Synthesis, Structure, and Ligand-Promoted Reductive Elimination in an Acylrhodium Ethyl Complex

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8-Quinolinecarboxaldehyde and $[(C_2H_4)_2RhCl]_2$ reacted to give a polymeric acylrhodium ethyl compound which was solubilized by pyridine to give chloroethyl(8-quinolinecarbonyl-*C,N*)(pyridine)rhodium. This compound was stable in the presence of amine ligands, but phosphine ligands caused rapid reductive elimination. Intermediates in the reductive elimination were observed at −40 °C by using ^1H, ^{13}C, and ^{31}P NMR in the case of the ligand PPh_3. In the first-formed intermediate PPh_3 displaced pyridine. The resulting five-coordinated Rh(III) complex reductively eliminated (with an observed first-order rate constant of 3.7×10^{-4} s^{-1} at −40 °C) to give an η^2-ketone Rh(I) intermediate. With excess phosphine $RhCl(PPh_3)_3$ and 8-quinolinyl ethyl ketone were the final products. Recrystallization of the starting pyridine complex from pyridine–ether gave $Cl(C_2H_5)Rh(C_{10}H_6NO)(C_5H_5N)_2 \cdot {}^1/_2C_4H_{10}O$ (chloroethyl(8-quinolinecarbonyl-*C,N*)bis(pyridine)rhodium–hemi(diethyl ether)), whose structure was determined by single-crystal X-ray diffraction. The compound crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell $a = 8.933$ (3) Å, $b = 17.573$ (8) Å, $c = 7.760$ (2) Å, $\alpha = 97.57$ (3)°, $\beta = 98.04$ (2)°, and $\gamma = 79.98$ (3)°. The least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms converged at $R_F = 0.046$ ($R_{wF} = 0.055$) for 2595 observed reflections and 262 parameters refined.

Introduction

Acylmetal alkyls are often intermediates in transition-metal-catalyzed routes to ketones.[1] As befits a catalytic intermediate, acylmetal alkyls tend to be unstable, undergoing facile reductive elimination.[2] This is because the product ketone can remain bound to the lower valent metal complex produced upon reductive elimination, thereby stabilizing the complex since the electron count around the metal is unchanged.[3] In contrast, reductive elimination in dialkylmetal complexes decreases the electron count around the metal by two electrons and frequently produces a high-energy, electron-deficient metal fragment. These resulting metal fragments can undergo many interesting reactions, including activation of alkyl and aryl carbon–hydrogen bonds.

There are several possible routes to acylmetal alkyls, including the one of more interest to us, metal insertion into an α-ketone carbon–carbon bond.[4] We wanted to find examples of stable acylmetal alkyls since they might suggest structural features or ligand types that would favor carbon–carbon bond activation in ketones. Furthermore, a study of reductive elimination in such compounds could illuminate the reverse reaction, oxidation addition of an α-ketone C–C bond, in the same way that the investigation of active olefin hydrogenation catalysts led to new ways to effect the reverse reaction, the activation of simple C–H bonds.[5] In this paper we describe the synthesis and structure of a stable acylrhodium(III) ethyl complex derived from 8-quinolinecarboxaldehyde and $[(C_2H_4)_2RhCl]_2$ and report on its stability and ligand-promoted reductive elimination.

Synthesis Chloroethyl(8-quinolinecarbonyl-*C,N*)(pyridine)-rhodium (4)

Various low-valent rhodium compounds catalyze the hydroacylation of 8-quinolinecarboxaldeyde (1) and related molecules.[1c] These hydroacylation reactions occur at elevated temperatures in the presence of excess olefin. They proceed by oxidative addition to produce an acylrhodium hydride, olefin insertion to give an acylrhodium alkyl, and reductive elimination to form the product ketone. We attempted to isolate acylmetal alkyl intermediates in this reaction by using a reactive metal–olefin complex at room temperature. For that reason we added to a benzene suspension of bis(μ-chloro)tetrakis(ethylene)dirhodium(I) (2) a solution of 8-quinolinecarboxaldehyde, which produced an immediate reaction. One mole of ethylene per mole of rhodium bubbled off, and a yellow solid, 3, formed in quantitative yield. Combustion analysis corresponding to the empirical formula $C_{12}H_{11}ClNORh$ showed 3 to be a complex of compound 1, Rh, Cl, and one C_2H_4. This insoluble polymeric material could be solubilized by pyridine to give ultimately a yellow-orange solid, 4. Combustion analysis of 4 was consistent with the empirical formula $C_{17}H_{16}ClN_2ORh$, indicating 3 had taken up one molecule of pyridine. The ^1H NMR showed 4 to be an acylrhodium(III) ethyl complex. In addition to the low-field quinoline resonances, there is a three-proton triplet at 0.3 ppm (an ethyl CH_3) and two one-proton multiplets at 1.7 and 2.1 ppm, corresponding to the diastereotopic CH_2 protons of the ethyl group. Chemical evidence for the

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Scheme I

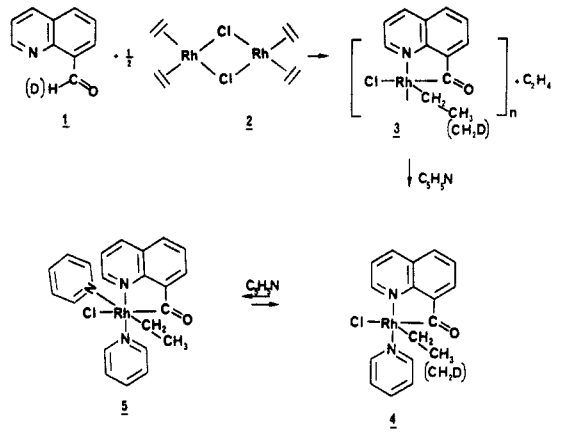

Table I. Crystal and Collection Data for 5

formula	$C_{22}H_{21}ClN_3ORh \cdot {}^1/_2C_4H_{10}O$
cryst system	triclinic
space group	$P\bar{1}$ (no. 2)
T, °C	23
a, Å	8.933 (3)
b, Å	17.573 (8)
c, Å	7.760 (2)
α, deg	97.57 (3)
β, deg	98.04 (2)
γ, deg	79.98 (3)
V, Å^3	1180.6
Z	2
d(calcd), g cm^{-3}	1.46
radiatn	Mo Kα (λ = 0.710 73 Å) graphite monochromator
cryst size, mm	0.15 × 0.20 × 0.25
diffractometer	Enraf-Nonius CAD 4
abs coeff, cm^{-1}	8.4
scan type	ω-2θ
scan rate	2-20°/min (in ω)
scan width, deg	0.6 + 0.350 tan θ
max 2θ	50.0
no. of reflctns	4269 total, 4203 unique
correctns	linear decay (1.00-1.06)
reflctns included ($F_o^2 > 3\sigma(F_o^2)$)	2595
parameters refined	262
R_F	0.046
R_{wF}	0.055
esd of observn of unit wt	1.36
highest peak in final diff Fourier	0.47 (7) e/Å^3

rhodium–ethyl bond was furnished by treating **4** with 1 equiv of Br_2 which cleanly gave ethyl bromide (identified by its ^{1}H NMR spectrum).

A plausible mechanism for the formation of **4** (Scheme I) involves **1** displacing ethylene or splitting the chlorine bridge in **2** and oxidative addition of the aldehyde C–H bond to the rhodium center. The remaining ethylene then would insert into the Rh–H bond, forming **3**.[6] In accord with this mechanism, the deuterated aldehyde **1D**[7] reacts with **2** to give ultimately the deuterated product **4D** in which all the molecules contain one deuterium in the methyl group (as shown by a ^{13}C–D coupling exclusively in the methyl group of **4D**). No scrambling of the deuterium label was seen even after **4D** was heated at 70 °C for 1 h in $CDCl_3$.

(6) Since bubbling argon through the solution during the reaction does not decrease the yield of the polymeric product, it seems likely that one ethylene remains bonded to rhodium long enough to trap the rhodium hydride.

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Table II. Table of Positional Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z
Rh	0.35309 (6)	0.26585 (3)	0.07936 (7)
Cl	0.5019 (2)	0.1919 (1)	−0.1660 (2)
O1	0.1760 (6)	0.3105 (3)	0.3719 (6)
N1	0.3425 (6)	0.3688 (3)	−0.0219 (6)
N2	0.3599 (6)	0.1634 (3)	0.1850 (6)
N3	0.1400 (6)	0.2426 (3)	−0.0855 (6)
C1	0.5617 (9)	0.2828 (4)	0.2222 (9)
C2	0.5706 (10)	0.3373 (5)	0.3816 (11)
C3	0.2331 (8)	0.3282 (4)	0.2522 (8)
C4	0.2033 (7)	0.4138 (4)	0.2190 (8)
C5	0.2617 (7)	0.4302 (4)	0.0703 (8)
C6	0.1229 (9)	0.4722 (4)	0.3187 (10)
C7	0.0983 (10)	0.5482 (4)	0.2741 (11)
C8	0.1508 (10)	0.5653 (4)	0.1305 (10)
C9	0.2363 (9)	0.5068 (4)	0.0228 (9)
C10	0.2948 (10)	0.5181 (4)	−0.1280 (10)
C11	0.3743 (10)	0.4569 (5)	−0.2164 (10)
C12	0.3988 (9)	0.3830 (4)	−0.1598 (8)
C13	0.3452 (8)	0.0976 (4)	0.0778 (9)
C14	0.3448 (9)	0.0283 (4)	0.1386 (10)
C15	0.3554 (10)	0.0248 (4)	0.3133 (11)
C16	0.3689 (10)	0.0915 (5)	0.4264 (10)
C17	0.3746 (9)	0.1589 (4)	0.3578 (9)
C18	0.1181 (8)	0.2487 (4)	−0.2573 (8)
C19	−0.0140 (8)	0.2362 (4)	−0.3618 (9)
C20	−0.1320 (8)	0.2172 (5)	−0.2878 (10)
C21	−0.1101 (8)	0.2089 (4)	−0.1138 (11)
C22	0.0244 (8)	0.2231 (4)	−0.0162 (8)
O2	0.0000	0.0000	0.5000
C23	−0.084 (3)	0.020 (1)	0.348 (3)
C24	−0.133 (2)	0.061 (1)	0.271 (3)
H1	0.6103	0.2334	0.2549
H2	0.6192	0.2995	0.1443
H3	0.6748	0.3371	0.4282
H4	0.5259	0.3881	0.3547
H5	0.5170	0.3220	0.4654
H6	0.0836	0.4612	0.4187
H7	0.0439	0.5886	0.3458
H8	0.1299	0.6172	0.1013
H9	0.2787	0.5681	−0.1675

[a] Estimated standard deviations in the least significant digits are shown in parentheses. Hydrogen atoms were included in calculated positions and were not refined. Positions were calculated by assuming idealized geometries with C–H = 0.95 Å. The "ether" molecule's hydrogen atoms were omitted. O2, C23, and C24 belong to the disordered ether molecule.

Structure of Chloroethyl(8-quinolinecarbonyl-*C*,*N*)bis(pyridine)rhodium (5)

Since few examples of acylmetal alkyl structures were known, it seemed appropriate to subject **4** to a single-crystal X-ray structure determination. Crystals suitable for X-ray analysis were grown by addition of ether to a pyridine solution of **4**. The crystals which grew were, however, the six-coordinate bis(pyridine) complex **5**. When crystals of **5** were dissolved in $CDCl_3$ for ^{1}H NMR studies, only the mono(pyridine) adduct **4** was observed (as shown by only one set of coordinated 2,6-pyridine resonances at 9.06 ppm). The solid **4** could be obtained as an analytically pure microcrystalline product, but we were not successful in growing sufficiently large single crystals of it for X-ray studies. The equilibrium concentration of **5** is low, since no resonances corresponding to **5** could be seen in the ^{1}H NMR spectrum of **4** even when it was cooled to −40 °C in the presence of 5 equiv of pyridine.

A drawing of the structure of **5** is given in Figure 1, and Tables II–IV give positional parameters, bond distances, and bond angles. The structure has a number of interesting features. There are three rhodium–nitrogen bond

Table III. Bond Distances (Å)[a]

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Rh	Cl	2.557 (1)	N3	C22	1.342 (7)	C13	C14	1.365 (9)
Rh	N1	2.047 (5)	C1	C2	1.462 (9)	C14	C15	1.354 (9)
Rh	N2	2.062 (5)	C3	C4	1.531 (8)	C15	C16	1.381 (10)
Rh	N3	2.209 (5)	C4	C5	1.413 (8)	C16	C17	1.373 (9)
Rh	C1	2.078 (7)	C4	C6	1.363 (8)	C18	C19	1.369 (8)
Rh	C3	1.938 (6)	C5	C9	1.415 (8)	C19	C20	1.377 (9)
O1	C3	1.218 (7)	C6	C7	1.395 (9)	C20	C21	1.361 (9)
N1	C5	1.366 (7)	C7	C8	1.355 (10)	C21	C22	1.371 (9)
N1	C12	1.313 (7)	C8	C9	1.420 (9)	O2	C23	1.36 (2)
N2	C13	1.347 (7)	C9	C10	1.397 (9)	O2	C23	1.36 (2)
N2	C17	1.340 (7)	C10	C11	1.343 (10)	C23	C24	0.99 (3)
N3	C18	1.336 (7)	C11	C12	1.398 (9)			

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Bond Angles (deg)[a]

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Cl	Rh	N1	91.1 (1)	Rh	N2	C17	123.0 (4)	C5	C9	C10	117.1 (6)
Cl	Rh	N2	90.2 (1)	C13	N2	C17	117.4 (5)	C8	C9	C10	125.7 (7)
Cl	Rh	N3	88.2 (1)	Rh	N3	C18	122.1 (4)	C9	C10	C11	118.9 (7)
Cl	Rh	C1	88.1 (2)	Rh	N3	C22	121.2 (4)	C10	C11	C12	121.1 (6)
Cl	Rh	C3	175.3 (2)	C18	N3	C22	116.7 (6)	N1	C12	C11	122.5 (6)
N1	Rh	N2	178.7 (2)	Rh	C1	C2	121.7 (5)	N2	C13	C14	122.6 (6)
N1	Rh	N3	91.4 (2)	Rh	C3	O1	131.7 (5)	C13	C14	C15	119.5 (6)
N1	Rh	C1	89.2 (2)	Rh	C3	C4	110.5 (4)	C14	C15	C16	119.2 (7)
N1	Rh	C3	84.7 (2)	O1	C3	C4	117.7 (5)	C15	C16	C17	118.7 (2)
N2	Rh	N3	88.3 (2)	C3	C4	C5	115.4 (5)	N2	C17	C16	122.5 (6)
N2	Rh	C1	91.2 (2)	C3	C4	C6	124.6 (6)	N3	C18	C19	123.3 (6)
N2	Rh	C3	94.0 (2)	C5	C4	C6	119.9 (6)	C18	C19	C20	119.1 (6)
N3	Rh	C1	176.2 (2)	N1	C5	C4	116.5 (5)	C19	C20	C21	118.2 (7)
N3	Rh	C3	89.8 (2)	N1	C5	C9	123.0 (5)	C20	C21	C22	119.7 (6)
C1	Rh	C3	94.0 (3)	C4	C5	C9	120.5 (6)	N3	C22	C21	122.9 (6)
Rh	N1	C5	112.8 (4)	C4	C6	C7	120.1 (6)	C23	O2	C23	180 (3)
Rh	N1	C12	129.8 (4)	C6	C7	C8	121.2 (7)	O2	C23	C24	150 (4)
C5	N1	C12	117.4 (5)	C7	C8	C9	121.1 (6)				
Rh	N2	C13	119.5 (4)	C5	C9	C8	117.2 (6)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

lengths in **5**. Rh–N(1) and Rh–N(2) are close to the value of 2.09 (2) Å found in *trans*-$[RhCl_2(py)_4]^+$.[8] The Rh–N(3) distance is significantly longer, 2.209 (5) Å, and illustrates the strong trans influence of the ethyl group.[9] The Rh–CH_2 bond length of 2.078 (7) Å is within the 2.05–2.08 Å range found for Rh(III) alkyls and equals the sum of the covalent radii of Rh and C (1.30 Å + 0.77 Å).[10] The Rh–COR bond length of 1.938 (6) Å is shorter than that seen in most other highly refined rhodium acyls, which range from 1.971 to 2.062 Å.[11] This shortness probably reflects efficient back-bonding in the chelate ring. While the rhodium–COR bond length value overlaps values for rhodium–carbene bond lengths,[12] the carbon–oxygen bond length of 1.218 (7) Å and the ν_{CO} of 1633 cm^{-1} suggest the Rh–COR unit is best described as a rhodium acyl. The rhodium–chlorine bond length in **5** is also exceptional, the 2.557 (1) Å distance being 10% longer than usual.[13] This is a consequence of the strong trans influence of the acyl group and has been seen in a related structure.[14] As a consequence of an acyl's strong trans influence, most rhodium acyls whose structures have been determined are five-coordinate square pyramids with apical acyl ligands.[11]

The strain of accommodating the small bite angle of approximately 60° in the five-membered chelate ring is apparent in its structure. The Rh–N(1) distance is slightly

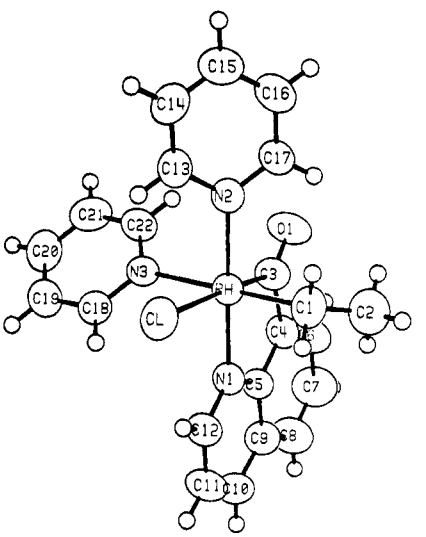

Figure 1. Drawing of the structure of the acylrhodium ethyl complex **5**, showing 40% probability thermal ellispoids. Hydrogen atoms are at calculated positions.

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compressed to 2.047 (9) Å, and the C(3)–C(4) distance of 1.531 (8) Å is larger than expected for an sp^2–sp^2 carbon–carbon bond (1.47 (2) Å). Within the chelate ring the ring strain is distributed so that the C(4)–C(3)–Rh angle is 110.5 (4)°, the C(5)–N(1)–Rh angle is 112.8 (4)°, and the N(1)–Rh–C(3) angle is 84.7 (2)°. The ethyl group exhibits some interesting features. As is the case for several other metal–ethyl structures, the Rh–C(1)–C(2) angle is greater than the tetrahedral value, in this case 121.7 (5)°.[15] The C(1)–C(2) distance is a very short 1.462 (9) Å, which, for comparison, is what one expects for an sp^3–sp carbon–carbon single bond.[16] We believe this value is an artifact, possibly due to a small amount of disorder in the ethyl group or to the inherently difficult problem of determining the structures of light atom fragments in a heavy-atom structure. The initial structure using isotropic refinement of non-hydrogen atoms ($R_1 = 0.063$; $R_2 = 0.077$) gave the C(1)–C(2) distance as 1.489 (1) Å. If we take the difference of 0.03 Å between the isotropic and anisotropic C(1)–C(2) values as a more realistic estimate of the uncertainty in this bond length, then the actual C(1)–C(2) distance could easily be 1.52 Å.

If the 1.46-Å bond length is taken to be correct, this would imply a distortion toward a β-elimination type of structure. However, there was no evidence for this in the NMR spectrum. The J_{C-H} for the CH_3 group is a normal 125 Hz.[17] If this number were an average of two large sp^2-like C–H coupling constants and one small C–H coupling due to a long C–H bond,[18] then in the Rh–CH_2CH_2D complex one would expect a site preference for deuterium at an sp^2 site and a deviation of J_{C-D} from its calculated value of 19 Hz to a higher value. This was not observed.

Given the structure of **5** it is clear that the pyridine which is lost in solution is the one trans to the ethyl group. Compound **4** is therefore most likely square pyramidal (as found for other five-coordinate Rh(III) structures[11]) with an apical ethyl group. In addition to trans influences which disfavor coordination of ligands in the alkyl–acyl plane, an inspection of Dreiding models shows that with ligands larger than pyridine, there would be as well significant steric interactions in that plane. Coordination of triphenylphosphine, for example, trans to the ethyl group gives close contacts between the triphenylphosphine hydrogens and the quinoline plane. The hydrogen at C(2) of the quinoline ring (C(12) in Figure 1) hinders coordination of large groups trans to the acyl group.

Ligand-Promoted Reductive Elimination of 4

The stability of **4** with respect to reductive elimination is not surprising since the resulting Rh(I) product would be coordinated only to two pyridyl nitrogens and a Cl and such hard-base, soft metal complexes should be high in energy.[19] The presence of the acyl group in a chelate ring could also hinder the formation of an η^2-ketone intermediate and further retard reductive elimination relative to other acylmetal alkyls. Compound **4** was found to be stable for days in solutions of chlorinated solvents or pyridine, and addition of other hard ligands such as triethylamine,

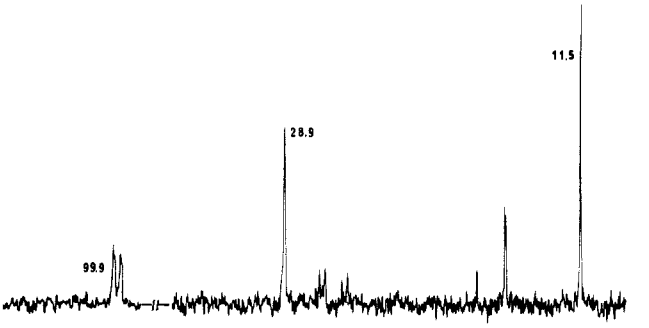
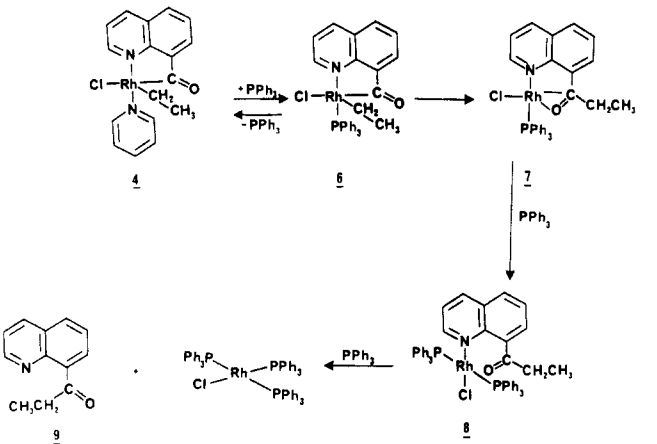


Figure 2. The high-field region of the ^{13}C NMR spectrum of the η^2-ketone **7**, showing the carbonyl carbon doublet at 99.9 ppm and the singlets at 28.9 and 11.5 ppm for the CH_2 and CH_3 carbons, respectively. There are also weaker resonances due to **6**, the precursor of **7**.

Scheme II



dimethyl sulfoxide or 4-(dimethylamino)pyridine did not cause rapid reductive elimination. In contrast, addition of soft ligands which stabilize Rh(I), such as phosphines, phosphites, or CO to **4**, caused rapid reductive elimination. Using ^1H, ^{13}C, and ^{31}P NMR spectroscopy, it was possible to follow the course of this reaction at −40 °C with the ligand PPh_3 and observe intermediates in this ligand-promoted reductive elimination reaction (see Scheme II).

The first compound formed upon addition of PPh_3 to **4** in $CDCl_3$ at −40 °C is the five-coordinate monophosphine Rh(III) complex **6**. This exhibits a single $^{31}P\{^1H\}$ doublet at 8.3 ppm with $J_{Rh-P} = 65$ Hz. The $^{13}C\{^1H\}$ NMR spectrum shows the CH_2 carbon as a doublet of doublets with $J_{P-C} = 82$ Hz and $J_{Rh-C} = 35$ Hz. We could not observe the acyl carbon. The chemical shifts and coupling constants in the ^1H, ^{31}P, and ^{13}C spectra were unchanged starting from several different pyridine derivatives of **4** (including 4-methylpyridine, 3,5-dimethylpyridine, and 4-(dimethylamino)pyridine) which indicates in **6** that pyridine is no longer bound to rhodium. The chemical shift of the hydrogen at C(2) of the quinoline ring shifts upfield from 9.1 ppm in 8-quinolinyl ethyl ketone to 10.5 ppm in **4**. In **6** this hydrogen appears at 10.04 ppm, indicating the quinoline nitrogen has not been displaced by PPh_3 and is still bonded to rhodium.

While the precise stereochemistry of **6** is unknown, the most likely position for the PPh_3 ligand is trans to the quinoline nitrogen, from both steric and electronic considerations. The precise equilibrium constant for the conversion of **4** to **6** was not measured, but ^1H NMR showed equilibrium was reached rapidly (within a few minutes at −40 °C) and **6** was favored by a ratio of better than six to one. With time, a second $^{31}P\{^1H\}$ signal appeared at 35.6 ppm with $J_{Rh-P} = 188$ Hz at the expense

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Table V. ^{103}Rh-^{31}P Coupling Constants (Hz) and (^{31}P Chemical Shifts (ppm)) at −40 °C for Intermediates in the Reductive Elimination of 4 with PPh_3 and Related Ligands

	PPh_3	$PMePh_2$	$P(p\text{-}CH_3C_6H_4)_3$	$P(p\text{-}ClC_6H_4)_3$
6	65.1 (8.3)	71.4 (−3.1)	66.0 (7.3)	64.4 (6.4)
7	188.0 (35.6)	186.2 (19.9)	187.7 (34.7)	190.0 (35.5)
8	116.3 (21.9)	139.7 (2.6)	116.5 (21.4)	129.5 (21.3)

of **6**. From the large rhodium–phosphorus coupling constant it must be a Rh(I) species,[20] to which we assign the η^2-ketone structure **7**. The $^{13}C\{^1H\}$ spectrum of **7** provides the most compelling evidence of η^2-ketone coordination. The CH_2 of the ethyl group no longer shows Rh–C or P–C coupling, appearing as a singlet at 28.9 ppm (with J_{C-H} = 120 Hz in the proton-coupled spectrum), showing that reductive elimination has taken place. Also indicative of the η^2-ketone formulation is continued nonequivalence of the CH_2 protons, which appear as multiplets at 1.3 and 1.55 ppm. However, the most compelling evidence for describing **7** as an η^2-ketone is the appearance of a $^{13}C\{^1H\}$ resonance at 99.9 ppm (d, J = 15 Hz; see Figure 2) which in the proton-coupled spectrum is not directly coupled to any protons and to which we assign the carbonyl carbon of an η^2-ketone. This resonance grows in and disappears with the other ^1H, ^{13}C, and ^{31}P resonances of **7**. Other η^2-ketone carbonyl resonances have been observed in the 69–111 ppm region,[21] while η^1-carbonyls bonded to a metal through an oxygen lone pair exhibit carbonyl ^{13}C chemical shifts within 20 ppm of their uncoordinated value.[22] Compound **7** does not persist above −10 °C under our reaction conditions. Either the η^2-bond is so weak it dissociates near −10 °C, or the pyridine present in the solution from **4** is able to displace the η^2-ketone carbonyl at this temperature.

In the presence of excess PPh_3 **7** is converted to **8** at −40 °C.[23] The clearest evidence for two trans phosphines in **8** is the Rh–P coupling constant variation in **6**, **7**, and **8** as the phosphine is changed (Table V). Since phosphorus coupling constants in metal complexes are most affected by the group trans to the phosphorus[20] and the group trans to the phosphorus does not change in **6** and **7**, the Rh–P coupling is similar for the different phosphines. However, in **8** the phosphines are trans to each other and there is a corresponding variation in J_{Rh-P} for different phosphines. In the presence of excess PPh_3 **8** is cleanly converted into $RhCl(PPh_3)_3$. 8-Quinolinyl ethyl ketone was the other product isolated at the end of the reaction. Other possible reductive elimination products were looked for spectroscopically, in particular ethyl chloride[24] and the ethyltriphenylphosphonium cation,[25] but these were never observed.

The kinetics of the reductive elimination of **6** were measured by following the disappearance of its $^{31}P\{^1H\}$ doublet at −40 °C. Under the reaction conditions of excess phosphine the observed first-order rate constant (Table VI) corresponds, within experimental error, to the rate of reductive elimination, assuming the mechanism shown in Scheme II. Considering the stability of **4** we were interested in seeing if replacement of the pyridine ligand by one triphenylphosphine was sufficient to promote reductive elimination or whether coordination of two phosphine ligands (to give the phosphine analogue of **5**) was necessary. The first-order kinetics for the conversion of **6** to **7** shows that only one phosphine is needed for reductive elimination.

Table VI. Observed First-Order Rate Constants for the Disappearance of **6** at −40 °C[a]

ligand	10^4k, s^{-1}	ligand	10^4k, s^{-1}
PPh_3	3.7	$PMePh_2$	6.6
PPh_3	3.8 (15 equiv)	$P(p\text{-}CH_3C_6H_4)_3$	3.7
PPh_3	3.6 (20 equiv)	$P(p\text{-}ClC_6H_4)_3$	1.1

[a] Ten equivalents of phosphine unless otherwise noted.

Reductive elimination from *cis*-$RhH(CH_2COCH_3)(PMe_3)_3Cl$ has been shown recently to proceed from a five-coordinate complex with three ligands in the reduction plane,[26] just as is the case with reductive elimination in **6**. For d^8 metal complexes there is theoretical justification for the observation that T-shaped cis three-coordinate metal complexes undergo facile reductive elimination.[27] It may be that the controlling factors are the same for d^8 and d^6 metal complexes and, as Milstein has suggested,[26] the ligands above and below the reduction plane in the d^6 rhodium(III) cases do not have a large influence on the course of the reaction (except to the extent they can stabilize the rhodium(I) product).

We attempted to reverse the reductive elimination and prepare **4** from **7**. The phosphorus sponge[28] $[Rh(COD)Cl]_2$ was added at −40 °C to a solution of **7** (prepared from **4** and 1 equiv of PPh_3). While the $^{31}P\{^1H\}$ resonance of **7** rapidly disappeared, no ^1H resonances corresponding to the rhodium ethyl group of **4** (or any similar rhodium–ethyl complex) appeared at −40 °C or upon warming to 25 °C. We have found subsequently that addition of the carbon–carbon bond of the ethyl ketone **10** can take place with $[RhCl(C_2H_4)_2]_2$, but temperatures above 80 °C are required.[4]

Table VI gives the observed first-order rate constants for reductive elimination with phosphines other than PPh_3. With the high concentration of phosphines used, the observed rates are dominated by the rate of reductive elimination and not by the differences in equilibrium constants for the various phosphines. The more basic phosphine $PMePh_2$ accelerates the rate of reductive elimination of **6**, while the less basic $P(p\text{-}C_6H_4Cl)_3$ slows down the rate of reductive elimination. The more rapid reductive elimination from the smaller, but more basic ligand $PMePh_2$ (relative to PPh_3) supports the idea that the reason for the instability of **6** relative to **4** is not due to the larger size of PPh_3 vs. pyridine (although this may be a factor) but rather the different electronic characteristics of the ligands. Other reductive elimination systems have exhibited analogous trends,[29] which may be expected, since electrons moving from metal–ligand bonds to ligand–ligand bonds should produce electron deficiency at the metal in the transition state. The activation parameters for PPh_3

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measured over the temperature range of −55 to −40 °C give $\Delta H^{\ddagger} = 17.3 \pm 2$ kcal/mol and $\Delta S^{\ddagger} = 0.2 \pm 4$ eu. Activation entropies close to zero have been measured for several other reductive elimination reactions.[30]

Conclusions

The reductive elimination of **4** promoted by phosphines and CO is similar to the ligand induced reductive elimination reactions of Cp_2ZrHR.[31] In both cases donors such as ethers or amines do not destabilize the higher valent metal center. Upon the addition of a donor ligand which coordinates well to the lower valent metal center, however, rapid reductive elimination takes place. With **4**, the transition state for reductive elimination appears to resemble the Rh(I) product, and, thus, the extent to which the ligands interact better with either a Rh(I) or Rh(III) center determines the stability of the acylrhodium alkyl.

The appearance of an η^2-ketone complex as an intermediate in the reductive elimination of an acylmetal alkyl is probably a specific example of a more general behavior of reductive elimination reactions with groups containing π-bonds or lone pairs. Recently Jones and Feher have shown, for example, that reductive elimination in an arylrhodium hydride complex generates a labile η^2-arene complex and a cyclopentenylrhodium hydride produces an η^2-olefin complex.[32] Unless special steric or conformational factors intervene, there should be no reason why, whenever reductive elimination generates a potential ligand, the ligand should not remain coordinated to the reduced metal fragment. Since recent work has shown C–H bonds and H_2 can serve as ligands for transition metals,[33] it seems likely that even in reductive eliminations of alkylmetal hydrides or dialkylmetal complexes, the resulting hydrocarbon can act as a weakly bound ligand to the reduced metal fragment.

Finally, reductive elimination from five-coordinate rather than six-coordinate Rh(III) complexes is beginning to look like the norm.[34] Thus, two strategies emerge for the stabilization and isolation of otherwise evanescent organometallic intermediates. Either one can use tightly binding ligands, such as PMe_3, which result in six-coordination, or one can use ligands which by their hard or soft nature favor one metal oxidation state over another.

Experimental Section

General Procedures. All operations with any Rh(I) compounds were carried out under an atmosphere of nitrogen or argon using either a Vacuum Atmospheres HE-43 drybox or Schlenk glassware. All new isolated compounds gave confirmatory combustion analyses (C, H, N) as performed by Schwartzkopf Laboratories. NMR spectra were measured on a Bruker WM250. ^1H and ^{13}C spectra are reported in parts per million vs. Me_4Si. The ^{31}P chemical shifts are referenced to H_3PO_4 by subtracting 1.2 ppm from the observed chemical shifts using external triethylphosphate as zero. No susceptibility corrections were made so the reported ^{31}P chemical shifts should be viewed as approximations, although they were reproducible under our conditions. All NMR spectra were recorded in $CDCl_3$.

Synthesis of 4. To a suspension of freshly prepared $[RhCl(C_2H_4)_2]_2$ (0.245 g, 0.63 mmol) in 20 mL of CH_2Cl_2 was added rapidly 8-quinolinecarboxaldehyde (0.204 g, 1.3 mmol) dissolved in 10 mL of CH_2Cl_2. Ethylene evolution was rapid, and in a separate experiment it was found to correspond to 1 mol/1 mol of aldehyde. A yellow solid was deposited; elemental analysis was consistent with the formula $C_{12}H_{11}ClNORh$ (0.398 g, 95%). Anal. Calcd C, 44.54; H, 3.43; N, 4.33. Found: C, 44.24; H, 3.49; N, 4.34. IR (Nujol): 1662 (s), 1498 (m), 1375 (s), 917 (s), 903 (s), 786 (s) cm^{-1}. This was insoluble in noncoordinating solvents and only darkened upon heating to 250 °C. Addition of excess pyridine and trituration with ether followed by recrystallization from CH_2Cl_2–ether gave **4**: IR ($CHCl_3$) 1640 (s), 1445 (m), 902 (s), 841 (s), 831 (s) cm^{-1}; ^1H NMR 10.54 (d, 1 H, J = 5.1 Hz, HC=N–), 7.3–8.3 (m, 5 H, quinoline), 9.06, 7.07, 6.72 (m, 5 H, pyridine), 2.13 (ddq, 1 H, J = 8, 6, 2 Hz, diastereotopic CH_2), 1.17 (ddq, 1 H, J = 8, 6, 2 Hz, diastereotopic CH_2), 0.27 (dt, 3 H, J = 8, 0.8 Hz, CH_3); ^{13}C NMR 234 (d, J_{Rh-C} = 41.6 Hz, CO), 12.7 (d, J_{Rh-C} = 26 Hz, CH_2), 11.8 (CH_3). Anal. Calcd $C_{24}H_{20}ClN_3O_{1.5}Rh$: C, 55.56; H, 5.05; N, 8.10. Found: C, 55.23; H, 4.87; N, 8.24. In the proton-coupled spectrum J_{C-H} = 130 Hz for CH_2 and J_{C-H} = 124 Hz for CH_3. **4** darkened but did not melt when heated to 250 °C. Compound **4D** was prepared from the deuterated aldehyde **1D**.[7] The ^{13}C NMR spectrum showed J_{C-D} = 19 Hz at the CH_2D group and no C–D coupling at the CH_2 group.

X-ray Crystal Structure Analysis. The crystals were grown from pyridine–ether as pale yellow prisms. The moderately air-stable prisms softened and turned red in air due to the loss of an ether of recrystallization, so the crystals were kept in the mother liquor during data collection. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement of the setting angles of 25 reflections in the range $4° < \theta < 14°$ using the computer-controlled diagonal slit method of centering. Lattice constants are summarized in Table I. There were no systematic absences; the space group was determined to be $P\bar{1}$ (no. 2).

The structure was solved by using the Patterson heavy-atom method which revealed the position of the Rh atom. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included at calculated positions (assuming idealized geometries with C–H = 0.95 Å) and were not refined. All non-hydrogen atoms were refined anisotropically. An ether molecule was located, disordered, about an inversion center. While it was poorly defined crystallographically, the NMR spectrum indicated its presence in the yellow crystals and its absence in the red, powdery solid. The structure was refined in full-matrix least squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weight w is defined as $4F_o^2/\sigma(F_o^2)$. All calculations were performed on linked PDP-11/45-11/60 computers using the Enraf-Nonius Structure Determination Package as well as private programs of the Molecular Structure Corp.

Kinetics Experiments. The first-order rate constants were obtained by measuring the disappearance of the doublet at 8.3 ppm due to **6** in the ^{31}P NMR spectrum. These were recorded by using a Bruker WM-250 NMR spectrometer equipped with a VT-1000 temperature control unit (±0.1 °C).

In a typical experiment, 15 mg (3.1×10^{-5} mol) of the rhodium complex **4** were dissolved in 1 mL of $CDCl_3$ and added to a 10-mm NMR tube. A microcell containing a $CDCl_3$ solution of $OP(OC_2H_5)_3$ (50 μL) as external reference was inserted into the NMR tube so that it just touched the solution containing **4**. A 1-mL $CDCl_3$ solution of PPh_3, 65–215 mg ($2.5–8.2 \times 10^{-4}$ mol), was pipetted into the NMR tube (above the microcell). The NMR tube was flushed with nitrogen, capped, and cooled to −60 °C. The two separate solutions, which did not mix due to the tight fit of the microcell, were thoroughly mixed at −60 °C by plunging the microcell up and down several times. The NMR tube was rapidly transferred to the cold NMR probe (−55 to −40 °C), and the spectra were recorded by using a standard Bruker kinetics microprogram. Each kinetics point corresponds to 64 FIDs (acquisition time per FID 0.819 s) with a 600-s delay between points. The half-life of **6** was on the order of 30 min at −40 °C, and the first-order plots of disappearance of **6** were linear for 3 half-lives.

The ^1H NMR of **6** at −40 °C showed: 1.8 and 2.25 (1 H each, m, diastereotopic CH_2), 1.06 (1 H, t, J = 7 Hz, CH_3), 10.04 ppm (1 H, d, J = 4 Hz, quinoline HC=N–). ^{13}C NMR: 26.05 (d of d, J_{Rh-C} = 21.1, J_{P-C} = 82.2 Hz, CH_2), 13.96 (d, J_{P-C} = 3.5 Hz, CH_3). We could not observe the acyl carbon of **6** due to its finite lifetime and limited solubility below −40 °C. **7**: ^1H NMR 1.33, 1.55 (1

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H each, m, diastereotopic CH_2), 0.95 (t, 3 H, J = 7 Hz, CH_3), 8.78 ppm (d, 1 H, J = 4 Hz, quinoline HC=N-); ^{13}C NMR 28.9 (CH_2, no P or Rh coupling, J_{C-H} = 120 Hz), 11.5 (CH_3, J_{C-H} = 127 Hz), 99.9 ppm (CO, doublet, J = 15 Hz). (No one-bond C-H coupling appeared in the proton-coupled spectrum. Some broading of the resonance occurred, but no two-bond couplings were resolved.) **8**: ^1H NMR 1.10 (t, 3 H, J = 7 Hz, CH_3), 9.22 ppm (d, 1 H, J = 4, quinoline HC=N-). **9**: ^1H NMR 8.94 (d of d, 1 H, J = 4.2, 1.8 Hz HC=N-), 8.2-7.4 (m, 5 H, quinoline ring), 3.45 (q, 2 H, J = 7.3 Hz, CH_2), 1.26 ppm (t, 3 H, J = 7.3 Hz, CH_3); ^{13}C NMR 206.9 (CO), 38.1 (CH_2), 8.5 ppm (CH_3).

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Supplementary Material Available: Tables of general temperature factor expressions (Tables A and B), table of root-mean-square amplitudes of thermal vibrations (Table C), table of torsion angles (Table D), and table of observed and calculated structure factors (Table E) (25 pages). Ordering information is given on any current masthead page.

Pyrazolyl-Bridged Iridium Dimers. 7.[1] Synthesis and Properties of Bridge-Substituted Analogues of $[Ir(COD)(\mu\text{-pz})]_2$ (pzH = Pyrazole), the "Mixed-Bridge" Complex $[Ir_2(COD)_2(\mu\text{-pz})(\mu\text{-fpz})]$ (fpzH = 3,5-Bis(trifluoromethyl)pyrazole), and the "Mixed-Metal" Dimer $[IrRh(COD)_2(\mu\text{-pz})_2]$. Crystal and Molecular Structures of Bis(cyclooctadiene)bis(μ-3-phenyl-5-methylpyrazolyl)-diiridium(I) (Dissymmetric Isomer) and Bis(cyclooctadiene)bis(μ-3,4,5-trimethylpyrazolyl)diiridium(I)

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Fifteen diiridium(I) complexes $[Ir(COD)(\mu\text{-L})]_2$ (**2**-**16**) (COD = cycloocta-1,5-diene) related to the prototypal compound $[Ir(COD)(\mu\text{-pz})]_2$ (**1**, pzH = pyrazole) have been synthesized by Cl displacement by LH from $[Ir(COD)(\mu\text{-Cl})]_2$ (L = 4-methylpyrazolyl (**2**), 3-methylpyrazolyl (**3**), 3,5-dimethylpyrazolyl (**4**), 3,5-diphenylpyrazolyl (**5**), 3-phenyl-5-methylpyrazolyl (**6**), 3-(trifluoromethyl)-5-methylpyrazolyl (**7**), 3,5-bis(trifluoromethyl)pyrazolyl (**8**), 3,4,5-trimethylpyrazolyl (**9**), 3,5-dimethyl-4-bromopyrazolyl (**10**), indazolyl (**11**), 3-(heptafluoropropyl)-5-*tert*-butylpyrazolyl (**12**), 3-(trifluoromethyl)-5-phenylpyrazolyl (**13**), 4-chloropyrazolyl (**14**), 4-iodopyrazolyl (**15**), and 4-nitropyrazolyl (**16**)). The products have been characterized by ^1H and ^{13}C NMR spectroscopy and UV/visible absorption spectrophotometry and have been subjected to study by cyclic voltammetry. Among complexes incorporating unsymmetrically substituted bridging ligands, dimers **3**, **7** and **11** exist as diastereoisomeric mixtures, while for **6** one diastereomer predominates and **12** and **13** appear to be formed as single isomers. The predominant diastereomer of compound **6** has been identified as the dissymmetric isomer (C_2 molecular symmetry); monoclinic, of space group $P2_1/n$ with a = 13.690 (4) Å, b = 14.617 (4) Å, c = 15.749 (10) Å, and β = 96.42 (4)°, in which the Ir_2 separation = 3.079 (2) Å. Intramolecular nonbonding approach to within 2.2 Å of hydrogen atoms attached to opposing terminal COD ligands has been identified in crystals of compound **9**, triclinic, of space group $P\bar{1}$, a = 11.116 (4) Å, b = 13.502 (5) Å, c = 11.006 (4) Å, α = 105.45 (4)°, β = 62.16 (3)°, and γ = 110.07 (4)°, in which the Ir_2 separation is 3.096 (1) Å. A marked increase in $E_{1/2}$ is observed compared with the parent compound **1** accompanying either 3,5 or 4 substitution with electron-withdrawing groups (CF_3 or NO_2) of the bridging pyrazolyl unit. Synthesis of the "mixed-bridge" analogue $[Ir(COD)(\mu\text{-pz})(\mu\text{-fpz})Ir(COD)]$ (**17**) and of the "mixed-metal" complex $[RhIr(COD)_2(\mu\text{-pz})_2]$ (**18**) is described, and stability and NMR properties of both these products are reported.

We are investigating the chemistry of compounds related to the pyrazolyl-bridged diiridium(I) complex $[Ir(COD)(\mu\text{-pz})]_2$ (**1**, COD = cycloocta-1,5-diene, pzH = pyrazole) as a model for electronic communication between

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