disorder in the imine, so that the most reliable metric parameters for the ligand should be obtained from it.

* Tables are available from the authors.

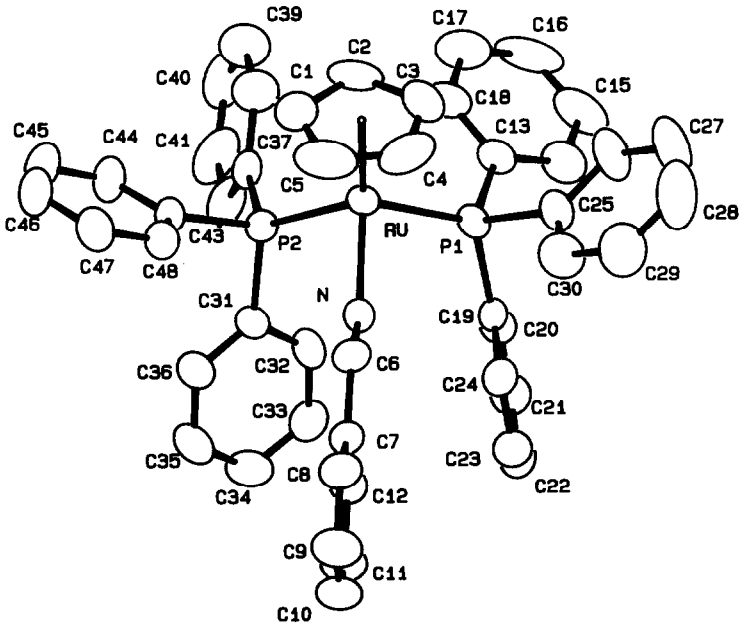



Fig. 1. The structure of the cation in $[CpRu(PPh_3)_2(HN{=}CHPh)]PF_6 \cdot CH_2Cl_2 \cdot 0.5C_5H_{12}$, **7″** showing 50% probability ellipsoids.

*X-Ray crystallographic analysis of* $[CpRu(PPh_3)_2(NH{=}CHPh)]PF_6 \cdot CH_2Cl_2 \cdot 0.5C_5H_{12}$, *7″*

Crystallization of **7** from a mixture of methylene chloride and pentane yielded **7″** in which the crystals contained both solvents. Using the methodology described for **7′**, a crystal which measured $0.37 \times 0.37 \times 0.13$ mm was used for a structure determination. The space group, based on the observed systematic extinctions, was $P2_1/c$. A 2:1 orientational disorder was found for the methylene chloride which was successfully modeled. Large thermal parameters for the pentane indicated some disorder for this solvate as well. In this structure, however, there did not appear to be a significant disorder in the benzylideneamine ligand. Anisotropic refinement of non-hydrogen atoms in the complex and inclusion of hydrogen atoms in calculated positions converged to $R = 0.049$ and $R_w = 0.069$. The structure of this cation is shown in Fig. 2. Positional parameters, bond distances and bond angles are given in Tables 2, 3, and 4. The conformation of the benzylidene ligand was approximately the same as the major conformer found for **7′**. The conformation of the phenyl rings in the phosphines showed only minor torsional distortions relative to those in **7′**, the largest distortion was a rotation of the C13–C18 ring. The major conformer of the imine ligand showed a similar orientation and similar bond angles to those of **7′**. Owing to the disorder, however, the metrical parameters for the benzylidene ligand in **7″** would appear to be the most reliable.

*X-Ray crystallographic analysis of* $[CpRu(PPh_3)(CO)(\eta^1\text{-}PhCH{=}CHCHO)]PF_6$, *3′*

Diffraction measurements for **3′** used a crystal which measured $0.36 \times 0.17 \times 0.12$ mm. The space group was determined to be $P2_1/c$ from the systematic absences. The cell parameters were $a = 11.613(2)$, $b = 15.628(4)$, $c = 18.484$ Å,

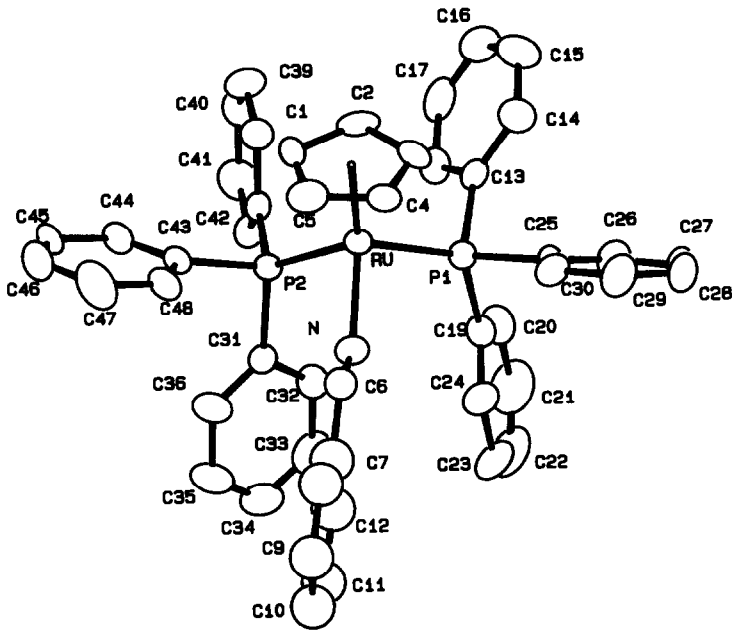



Fig. 2. The structure of the cation in $[CpRu(PPh_3)_2(HN{=}CHPh)]PF_6$, **7′** showing 50% probability ellipsoids. The major conformation of the disordered benzylidene imine is shown.

$\beta = 92.88(2)°$, $V = 3350(2)$ Å$^3$, $Z = 4$. Anisotropic refinement of non-hydrogen atoms and inclusion of hydrogen atoms in calculated positions converged to $R = 0.040$ and $R_w = 0.040$. Large thermal parameters for the carbons in the CH=CHCHO fragment suggested a disorder in this fragment. Peaks in the difference Fourier were consistent with a crankshaft disorder of the fragment with the phenyl approximately in the same location. Attempts to find a suitable disorder model were unsuccessful, although the structure clearly showed that an $\eta^1$-carbonyl was involved. The structure served to prove the connectivity of the atoms and the mode of carbonyl attachment. As the metrical parameters within the cinnamaldehyde ligand were unreliable, however, details of the structure have not been included here.

## Results

*Preparation of $\eta^1$-carbonyl complexes*

The cationic complexes of the type $[CpRu(PPh_3)(CO)(\eta^1\text{-acetone})]SbF_6$, **1** and $[CpRu(PPh_3)(CO)(\eta^1\text{-benzaldehyde})]SbF_6$, **2** were easily prepared in high yield by the route shown in eq. 1. There are some noteworthy general trends in the

$$CpRu(PPh_3)(CO)I + AgSbF_6 + RR'C{=}O \rightarrow [CpRu(PPh_3)(CO)(RR'C{=}O)]SbF_6 + AgI \quad (1)$$

properties of these complexes. In the $^1$H NMR spectra of all of the compounds, an upfield shift was observed for the aldehydic proton and acetone methyl protons in the complexes with respect to the shifts of the uncoordinated species. The complexes are reasonably stable in the air in the solid state and can be stored

under nitrogen at room temperature indefinitely. In solution, however, the acetone and benzaldehyde ligands are easily displaced by other Lewis base ligands. About 10% dissociation was observed when dissolved in rigorously dried deuteriochloroform, indicating a rather labile M–O=C bond.

Attempts were made to prepare the bisphosphine analogues of complex **1** and **2**, but without success. We examined two methods, which differed in the manner in which the halide was displaced from the starting material. When $NH_4PF_6$ was used, near quantitative conversion to the imine complex was observed, *vide infra*, but neither aldehyde nor acetone complexes were isolated. Alternatively, when $AgPF_6$ was used to dehalogenate the starting material, a singlet at $\delta$ 4.96 indicated the presence of a new cyclopentadienyl-containing compound, but no resonances were observed which could be assigned to coordinated benzaldehyde or acetone. This latter dehalogenated material was not stable enough to be isolated, and decomposed in solution to a dark green compound which was paramagnetic. Considering the lability of its more acidic analogue $[CpRu(PPh_3)(CO)(base)]^+$, this might have been anticipated.

*Preparation of aldimine complexes*

$[CpRu(PPh_3)(CO)(\eta^1\text{-MeN=CHPh})]SbF_6$, **4** can be readily synthesized by a metathesis reaction between **2** and benzylidenemethylamine in chloroform as shown in eq. 2. Both **1** and **2** are excellent starting materials for the reactions and

$$[CpRu(PPh_3)(CO)(PhCH{=}O)]^+ + PhCH{=}NMe \rightarrow [CpRu(PPh_3)(CO)(MeN{=}CHPh)]^+ \quad (2)$$

the use of either is a matter of convenience. The reaction was quantitative by NMR within a few minutes. The product was easily isolated owing to its low solubility in chloroform and was characterized by conventional spectroscopic techniques and chemical analysis. Compound **4** is very stable both as a solid and in solution. This clearly suggests that an imine ligand is a much stronger base toward $[CpRu(PPh_3)(CO)]^+$ than the aldehyde or ketone from which it is derived. We were especially surprised by its stability, even under prolonged heating at 60 °C, when dissolved in acetonitrile, which is a fairly good ligand and Lewis base. This observation is contrary to the long-standing belief stated in the literature which has attributed the scarcity of imine complexes to low Lewis basicity of the imine nitrogen [9,15].

The benzaldimine analogue derived from ammonia, **6**, was obtained from the reaction between the ammine complex **5** and benzaldehyde at room temperature; however, the presence of a base such as sodium methoxide is essential for the conversion. A disadvantage of methoxide was that it also reacted slowly with $SbF_6^-$

$$\underset{(5)}{[CpRu(PPh_3)(CO)(NH_3)]SbF_6} + PhCHO \rightarrow \underset{(6)}{[CpRu(PPh_3)(CO)(HN{=}CHPh)]SbF_6} + H_2O \quad (3)$$

to form the new counterion $SbF_4(OMe)_2^-$, the presence of which could be detected by a resonance at $\delta$ 3.80 in the $^1H$ NMR spectrum of the reaction mixture. This species with the unusual counterion could be isolated and was

characterized by elemental analysis; however, this counterion was easily exchanged by addition of a large excess of $NaSbF_6$ to the reaction mixture before workup. Hence **6** was usually isolated as the pure hexafluoroantimonate salt. Complex **6** proved to be as equally robust as the methyl analogue, **4**, and could withstand prolonged heating in both acetone or acetonitrile without decomposition. The ammine compound **5** was prepared by purging $NH_3$ through a solution of **1** (eq. 4). The reaction was complete within a few minutes and analytically pure **5** was isolated almost quantitatively.

$$\underset{(\mathbf{1})}{[CpRu(PPh_3)(CO)(Me_2C{=}O)]SbF_6} + NH_3 \rightarrow \underset{(\mathbf{5})}{[CpRu(PPh_3)(CO)(NH_3)]SbF_6} + Me_2CO \quad (4)$$

We first obtained the ammonia benzaldimine complex of the bisphosphine analogue while attempting the preparation of a benzaldehyde complex as shown in eq. 5. In modified form this developed into a very effective way of generating imine species. We initially found this reaction occurred at room temperature in ~ 24 h, but 40% of the ruthenium containing material was in the form of the ammine

$$CpRu(PPh_3)_2Cl + NH_4PF_6 + PhCHO \rightarrow \underset{(\mathbf{7})}{[CpRu(PPh_3)_2(PhCH{=}NH)]PF_6} \quad (5)$$

complex at the end of the reaction. It was also found that the rate of the formation could be significantly enhanced by the use of an excess of the aldehyde reagent. In refluxing methanol with a two-fold excess of ammonium ion and a ten-fold excess of aldehyde, a yield of > 95% was realized after only 1 h of reaction time. An intermediate was observed by NMR before the formation of the benzaldimine complex. The formation of this intermediate was independent of the presence of aldehyde. Additionally, the formation of the intermediate was not observed if the chloride compound $CpRu(PPh_3)_2Cl$ were dehalogenated by silver salt. Suggested by the role of **5** in the formation of **6**, the above observation strongly implied that the ammine complex was this intermediate. To prove this point, the reaction was carried out in the absence of benzaldehyde and the intermediate, **8**, was isolated and characterized both spectroscopically and analytically as the ammine complex. This complex has recently been prepared in lower yield and characterized by others [17].

$$CpRu(PPh_3)_2Cl + NH_4PF_6 \rightarrow \underset{(\mathbf{8})}{[CpRu(PPh_3)_2(NH_3)]PF_6} \quad (6)$$

As evidenced by ~ 25% displacement of the imine ligand upon heating for 1 h at 60 °C in deuterated acetonitrile, compound **7** appears to be less stable than **3** or **6**, which can be attributed to the reduced acidity of $[CpRu(PPh_3)_2]^+$ compared to $[CpRu(PPh_3)(CO)]^+$.

## Discussion

*IR spectra*

Whether the mode of binding of an aldehyde is via the $\sigma$- or $\pi$-system of the carbonyl can be assessed by several spectroscopic methods. The principal differen-

tiating feature of the $\eta^2$ versus the $\eta^1$ geometry which affects the IR spectrum is the result of a change in the integrity of the $\pi$-electron system of the carbonyl. For the $\eta^2$-bound aldehyde attached to a Lewis acid transition metal cation, the salient features of the resulting IR spectrum are fairly obvious: the $\pi$-electrons serve as the Lewis base donor pair, and along with the resulting $\pi$-orbital overlap, there is appreciable back-donation from a filled *d*-orbital on the metal into the $\pi^*$-orbital of the carbonyl. The filling of this antibonding orbital leads to weakening of the C=O double bond, and a substantial lowering of the $\nu$(C=O) stretching frequency. In the case of the $\eta^1$-aldehyde complexes, the primary ligand–metal interaction would be through a lone pair of electrons on the carbonyl oxygen and involve a $\sigma$-type donation to the metal. Here, one would still expect some lowering of $\nu$(C=O) by back-donation from a filled *d*-orbital on the metal into the $\pi^*$-orbital of the carbonyl. This effect is less important in an end-on geometry than in a side-on geometry, owing to a significant disparity in the extent of orbital overlap for these two binding geometries. Therefore, this lowering of $\nu$(C=O) in an $\eta^1$-complex should be smaller by comparison to that from the direct $\pi$-electron donation and $\pi^*$-backbonding in the $\eta^2$-complexes. For the $\eta^1$-bound aldehyde complexes, the difference between bound and complexed C=O stretching frequency, $\Delta\nu$, is in the range 50–100 $cm^{-1}$ [16]. On the other hand, the $\eta^2$-bound aldehydes and ketones have a much greater $\Delta\nu$, which is between 500 to 750 $cm^{-1}$ [18]. The C=O stretching frequencies of the acetone in **1** and benzaldehyde in **2** are 1658 and 1621 $cm^{-1}$, respectively. These represent only a modest change from the stretching frequencies of their corresponding free species, which are observed at 1711 and 1702 $cm^{-1}$, respectively. According to the argument above, it is clear that both compounds adopt an $\eta^1$-mode of metal-carbonyl coordination. By the same argument, the C=N stretching frequencies of the imine complexes would also be expected to produce a modest change upon coordination through the nitrogen lone pair. A substantial decrease of C=N stretching frequency would be expected in a $\pi$-bound imine complex [19]. With the $\nu$(C=N) for **3** and **6** occurring at 1630 and 1618 $cm^{-1}$, respectively, one can reasonably assert that these compounds adopt an $\eta^1$-type of interaction. An ambiguous assignment of $\nu$(C=N) for **7** was hampered by the presence of other aromatic absorptions between 1600 and 1550 $cm^{-1}$. The magnitude of this decrease in $\nu$(C=N) is certainly in agreement with an increase in backbonding because the bis-phosphine ligand environment offers a more electron rich metal center than the carbonyl-phosphine combination.

*NMR spectra*

In the $^1$H NMR spectra of the N-protio imine species, large couplings were observed between the two protons of the N-protio benzaldimine functional group, as has also been noted in the other imine complexes [12a]. The couplings for **6** and **7** are 21.4 and 22.0 Hz, respectively. The exceptionally large coupling constants indicate a *trans* or *anti* relationship of the two protons across the C=N bond. This stereochemical outcome would be predicted from steric considerations in forming the imine ligand such that the much bulkier phenyl group is *trans* to the metal. The two doublets are at a particularly low field and appear in the range of $\delta$ 7.5 to 10.7, which indicates a high degree of deshielding, as expected from an uncoordinated double bond. In each compound, the doublet at lowest field has a much

broader line width indicative of coupling to $^{31}P$ and $^{14}N$, a quadrupolar nucleus; consequently, it has been assigned to the =NH proton in the imine complex.

It is also noteworthy that counterion-dependent chemical shifts were observed when less polar solvents, such as $CDCl_3$, were used. These variations in shift suggest that ion pair interactions are responsible for the shifts and the =NH and =CH imine protons are the most sensitive in this regard. This might suggest some hydrogen bonding interaction of the =NH proton with the fluoride, although there is no indication of this in the crystal structures of **7**. For example, for $[CpRu(PPh_3)(CO)(\eta^1\text{-HN=CHPh})]^+$, the imine nitrogen proton shifted downfield by as much as 0.60 ppm upon changing from $SbF_6^-$ to $SbF_4(OMe)_2^-$, while the coupling constant stayed virtually unchanged, an indication of retention of the integrity of the C=N bond. The process is reversible and continuous depending on the ratio of the two counterions. On the other hand, the shift is barely perturbed in a more polar solvent, e.g., acetone-$d_6$, with variation of counterion.

The $^1H$ NMR data are also of great use in determining different modes of bonding interaction. Aldehyde and aldimine-CH protons on the $\eta^2$-bound complexes experience large upfield shifts of 4 to 7 ppm [19], whereas the $\eta^1$ compounds have aldehyde proton shifts within one ppm of the value for the free aldehyde [18]. To a lesser degree, a similar trend should also be true for the ketone complexes. The $^1H$ NMR data of the complexes discussed here are all consistent with an $\eta^1$-geometry, as we also found in the infrared analyses. The direction of the coordination shifts observed in the $^1H$ NMR are not as diagnostic of a particular mode of bonding, however, as found for the $\nu$(C=O) in the infrared spectra. There are reports of both upfield and downfield shifts for $\eta^1$-bound species. Upon coordination of a carbonyl or imine to a cationic metal center, there are two conflicting factors which influence the chemical shifts of substituents. One is the inductive electron-withdrawing effect from a positive metal center which exerts a deshielding influence. The other effect arises from the backbonding from a filled-*d*-orbital on the metal into the $\pi^*$-orbital of the carbonyl group. This $\pi$-effect in a $\eta^1$-complex may counteract the inductive effect by reducing the order of the double bond. When the latter effect dominates, an upfield shift results, as in the cases of **1**, **2**, and their CpFe analogues [16c], whereas in some dicationic systems, the former effect dominates resulting in downfield shifts. Such is the case for compounds $[HCpy_3M(NO)_2(\eta^1\text{-acetone})]^{2+}$ and $[HCpy_3M(NO)_2(\eta^1\text{-benzaldehyde})]^{2+}$ [20].

**Stereochemistry and conformational isomers**

*$[CpRu(L)_2(imine)]^+$*

The structure of $[CpRu(PPh_3)_2(HN=CHPh)]^+$ as found in crystals containing solvent, **7″**, is shown in Fig. 1 as a view with the vector from the centroid of the Cp ring (Ct) to Ru axis tilted 50° from the perpendicular to the page. It has a piano-stool structure with two phosphorus and one nitrogen ligand as legs. Although the ligands opposite the Cp ring would generally be expected to have angles between them of 90°, the large cone angle of the phosphine increases the P1–Ru–P2 angle to 105.0°, (100.9° in **7′**). If one ignores the phenyls, as a crude approximation the molecule has a plane through the ruthenium, Ct, and the imine ligand. Although the Ct–Ru–P–C torsional angles are nearly mirror images, the

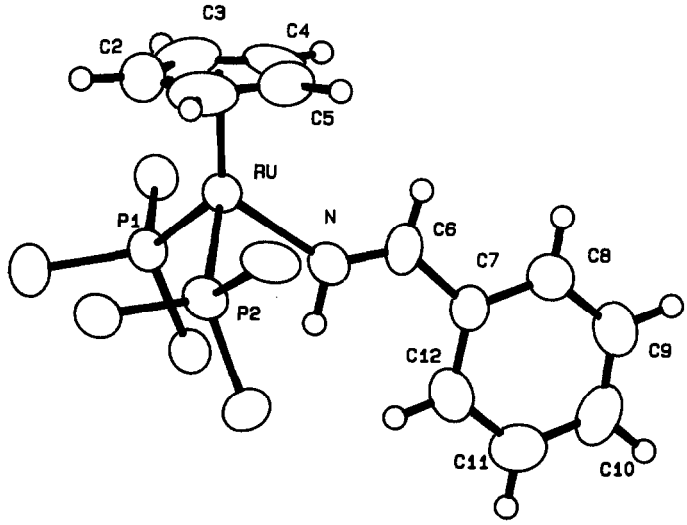



Fig. 3. The conformation of the imine ligand in $[CpRu(PPh_3)_2(HN{=}CHPh)]PF_6 \cdot CH_2Cl_2 \cdot 0.5C_5H_{12}$, **7″** showing 50% probability ellipsoids. Only the *ipso* carbons of the phenyls on the phosphines are shown for clarity.

orientation of the phenyl rings are different, such that the interligand interactions tend to have the phenyls oriented approximately perpendicular to each other. Thus, the $P1Ph_3$ and $P2Ph_3$ ligands are not mirror images. Although the conformations in the $P2Ph_3$ ligands are quite similar in **7″** and **7′**, there are some significant differences in $P1Ph_3$ owing to torsions about the P1–Ph bonds.

The two N–Ru–P angles are not equal, 84.9 and 88.9°. (In the non-solvated structure **7′** these angles were 85.8 and 94.4°.) A different orientation of the cation in **7″** and the major conformer in **7′** are shown in Figs. 3 and 4, where it is

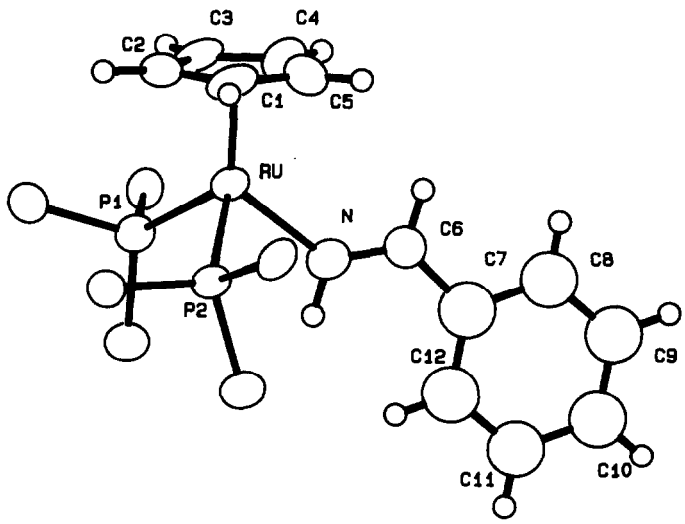
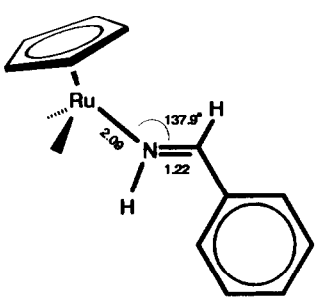
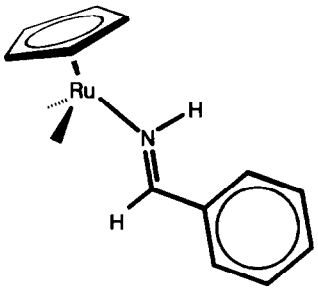



Fig. 4. The major conformation of the imine ligand found in $[CpRu(PPh_3)_2(HN{=}CHPh)]PF_6$, **7′** showing 50% probability ellipsoids.




*synperiplanar*




*antiperiplanar*

readily seen that aside from the phenyl group orientations, the two solid state structures are qualitatively indistinguishable.

In agreement with the coupling constants in the $^1$H NMR, the *E* isomer is found in the coordinated imine (see Fig. 3). This stereochemistry, which has an *anti* disposition of protons in the HN=CH moiety, is also maintained in solution as indicated by the 22 Hz *vicinal* coupling constant.

The entire imine ligand in **7″** is nearly planar and aligned with the vector from the Ru to the centroid of the Cp ligand, Ru–Ct, with torsion angles: $\phi$(Ru–N–C6–C7) = 177.0(7)°, $\phi$(Ct–Ru–N–C6) = −5(1)°, and $\phi$(N–C6–C7–C8) = 178(1)°. The preferred conformer in **7′** and the conformer in **7″** found in the solid and presumably that observed in solution is the synperiplanar conformer *sp*-**7** with $\phi$(Ct–Ru–N–C6) ~ 180°. As found in the crystal structure of **7′**, (Fig. 5) there appears to be a moderately stable antiperiplanar conformer with $\phi$(Ct–Ru–N–C6) ~ 0°, *ap*-**7**. The cleft between the triphenylphosphine ligands and the large Ru–N–C6 bond angle of 138° keeps the benzylidene ligand from having exces-

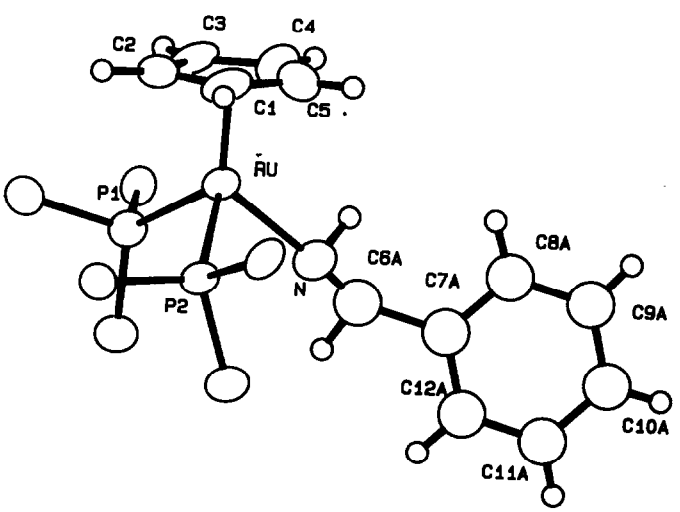
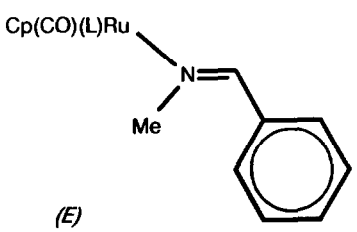



Fig. 5. The minor conformation found in the crystal structure of **7′**.

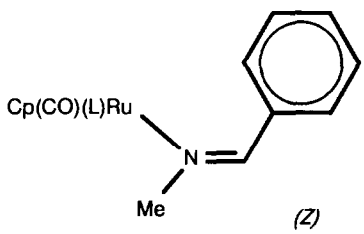
sively large interactions with the phenyls of the phosphine in both the *sp* and *ap* conformations. The predominance of the *sp* conformation in solution is indicated by the observation of a modest nuclear Overhauser effect upon the *ortho* protons of the $PPh_3$ upon irradiation of HN=C of ~2%. A comparable effect was also noted in the *ortho* protons of PhC=N. A weak effect (0.5–1%) was noted in the $Ph_3P$ *ortho* protons upon irradiation of benzylidene H suggesting that some population of the *ap* conformation also was present. An attempt to directly observe the spectra of the conformers by slowing the rotation rate at lower temperatures (−65 °C) was unsuccessful.

*[CpRu(L)(CO)(imine)]* $^+$

The (*N*)-benzylidenemethylamine complex, **4**, is prepared from the preformed ligand. Consideration of steric interactions suggests that an *anti* arrangement of the methyl and phenyl would be most stable in the free ligand. If no isomerization occurred and this stereochemistry were retained in the complex, (*Z*)-**4** would result. In the complex, however, one might anticipate that the metal might prefer an *anti* disposition relative to the phenyl, as found in **7**, which would give the (*E*) isomer of **4**. The formation of this presumably more stable isomer, however, would require isomerization to occur about the C=N bond. Although the data are limited, it appears that the *anti* arrangement of methyl and phenyl has been retained on additions to some other metal centers [21].

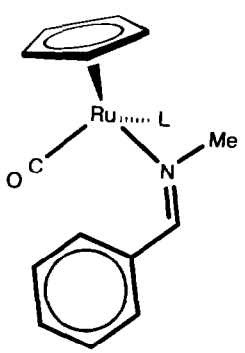



*(E)*




*(Z)*

It is clear from the 14% nuclear Overhauser effect on the benzylidene proton, N=CH upon irradiating the methyl that the methyl is proximate to the N=CH. Therefore, **4** is the *Z* isomer. The preferred conformation in (*Z*)-**4** might well be different than that found in **7**. In fact, since there is no longer a cleft between the two ligands, other orientations than synperiplanar and antiperiplanar are likely.



The absence of steric interaction in the region near the carbonyl, as well as the better $\pi$-backbonding when the *p*-orbital is aligned with the Ru–P vector [18,22,23] would suggest that an *anticlinal* orientation might well be preferred. Irradiation of the methyl group produced a modest ($\sim 2\%$) effect on the *ortho* protons of the phenyls of $PPh_3$, indicating the proximity of the methyl to the $PPh_3$ as expected for *ac*-**4**.

The back donation in these ruthenium complexes is exceptionally large and it serves, not only to orient the imine in some cases, but to counteract the effect of binding to an acid. Whereas bonding to a conventional Lewis acid would greatly enhance the reactivity of the imine, for these ruthenium complexes the polarization induced by $\sigma$-donation is compensated by $\pi$-effects. Thus, the imine complexes are quite stable and do not show the high reactivity associated with a free imine. We are currently exploring the reactivity of these complexes.

## Acknowledgements

This work was supported in part by a grant from the National Science Foundation. We also acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society for support of this research.

## References

1 (a) J.M. Fernández and J.A. Gladysz, Inorg. Chem., 8 (1989) 207; (b) C.M. Garner, N. Quirós Méndes, J.J. Kowalczyk, J.M. Fernández, K. Emerson, R.D. Larsen and J.A. Gladysz, J. Am. Chem. Soc., 112 (1990) 5146; (c) D.M. Dalton, J.M. Fernández, K. Emerson, R.D. Larsen and A.M. Arif, ibid., 112 (1990) 9198; (d) J.W. Faller and D.L. Linebarrier, ibid., 111 (1989) 1937; (e) J.W. Faller, J.A. John and M.R. Mazzieri, Tetrahedron Lett., 30 (1989) 1769; (f) R.V. Honeychuck, P.V. Bonnesen, J. Farahi and W.H. Hersh, J. Org. Chem., 52 (1987) 5296; (g) P.V. Bonnesen, C.L. Puckett, R.V. Honeychuck and W.H. Hersh, J. Am. Chem. Soc., 111 (1989) 6070.

2 (a) S.J. Danishefsky, E. Larson, D. Askin and N. Kato, J. Am. Chem. Soc., 107 (1985) 1246; (b) M. Bednarski and S. Danishefsky, J. Am. Chem. Soc., 105 (1983) 3716; (c) M.G. Vinogradov, A.B. Tuzikov, G.I. Nikishin, B.N. Shelimov and V.B. Kazansky, J. Organomet. Chem., 348 (1988) 123; (d) E.C. Ashby and J.T. Laemmle, Chem. Rev. 75 (1975) 521.

3 G.E. Keck and E.J. Enholm, J. Org. Chem., 50 (1985) 147.

4 (a) Y. Yamamoto, T. Komatsu and K. Maruyama, J. Org. Chem., 50 (1985) 3115; (b) Y. Yamamoto, S. Nishii, K. Maruyama, T. Komutsu and W. Ito, J. Am. Chem. Soc., 108 (1986) 7778.

5 (a) G. Guanti, E. Narisano and L. Banfi, Tetrahedron Lett., 28 (1987) 4331; (b) G. Guanti, E. Nairsano and L. Banfi, ibid., 28 (1987) 4335; (c) C. Gennari, I. Venturini, G. Gislon and G. Schimperna, ibid., 28 (1987) 227; (d) I. Ojima, S. Inaba and K. Yoshida, ibid., 41 (1977) 3643; (e) K. Ikeda, K. Archiwa and M. Sekiya, ibid., 24 (1983) 4707; (f) L.S. Hegedus, L.M. Schultze, J. Toro and Y. Chen, Tetrahedron, 41 (1985) 5833.

6 H. Schiff, Ann. Chem., 150 (1869) 193.

7 J.M. Fernandez-G, M.J. Rosales-Hoz, M.F. Rubio-Arroyo, R. Salcedo, R.A. Toscano and A. Vela, Inorg. Chem., 26 (1987) 349.

8 L.F. Lindoy, Quart. Rev. 25 (1971) 379.

9 R.C. Mehrotra, in G. Wilkinson, R.D. Gillard and J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, Vol. 2, Pergamon, Oxford, 1987, pp. 269–287.

10 (a) M. Pasquali, C. Floriani, A. Chiese-Villa and C. Guastini, J. Am. Chem. Soc., 101 (1979) 4740; (b) F. Muller, G. van Koten, K. Vrieze, B. Krijneri and C.H. Stam, J. Chem. Soc., Chem. Commun., (1986) 150; (c) R.C. Bennett, M.I. Bruce, B.C. Goodall, M.Z. Iqbal and F.G.A. Stone, J. Chem. Soc., Dalton, (1972) 1787; (d) H. van der Poel, G. van Koten and K. Vrieze, Inorg. Chem., 19 (1980) 1145; (e) J.M. Klerks, D.J. Stufkens, G. van Koten and K. Vrieze, J. Organomet. Chem., 181 (1979) 271.

11 (a) R. Grigg and J. Devlin, J. Chem. Soc., Chem. Commun., (1986) 631; (b) I.R. Girling and D.A. Widdenowson, J. Chem. Soc., Perkin Trans I, (1988) 1317.
12 (a) L. Knauss and E.O. Fischer, Chem. Ber., 103 (1970) 3744; (b) E.O. Fischer and L. Knauss, ibid., 103 (1970) 1262; (c) R.B. King and W.M. Douglas, J. Am. Chem. Soc., 95 (1973) 7528; (d) R.B. King and W.M. Douglas, Inorg. Chem., 13 (1974) 1339; (e) W.A. Herrmann, Chem. Ber., 107 (1974) 2899; (f) D. Sellmann and E. Thallmair, J. Organomet. Chem., 164 (1979) 337; (g) D. Czarkie and Y. Shvo, ibid., 280 (1985) 123; (h) H. Fischer and S. Zeuner, ibid., 286 (1985) 201; (i) H.G. Raubenheimer, G.J. Kruger, F. Scott and R. Otte, Organometallics, 6 (1987) 1789; (j) L. Knoll, J. Organomet. Chem., 155 (1978) C63.
13 S.G. Davies and S.J. Simpson, J. Chem. Soc., Dalton Trans., (1984) 993.
14 M.I. Bruce, C. Hameister, A.G. Swincer, R.C. Wallis and S.D. Ittel, Inorg. Synth., 21 (1982) 78.
15 G.C. Martin and J.M. Boncella, Organometallics, 8 (1989) 2968.
16 (a) M. Appel, W. Sacher and W. Beck, J. Organomet. Chem., 322 (1987) 351; (b) B.M. Foxman, P.T. Klemarczyk, R.E. Liptrot and M. Rosenblum, ibid., 187 (1980) 253; (c) E.K.G. Schmidt and C.H. Thiel, ibid., 209 (1981) 373; (d) W.L. Driessen and W.L. Groeneveld, Recl. Trav. Chim. Pays-Bas, 90 (1971) 87.
17 F.M. Conroy-Lewis and S.J. Simpson, J. Organomet. Chem., 396 (1990) 83.
18 Y.-H. Huang and J.A. Gladysz, J. Chem. Ed., 65 (1988) 298.
19 (a) S.P. Molnar, M. Orchin, J. Organomet. Chem., 16 (1969) 196; (b) W.P. Mul, C.J. Elsevier, K. Vrieze, W.J.J. Smuts and A.L. Spek, Recl. Trav. Chim. Pays-Bas, 107 (1988) 297.
20 J.W. Faller and Y. Ma, J. Am. Chem. Soc., 113 (1991) 1579.
21 D. Hottentot and C.H. Stam, Cryst. Struct. Commun., 4 (1975) 421.
22 B.E.R. Shilling, R. Hoffmann and J.W. Faller, J. Am. Chem. Soc., 101 (1979) 592.
23 J.W. Faller, C. Lambert and M.R. Mazzieri, J. Organomet. Chem., 383 (1990) 161.