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# Reversible Dehydrogenation of a Heterobimetallic Polyhydride Compound

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Li[$RuH_3(PPh_3)_3$] reacts with $[Ir(COD)Cl]_2$ to form a kinetic product, $(COD)Ir(\mu\text{-}H)_3Ru(PPh_3)_3$, which then isomerizes to $(COD)Ir(\mu\text{-}H)_2RuH(PPh_3)_3$ (1) as the thermodynamic product. The phosphines in this structure have the *mer* configuration. The ortho phenyl protons of the trans phosphine of 1 show temperature-dependent $^1H$ NMR behavior which may be related to subsequent reactivity observed at these positions. In solution at room temperature, 1 is in equilibrium with free $H_2$ and a dehydrogenated species. Upon removal of $H_2$, a new species (2) is formed. When 2 is placed under $H_2$, it reverts to 1, demonstrating the reversibility of this transformation. Spectroscopic data, as well as labeling studies, suggest that 2 contains a phosphine ortho metalated to ruthenium. The $\pi$-cloud of the ortho-metalated phenyl ring may play a role in donation to iridium. Crystal data for 1 (at −172 °C): $a = 21.150$ (8) Å, $b = 22.186$ (6) Å, $c = 12.638$ (3) Å, $\alpha = 91.55$ (1)°, $\beta = 90.85$ (1)°, $\gamma = 111.71$ (1)° with $Z = 4$ in space group $P\bar{1}$.

## Introduction

Transition-metal polyhydrides are involved in a variety of stoichiometric and catalytic transformations.[1] The coordinative saturation of such compounds has limited their applicability under very mild conditions, and we have therefore investigated various means to create, under mild conditions, an open coordination site for the binding of a potential substrate. These methods include photolysis (which can lead to loss of either $H_2$ or phosphine)[2] and protonation (with subsequent loss of $H_2$).[3] As an alternative approach to the creation of an open coordination site, we have initiated efforts to incorporate a second unsaturated metal center into these molecules.[4] The preference of the hydride ligand to bridge two metals provides a natural means for holding two metals together.[5] Several hydride-bridged bimetallic molecules have been characterized by the group of Venanzi,[5] as well as others.[6] In addition to serving as a potential substrate binding site, the presence of a second metal offers the additional advantage of possible cooperativity between the two adjacent metal centers. Such cooperativity could prove helpful in the reduction of dipolar substrates such as $CO_2$ or CO. While many heterobimetallics are known,[7] few have shown such reactivity, possibly due to the absence of reducing hydride ligands. Efforts have been made to introduce $H_2$ into preformed bimetallic molecules.[8] The synthetic strategy we have employed to make heterobimetallic polyhydride compounds involves the salt elimination reaction between an anionic transition-metal polyhydride[9] and an unsaturated organometallic halide. The synthesis, characterization, and reversible dehydrogenation of one such molecule are reported here.

## Experimental Section

All manipulations were carried out using standard Schlenk and glovebox procedures under prepurified nitrogen. Bulk solvents (toluene, hexane) were dried and deoxygenated over sodium or potassium benzophenone and subjected to three freeze–pump–thaw cycles prior to use. Deuterated solvents were dried (benzene and toluene over sodium/potassium alloy and methylene chloride over $P_2O_5$) and vacuum-transferred prior to use. Tris(2,6-dideuteriophenyl)phosphine ($PPh_3'$) was received as a generous gift from Ulrich Klabunde (Du Pont Central Research) and sublimed prior to use. $^1H$, $^2H$, and $^{31}P$ NMR spectra were recorded on a Nicolet NT-360 spectrometer operating at 360, 55, and 146 MHz, respectively. $^{13}C$ NMR spectra were recorded on a Bruker AM-500 spectrometer operating at 125 MHz. Li[$RuH_3(PPh_3)_3$][10] and $[Ir(COD)Cl]_2$[11] (COD = 1,5-cyclooctadiene) were prepared according to literature procedures. Infrared spectra were recorded as Nujol mulls on a Nicolet 510P FTIR spectrometer.

**Synthesis of $(COD)Ir(\mu\text{-}H)_3Ru(PPh_3)_3$.** To a slurry of Li[$RuH_3(PPh_3)_3$] (0.100 g, 0.11 mmol) in 20 mL of toluene was added solid $[Ir(COD)Cl]_2$ (0.037 g, 0.055 mmol). After it was stirred for 10 min, the resulting burgundy solution was filtered through a frit of medium porosity to remove LiCl. $^1H$ NMR (360 MHz, 25 °C, $C_6D_6$): $\delta$ −8.2 (AA'A''XX'X'', 3 H), 1.63 (m, $CH_2$ COD, 4 H), 2.35 (m, $CH_2$ COD, 4 H), 4.20 (s, vinyl COD, 4 H), 7.0–7.5 (m, phenyl H). $^{31}P\{^1H\}$ NMR (146 MHz, 25 °C, $C_6D_6$): $\delta$ 72.8 (s, 3 P).

**Synthesis of $(COD)Ir(\mu\text{-}H)_2RuH(PPh_3)_3$ (1).** When it stands, a solution of $(COD)Ir(\mu\text{-}H)_3Ru(PPh_3)_3$ isomerizes ($t_{1/2}$ = 10 min) to give $(COD)Ir(\mu\text{-}H)_2RuH(PPh_3)_3$ (1). $^1H$ NMR spectra (360 MHz, 25 °C, $C_6D_6$), including selective decoupling studies, reveal the following: $\delta$ −10.7 (dt, $J_P = J_{P'} = 17$ Hz, 1 H), −9.5 (dt,

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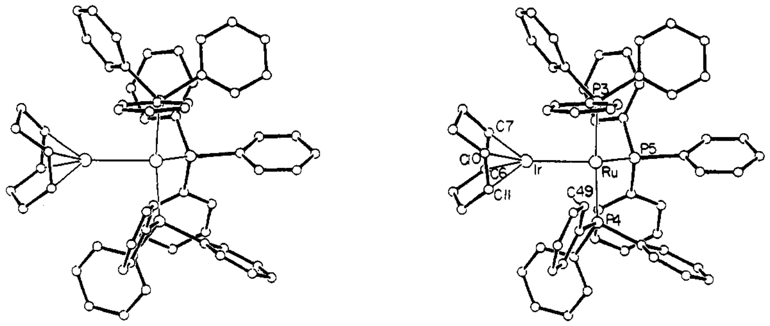

**Figure 1.** Stereo ORTEP drawing of the non-hydrogen atoms of $(COD)Ir(H)_2RuH(PPh_3)_3$, showing selected atom labeling. The hydride hydrogens are suggested to lie in a horizontal plane perpendicular to the plane of the paper, and this plane contains atoms Ru and Ir.

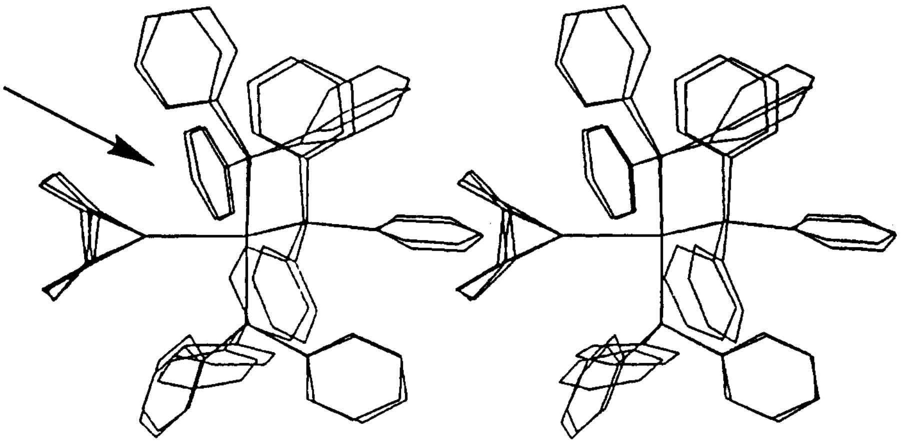

**Figure 2.** Stereo drawing of a superposition of the two crystallographically independent molecules of $(COD)Ir(H)_2RuH(PPh_3)_3$. The arrow designates the phenyl ring which is "prepared" for ortho metalation.

$J_P$ = 14 Hz, $J_{P'}$ = 42 Hz, 1 H), -3.6 (dt, $J_P$ = 4.4 Hz, $J_{P'}$ = 8.8 Hz, 1 H), 1.17 (m, $CH_2$ COD, 2 H), 1.47 (m, $CH_2$ COD, 2 H), 1.81 (m, $CH_2$ COD, 4 H), 3.27 (s, vinyl COD, 2 H), 4.41 (s, vinyl COD, 2 H), 6.77 (t, phenyl H), 6.98 (m, phenyl H), 7.04 (t, phenyl H), 7.23 (t, phenyl H), 7.65 (br s, phenyl H). $^{31}P\{^1H\}$ NMR (146 MHz, 25 °C, $C_6D_6$): $\delta$ 52.1 (d, $J_{P-P}$ = 27 Hz, 2 P), 70.0 (t, $J_{P-P}$ = 27 Hz, 1 P). $^{13}C\{^1H\}$ NMR (125 MHz, 25 °C, $CD_2Cl_2$): $\delta$ 31.1 (s, aliphatic COD, 2 C), 32.5 (s, aliphatic COD, 2 C), 64.1 (s, olefinic COD, 2 C), 65.5 (s, olefinic COD, 2 C), 127.1 (s, phenyl C), 128.5 (s, phenyl C), 134.6 (d, phenyl C), 135.0 (s, phenyl C), 140.0 (s, phenyl C). IR: 1823 $cm^{-1}$ ($\nu_{Ru-H}$). Anal. Calcd for $C_{62}H_{60}IrRuP_3\cdot 1.5CH_2Cl_2$: C, 58.68; H, 4.86. Found: C, 58.15; H, 4.80. Compound 1 was prepared on a larger scale as follows: To a slurry of 2.0 g of $LiRuH_3(PPh_3)_3$ (2.22 mmol) in 50 mL of toluene was added 0.736 g of $[Ir(COD)Cl]_2$ (1.10 mmol). After it was stirred for 3 h, the burgundy-colored solution was filtered to remove LiCl. The solution volume was reduced to 10 mL and 40 mL hexane added to precipitate the product as an orange powder, which was collected by filtration (yield 1.71 g, 65%).

**X-ray Structure Determination of $(COD)Ir(\mu\text{-}H)_2RuH(PPh_3)_3$.** A crystal of suitable size (grown from a saturated solution in $CH_2Cl_2$) was selected in a nitrogen atmosphere glovebag. The crystal was transferred to the goniostat, where it was cooled to -172 °C for characterization[12] and data collection. A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which exhibited no symmetry (other than $\bar{1}$) or systematic extinctions. The choice of the triclinic, centrosymmetric space group $P\bar{1}$ was confirmed by the successful solution and refinement of the structure. Unit cell dimensions were determined using 39 reflections having 19° < $2\theta$ < 36°. Data collection (6° ≤ $2\theta$ ≤ 45°) was undertaken as detailed in Table I. From the usual data processing[12] and averaging of equivalent reflections, a unique set of 14 462 reflections was obtained. The $R$ value for averaging was 0.049 for 2868 redundant data. A plot of the four standard reflections measured every 400 reflections showed no systematic trends. A correction for absorption was carried out.

**Table I. Crystallographic Data for $(C_8H_{12})IrH_3Ru(PPh_3)_3\bullet 1.5CH_2Cl_2$**

| | |
|---|---|
| chemical formula | $C_{62}H_{60}IrP_3Ru\cdot 1.5CH_2Cl_2$ |
| $a$, Å | 21.150 (8) |
| $b$, Å | 22.186 (6) |
| $c$, Å | 12.638 (3) |
| $\alpha$, deg | 91.55 (1) |
| $\beta$, deg | 90.85 (1) |
| $\gamma$, deg | 111.71 (1) |
| $V$, Å$^3$ | 5505.16 |
| $Z$ | 4 |
| fw | 2637.53 |
| space group | $P\bar{1}$ |
| $T$, °C | -172 |
| $\lambda$, Å | 0.71069 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.591 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 29.5 |
| $R$ | 0.0630 |
| $R_w$ | 0.0664 |

The structure was solved using the usual combination of direct methods and Fourier techniques. The Ir and Ru atoms were located in the initial $E$ map, and the remaining non-hydrogen atoms were revealed in successive Fourier iterations. The asymmetric unit contains two Ir–Ru molecules as well as three molecules of $CH_2Cl_2$, for a total of 143 non-hydrogen atoms. The full-matrix least-squares refinement was completed in a cyclical manner; all non-hydrogen atoms were refined using anisotropic thermal parameters, except for C(32) in molecule 1. This atom behaved in an abnormal manner throughout the refinement, and in the final cycles it was assigned an isotropic thermal parameter. No hydrogen atoms were introduced in calculated positions. The final difference map contains two rather large residuals of 4.21 and 2.47 e/Å$^3$ near the abnormal atom C(32), perhaps an indication of some disorder. There is no evidence of the hydride atoms. The results of the structure determination are shown in Tables II and III and Figures 1 and 2.

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**Table II. Fractional Coordinates[a] and Isotropic Thermal Parameters[b] for $(C_8H_{12})IrH_3Ru(PPh_3)_3 \bullet 1.5CH_2Cl_2$**

| | *x* | *y* | *z* | 10$B_{iso}$, Å$^2$ | | *x* | *y* | *z* | 10$B_{iso}$, Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| Ir(1) | 7781.9 (2) | 1530.5 (2) | 3140.9 (3) | 15 | C(6)′ | 9066 (5) | 8367 (5) | 2135 (9) | 20 |
| Ru(2) | 7222.9 (4) | 1851.0 (4) | 4782 (1) | 13 | C(7)′ | 8858 (5) | 7712 (5) | 2443 (8) | 14 |
| P(3) | 7163 (1) | 904 (1) | 5589 (2) | 14 | C(8)′ | 8630 (6) | 7469 (6) | 3545 (8) | 22 |
| P(4) | 6790 (1) | 2436 (1) | 3680 (2) | 17 | C(9)′ | 8089 (6) | 7732 (5) | 3968 (8) | 18 |
| P(5) | 7602 (1) | 2561 (1) | 6226 (2) | 13 | C(10)′ | 7657 (5) | 7833 (5) | 3055 (8) | 16 |
| C(6) | 8711 (5) | 1912 (5) | 2258 (8) | 19 | C(11)′ | 7803 (6) | 8433 (5) | 2554 (8) | 19 |
| C(7) | 8709 (5) | 1383 (6) | 2870 (9) | 23 | C(12)′ | 8410 (6) | 9043 (5) | 2874 (8) | 23 |
| C(8) | 8586 (6) | 711 (6) | 2444 (10) | 26 | C(13)′ | 9091 (6) | 8934 (5) | 2904 (9) | 22 |
| C(9) | 7938 (6) | 443 (6) | 1689 (10) | 26 | C(14)′ | 6861 (6) | 5541 (5) | −611 (8) | 19 |
| C(10) | 7409 (6) | 734 (5) | 2001 (9) | 21 | C(15)′ | 7035 (6) | 5008 (5) | −423 (9) | 24 |
| C(11) | 7356 (6) | 1285 (5) | 1570 (8) | 20 | C(16)′ | 6909 (6) | 4511 (6) | −1171 (9) | 25 |
| C(12) | 7841 (6) | 1695 (7) | 739 (9) | 30 | C(17)′ | 6624 (6) | 4542 (6) | −2158 (9) | 26 |
| C(13) | 8601 (6) | 1846 (6) | 1049 (9) | 29 | C(18)′ | 6433 (5) | 5069 (5) | −2361 (8) | 19 |
| C(14) | 6825 (5) | 783 (5) | 6927 (8) | 19 | C(19)′ | 6562 (5) | 5575 (5) | −1586 (8) | 20 |
| C(15) | 7078 (6) | 473 (5) | 7715 (8) | 21 | C(20)′ | 7559 (6) | 5984 (5) | 1339 (8) | 18 |
| C(16) | 6828 (6) | 418 (6) | 8736 (9) | 23 | C(21)′ | 8266 (6) | 6198 (5) | 1310 (8) | 21 |
| C(17) | 6324 (6) | 663 (5) | 9009 (8) | 23 | C(22)′ | 8638 (8) | 5968 (6) | 1997 (9) | 33 |
| C(18) | 6073 (6) | 953 (6) | 8238 (9) | 24 | C(23)′ | 8303 (8) | 5518 (6) | 2752 (9) | 32 |
| C(19) | 6318 (5) | 1016 (5) | 7221 (8) | 17 | C(24)′ | 7584 (7) | 5312 (6) | 2799 (9) | 31 |
| C(20) | 7919 (6) | 682 (5) | 5698 (8) | 19 | C(25)′ | 7214 (7) | 5530 (5) | 2109 (9) | 31 |
| C(21) | 8564 (5) | 1186 (5) | 5673 (8) | 17 | C(26)′ | 6319 (6) | 6162 (5) | 967 (9) | 18 |
| C(22) | 9155 (6) | 1042 (6) | 5755 (8) | 24 | C(27)′ | 6358 (7) | 6424 (6) | 1999 (10) | 31 |
| C(23) | 9119 (6) | 397 (6) | 5804 (8) | 22 | C(28)′ | 5778 (7) | 6431 (6) | 2512 (11) | 35 |
| C(24) | 8480 (6) | −100 (6) | 5816 (9) | 25 | C(29)′ | 5153 (7) | 6176 (6) | 1990 (11) | 36 |
| C(25) | 7885 (6) | 38 (6) | 5776 (9) | 27 | C(30)′ | 5090 (7) | 5892 (6) | 961 (11) | 35 |
| C(26) | 6543 (6) | 170 (5) | 4905 (8) | 19 | C(31)′ | 5687 (6) | 5894 (5) | 455 (9) | 24 |
| C(27) | 6779 (6) | −147 (5) | 4089 (9) | 24 | C(32)′ | 7021 (5) | 8253 (5) | −2156 (8) | 18 |
| C(28) | 6311 (7) | −712 (6) | 3573 (10) | 31 | C(33)′ | 7384 (7) | 8272 (6) | −3065 (9) | 27 |
| C(29) | 5626 (7) | −938 (6) | 3832 (10) | 35 | C(34)′ | 7104 (6) | 8299 (5) | −4090 (9) | 25 |
| C(30) | 5412 (7) | −642 (7) | 4624 (11) | 36 | C(35)′ | 6468 (7) | 8301 (7) | −4154 (10) | 38 |
| C(31) | 5877 (6) | −81 (6) | 5172 (9) | 27 | C(36)′ | 6102 (8) | 8300 (10) | −3283 (12) | 56 |
| C(32) | 6408 (4) | 2690 (4) | 4322 (7) | 3 | C(37)′ | 6370 (7) | 8253 (8) | −2270 (11) | 42 |
| C(33) | 6645 (6) | 3549 (6) | 4601 (8) | 21 | C(38)′ | 8089 (5) | 9062 (5) | −773 (8) | 13 |
| C(34) | 6287 (7) | 3899 (6) | 5100 (10) | 32 | C(39)′ | 8135 (6) | 9530 (5) | −1494 (8) | 19 |
| C(35) | 5592 (8) | 3585 (8) | 5316 (10) | 40 | C(40)′ | 8668 (5) | 10147 (5) | −1388 (9) | 19 |
| C(36) | 5267 (6) | 2945 (7) | 5039 (9) | 29 | C(41)′ | 9133 (5) | 10293 (5) | −553 (9) | 19 |
| C(37) | 5622 (7) | 2582 (7) | 4533 (9) | 31 | C(42)′ | 9076 (5) | 9812 (5) | 175 (9) | 19 |
| C(38) | 7290 (6) | 3043 (5) | 2727 (8) | 21 | C(43)′ | 8559 (5) | 9207 (5) | 75 (8) | 17 |
| C(39) | 7031 (7) | 3482 (5) | 2294 (9) | 25 | C(44)′ | 6755 (5) | 8355 (5) | −5 (8) | 16 |
| C(40) | 7394 (7) | 3914 (6) | 1538 (9) | 31 | C(45)′ | 6777 (6) | 8994 (5) | 228 (9) | 23 |
| C(41) | 8033 (7) | 3921 (6) | 1211 (9) | 32 | C(46)′ | 6242 (6) | 9063 (6) | 789 (10) | 30 |
| C(42) | 8295 (7) | 3490 (6) | 1678 (9) | 31 | C(47)′ | 5699 (6) | 8522 (6) | 1124 (9) | 24 |
| C(43) | 7922 (6) | 3054 (6) | 2423 (9) | 22 | C(48)′ | 5695 (6) | 7899 (6) | 907 (9) | 26 |
| C(44) | 6105 (6) | 1861 (5) | 2794 (8) | 19 | C(49)′ | 6225 (5) | 7827 (5) | 342 (8) | 19 |
| C(45) | 5951 (7) | 2045 (6) | 1799 (10) | 35 | C(50)′ | 8642 (5) | 6627 (5) | −1434 (8) | 16 |
| C(46) | 5437 (8) | 1612 (6) | 1142 (11) | 42 | C(51)′ | 8387 (6) | 5953 (6) | −1518 (9) | 23 |
| C(47) | 5062 (6) | 993 (6) | 1472 (10) | 31 | C(52)′ | 8771 (7) | 5603 (6) | −1106 (9) | 27 |
| C(48) | 5226 (7) | 786 (6) | 2422 (11) | 39 | C(53)′ | 9393 (7) | 5934 (6) | −620 (10) | 29 |
| C(49) | 5749 (6) | 1231 (6) | 3081 (10) | 31 | C(54)′ | 9660 (6) | 6619 (6) | −563 (9) | 25 |
| C(50) | 8325 (5) | 2467 (5) | 6967 (8) | 17 | C(55)′ | 9276 (6) | 6962 (6) | −950 (8) | 22 |
| C(51) | 8185 (6) | 2017 (5) | 7776 (8) | 18 | C(56)′ | 8737 (5) | 7814 (5) | −2358 (7) | 11 |
| C(52) | 8700 (6) | 1884 (6) | 8269 (8) | 21 | C(57)′ | 8891 (5) | 7856 (5) | −3438 (9) | 18 |
| C(53) | 9383 (6) | 2219 (6) | 7998 (9) | 26 | C(58)′ | 9359 (5) | 8422 (5) | −3818 (8) | 20 |
| C(54) | 9527 (6) | 2675 (5) | 7212 (9) | 22 | C(59)′ | 9686 (6) | 8961 (5) | −3142 (9) | 22 |
| C(55) | 8993 (6) | 2795 (5) | 6679 (9) | 21 | C(60)′ | 9538 (5) | 8918 (6) | −2055 (9) | 20 |
| C(56) | 7977 (5) | 3418 (5) | 5916 (9) | 18 | C(61)′ | 9069 (5) | 8343 (5) | −1678 (8) | 15 |
| C(57) | 7880 (6) | 3923 (5) | 6530 (9) | 20 | C(62)′ | 7641 (5) | 6656 (5) | −3020 (8) | 16 |
| C(58) | 8156 (7) | 4557 (5) | 6243 (9) | 27 | C(63)′ | 7025 (6) | 6713 (5) | −3298 (8) | 19 |
| C(59) | 8553 (6) | 4718 (6) | 5335 (9) | 27 | C(64)′ | 6673 (6) | 6421 (6) | −4257 (9) | 25 |
| C(60) | 8667 (7) | 4244 (6) | 4718 (10) | 31 | C(65)′ | 6948 (6) | 6082 (6) | −4925 (9) | 27 |
| C(61) | 8367 (5) | 3598 (5) | 4996 (8) | 20 | C(66)′ | 7571 (6) | 6014 (5) | −4637 (9) | 27 |
| C(62) | 7036 (5) | 2611 (5) | 7297 (8) | 15 | C(67)′ | 7917 (6) | 6314 (5) | −3704 (8) | 19 |
| C(63) | 6375 (5) | 2524 (5) | 7008 (9) | 17 | Cl(135) | 9875 (2) | 3706 (2) | 3225 (3) | 44 |
| C(64) | 5927 (5) | 2602 (5) | 7783 (8) | 14 | C(136) | 9965 (7) | 3065 (7) | 3986 (12) | 42 |
| C(65) | 6148 (5) | 2734 (5) | 8835 (8) | 18 | Cl(137) | 10529 (2) | 3429 (2) | 5073 (3) | 43 |
| C(66) | 6804 (5) | 2818 (5) | 9134 (9) | 19 | Cl(138) | 327 (2) | 4978 (2) | 7991 (3) | 47 |
| C(67) | 7254 (5) | 2757 (5) | 8364 (8) | 16 | C(139) | −511 (8) | 4455 (8) | 7712 (13) | 55 |
| Ir(1)′ | 8063.7 (2) | 7797.3 (2) | 1508.6 (3) | 11 | Cl(140) | −908 (2) | 4041 (2) | 8847 (3) | 43 |
| Ru(2)′ | 7556.6 (4) | 7288.1 (4) | −358 (1) | 10 | Cl(141) | 5077 (4) | 4316 (4) | 2609 (6) | 108 |
| P(3)′ | 7113 (1) | 6254 (1) | 317 (2) | 16 | C(142) | 4817 (16) | 3498 (12) | 2316 (21) | 111 |
| P(4)′ | 7409 (1) | 8234 (1) | −849 (2) | 12 | Cl(143) | 5369 (5) | 3405 (5) | 1316 (6) | 144 |
| P(5)′ | 8094 (1) | 7085 (1) | −1801 (2) | 13 | | | | | |

[a] Fractional coordinates are ×10$^4$. Primes indicate atoms in the second independent molecule. [b] Isotropic values for those atoms refined anisotropically are calculated using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

**Table III. Selected Bond Distances (Å) and Angles (deg) for (COD)IrH$_3$Ru(PPh$_3$)$_3$**

| | molecule 1 | molecule 2 |
|---|---|---|
| Ir(1)–Ru(2) | 2.6114 (6) | 2.6227 (11) |
| Ir(1)–C(6) | 2.170 (10) | 2.151 (10) |
| Ir(1)–C(7) | 2.134 (11) | 2.107 (10) |
| Ir(1)–C910) | 2.149 (10) | 2.158 (10) |
| Ir(1)–C(11) | 2.139 (10) | 2.130 (10) |
| Ru(2)–P(3) | 2.3228 (27) | 2.327 (3) |
| Ru(2)–P(4) | 2.324 (3) | 2.331 (3) |
| Ru(2)–P(5) | 2.3071 (27) | 2.2842 (27) |
| C(6)–C(7) | 1.422 (16) | 1.420 (15) |
| C(6)–C(13) | 1.537 (15) | 1.554 (15) |
| C(7)–C(8) | 1.500 (16) | 1.526 (14) |
| C(8)–C(9) | 1.572 (17) | 1.559 (15) |
| C(9)–C(10) | 1.533 (16) | 1.533 (15) |
| C(10)–C(11) | 1.394 (16) | 1.420 (15) |
| C(11)–C(12) | 1.542 (16) | 1.521 (15) |
| C(12)–C(13) | 1.556 (17) | 1.546 (17) |
| Ru(2)–Ir(1)–C(6) | 139.2 (3) | 135.0 (3) |
| Ru(2)–Ir(1)–C(7) | 135.3 (3) | 131.29 (28) |
| Ru(2)–Ir(1)–C(10) | 132.0 (3) | 135.6 (3) |
| Ru(2)–Ir(1)–C(11) | 127.2 (3) | 130.9 (3) |
| C(6)–Ir(1)–C(10) | 88.7 (4) | 89.4 (4) |
| C(6)–Ir(1)–C(11) | 80.9 (4) | 81.2 (4) |
| C(7)–Ir(1)–C(10) | 80.9 (4) | 81.0 (4) |
| C(7)–Ir(1)–C(11) | 97.5 (4) | 97.8 (4) |
| Ir(1)–Ru(2)–O(3) | 90.05 (5) | 91.33 (8) |
| Ir(1)–Ru(2)–O(4) | 88.89 (7) | 92.10 (7) |
| Ir(1)–Ru(2)–P(5) | 135.80 (7) | 129.55 (8) |
| P(3)–Ru(2)–P(4) | 152.47 (8) | 149.66 (10) |
| P(3)–Ru(2)–P(5) | 98.61 (9) | 99.98 (10) |
| P(4)–Ru(2)–P(5) | 101.25 (10) | 100.92 (10) |

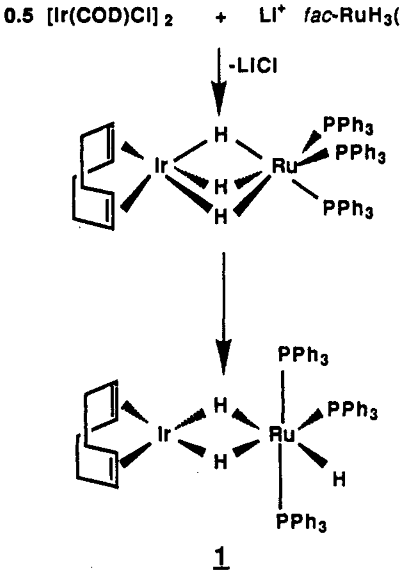
**Synthesis of 1-*d*$_{21}$.** This compound was prepared as above from [Ir(COD)Cl]$_2$ and Li[RuD$_3$(PPh$_3$')$_3$], where PPh$_3$' = tris(2,6-dideuteriophenyl)phosphine. Li[RuD$_3$(PPh$_3$')$_3$] was prepared from RuCl$_2$(PPh$_3$')$_3$ according to the method of Chan[10] with LiBEt$_3$D used in place of LiBEt$_3$H. RuCl$_2$(PPh$_3$')$_3$ was prepared from commercially available ruthenium trichloride hydrate and PPh$_3$'.[13a] IR: 1283 cm$^{-1}$ ($\nu_{Ru-D}$).

**Synthesis of (COD)IrH$_2$Ru{PPh$_2$(C$_6$H$_4$)}(PPh$_3$)$_2$ (2).** To a solution of 1 (0.5 g, 0.4 mmol) in 10 mL of toluene was added a 5-fold excess (0.27 mL, 2.1 mmol) of 3,3-dimethyl-1-butene. The solution was heated to 60 °C for 6 h, after which the solvent was removed under vacuum. Washing the crude product once with hexane yielded a light orange powder (yield 0.46 g, 92%). $^1$H NMR spectra (360 MHz, 25 °C, C$_6$D$_6$), including selective decoupling studies, reveal the following: $\delta$ −3.4 (ddd, $J_{P_a}$ = 4.4 Hz, $J_{P_b}$ = $J_{P_c}$ = 8.8 Hz, 1 H), −7.0 (ddd, $J_{P_a}$ = $J_{P_b}$ = $J_{P_c}$ = 17 Hz, 1 H), 0.50 (m, C$H_2$ COD, 1 H), 1.15 (m, C$H_2$ COD, 1 H), 1.52 (m, C$H_2$ COD, 2 H), 1.85 (m, C$H_2$ COD, 1 H), 2.15 (m, C$H_2$ COD, 1 H), 2.53 (m, C$H_2$ COD, 1 H), 2.79 (m, C$H_2$ COD, 1 H), 2.62 (s, vinylic COD, 1 H), 3.79 (s, vinylic COD, 1 H), 4.26 (s, vinylic COD, 1 H), 5.61 (s, vinylic COD, 1 H), 6.07 (t, phenyl H), 6.26 (t, phenyl H), 6.72–7.15 (m, phenyl H), 7.45 (m, phenyl H, 7.74 (t, phenyl H), 8.17 (t, phenyl H). $^{31}$P{$^1$H} NMR (146 MHz, 25 °C, C$_6$D$_6$): $\delta$ 4.7 (dd, $J$ = 32 Hz, $J$ = 242 Hz, 1 P), 62.0 (dd, $J$ = 24 Hz, $J$ = 242 Hz, 1 P), 86.8 (dd, $J$ = 24 Hz, $J$ = 32 Hz, 1 P). $^{13}$C{$^1$H} NMR (125 MHz, 25 °C, CH$_2$Cl$_2$): $\delta$ 30.7 (s, $C$H$_2$ COD, 1 C), 31.0 (s, $C$H$_2$ COD, 1 C), 32.6 (s, $C$H$_2$ COD, 1 C), 32.8 (s, $C$H$_2$ COD, 1 C), 54.0 (s, vinylic COD, 1 C), 67.3 (s, vinylic COD, 1 C), 67.8 (s, vinylic COD, 1 C), 68.4 (s, vinylic COD, 1 C), 117.3 (d, phenyl C), 127–129 (m, phenyl C), 133.5 (d, phenyl C), 134.3 (d, phenyl C), 134.8 (d, phenyl C), 137.6 (d, phenyl C), 142.1 (d, phenyl C), 146.4 (d, phenyl C), 154.3 (m, phenyl C).

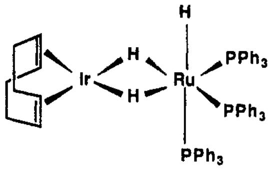
## Results

**Synthesis and Characterization of the Isomeric Heterobimetallic Compounds.** The reaction of [Ir(COD)Cl]$_2$ with Li[RuH$_3$(PPh$_3$)$_3$] (Ir:Ru ratio of 1:1) results initially in the formation of a kinetic product formulated as (COD)Ir($\mu$-H)$_3$Ru(PPh$_3$)$_3$. This product exhibits a single hydride chemical shift with a characteristic[13b] second-order AA'A''XX'X'' multiplet structure. The $^{31}$P{$^1$H} NMR spectrum displays one resonance indicative of three chemically equivalent phosphorus atoms. When this reaction was performed in an NMR tube and the solution immediately frozen, both the $^{31}$P{$^1$H} and $^1$H NMR spectra recorded at −80 °C were unchanged from the room-temperature spectra. This result tends to rule out a less symmetric but fluxional structure such as A for the kinetic product. At 25 °C in solution, this kinetic product undergoes isomerization with a half-life of 10 min to give (COD)Ir($\mu$-H)$_2$RuH(PPh$_3$)$_3$ (1) as the thermodynamic product (Scheme I).

**Scheme I**



1



A

The structure for 1 has been confirmed by a single-crystal X-ray diffraction study (Figure 1 and supplementary material). The unit cell contains two independent molecules of (COD)Ir($\mu$-H)$_2$RuH(PPh$_3$)$_3$ as well as three noninteracting CH$_2$Cl$_2$ solvent molecules. For the purpose of the following discussion, the bond lengths and angles of one of the bimetallic units have been chosen, since the two independent molecules are virtually identical. A drawing of both molecules superimposed is shown in Figure 2. The structural study shows that each metal in 1 retains the geometry present in the respective monometallic starting materials, i.e., square planar for Ir$^I$ and octahedral for Ru$^{II}$. The molecule possesses an approximate mirror plane of symmetry containing both metal atoms and the unique phosphorus. The angles around iridium sum to 360.0°; iridium is thus coplanar with ruthenium and the two COD olefinic midpoints. The average iridium to olefinic carbon distance of 2.141 Å is somewhat longer than the value of 2.086 Å found in [Ir(COD)Cl]$_2$.[14] The two trans phosphines are each bent by 15° from

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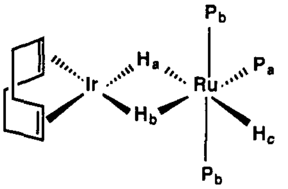
(13) (a) Wilkinson, G.; Stephenson, T. *J. Inorg. Nucl. Chem.* **1966**, *28*, 945. (b) *Transition Metal Hydrides*; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; p 80.

(14) Cotton, F. A.; Lahnerta, P.; Sanau, M.; Schwotzer, W. *Inorg. Chim. Acta* **1980**, *120*, 153.

**Chart I**



$^1$H NMR
H$_a$ d=-3.6 d of t $J_{Pa}$=4.4Hz
$J_{Pb}$=8.8Hz
H$_b$ d=-9.5 d of t $J_{Pa}$=42Hz
$J_{Pb}$=14Hz
H$_c$ d=-10.7 d of t $J_{Pa}$=17Hz
$J_{Pb}$=17Hz

1

idealized octahedral geometry due to steric repulsion caused by the unique phosphine. The ruthenium to unique phosphorus distance of 2.284 Å is slightly shorter than the average Ru–P distance of 2.330 Å for the two trans phosphorus atoms. Both values are quite similar to the average Ru–P distance of 2.323 Å found in K[*fac*-RuH$_3$(PPh$_3$)$_3$].[10] The Ru–Ir distance is 2.623 Å, while the sum of the atomic radii[15] of Ru and Ir is 2.69 Å.

The $^{31}$P{$^1$H} NMR spectrum of 1 is an AB$_2$ pattern at both −80 °C and +80 °C, consistent with a mirror plane of symmetry being present in solution. This conclusion is supported by the resolution of five of the six $^1$H NMR chemical shifts expected for the protons of the COD ligand.

Although the three hydrides were not located in the X-ray structure, the $^1$H NMR data support the positions shown in Scheme I. All three hydrides show distinct signals in the temperature range −80 to +80 °C; that is, the molecule is stereochemically rigid. Selective decoupling studies have allowed determination of all proton–phosphorus coupling constants, and from these, it is possible to deduce the hydride positions with respect to the phosphorus sites. The $^1$H NMR data are summarized in Chart I. Because the hydride signal at $\delta$ −9.5 shows a large P–H coupling constant of 42 Hz, it is assigned to the H$_b$ position, trans to the unique phosphine. The assignment of the signal at $\delta$ −10.7 ppm to the H$_c$ position terminal on ruthenium follows from the magnitude of $J$(P–H). The smaller magnitude of the $J$ values observed for the signal at $\delta$ −3.6 ppm ($J$ = 4.4, 8.8 Hz) suggests that it is not terminal on ruthenium. It is therefore assigned to the bridging H$_a$ position. The small magnitude of the coupling constants of H$_a$ is attributed to the fact that H$_a$ is trans to a terminal hydride and is therefore expected to couple more weakly with the three phosphorus nuclei. No H–H coupling was resolved. The infrared spectrum of 1 shows a peak assigned to a terminal hydride at 1820 cm$^{-1}$. The terminal metal hydride stretches of RuH$_3$(PPh$_3$)$_3^-$ occur at 1857 and 1815 cm$^{-1}$.[16a] The 1820-cm$^{-1}$ peak of 1 is replaced by one at 1283 cm$^{-1}$ in the selectively deuterated isotopomer of 1 (1-$d_{21}$), in which hydrogen has been replaced by deuterium in all 18 ortho phenyl positions as well as the three hydridic sites. No other metal hydride stretches could be assigned.

Despite the fact that the $^{31}$P{$^1$H} NMR spectrum and the hydride region of the $^1$H NMR spectrum of 1 are temperature-invariant, certain of its $^1$H NMR signals do exhibit temperature dependance. At −30 °C, the peak (7.65 ppm) which is noticeably broad (0.15 ppm in full width at half-height) at 25 °C (see supplementary material) is resolved into two signals. Because the $^{31}$P{$^1$H} NMR spectrum does not change with temperature, the most plausible explanation for the temperature-dependent behavior of the phenyl region involves the freezing out of rotational motion around the Ru–P and/or P–C$_{ipso}$ bonds of the triphenylphosphines. Because this behavior is somewhat unusual and, more importantly, indicative of steric hindrance experienced by specific phenyl protons, an effort was made to explicitly identify which phenyl protons were responsible for the temperature-dependent signal. Upon selective decoupling of the two trans phosphorus nuclei from the $^1$H NMR spectrum, the signal at $\delta$ 7.65 narrows. No other noticeable changes occur. This observation allows the assignment of the signal at $\delta$ 7.65 to the ortho protons of the trans phosphines. This assignment was confirmed by recording the $^1$H NMR spectrum of the previously mentioned selectively deuterated compound 1-$d_{21}$. The signals at $\delta$ 7.65 and 7.23 are absent in this spectrum. Since they can be integrated in a ratio of 2:1, unequivocal assignment of the phenyl signal at $\delta$ 7.65 to the ortho protons of the trans phosphines is established. The assignment of the signal at $\delta$ 7.23 to the ortho protons of the unique phosphine follows as well, and from the relative sharpness of this signal, it is apparent that these ortho protons are not experiencing any hindered rotation.

**Reactivity of (COD)Ir($\mu$-H)$_2$RuH(PPh$_3$)$_3$.** In an effort to obtain fundamental information concerning the reactivity of 1, exchange of the hydrogen atoms of 1 with deuterium was investigated. When a C$_6$D$_6$ solution of 1 is sealed in an NMR tube under 2 equiv of D$_2$, $^1$H NMR spectroscopy after 8 h reveals a slight decrease in the intensity of all three hydride signals. Also noticeable as the deuteration proceeds further is the appearance of new satellite lines adjacent to all three hydride signals. These are attributed to the isotope effect of an adjacent deuterium atom on the hydride chemical shift of partially deuterated material.[16b] To further confirm that deuterium was being incorporated into all three hydride sites, the experiment was repeated in C$_6$H$_6$ and monitored by $^2$H NMR spectroscopy. The $^2$H NMR spectrum, recorded after 6 h, clearly revealed deuterium incorporation at all three metal sites. After 24 h, a new peak had begun to appear in the phenyl region of the $^2$H NMR spectrum. This observation later proved to be quite important.

The exchange observed between 1 and D$_2$ could occur by either associative (eq 1) or dissociative (eq 2) mechanisms. *In an effort to distinguish between these two*

$$\text{(COD)IrRu(PPh}_3)_3\text{H}_3 + \text{D}_2 \rightleftarrows \text{(COD)IrRu(PPh}_3)_3\text{H}_3\text{D}_2 \quad (1)$$

$$\text{(COD)IrRu(PPh}_3)_3\text{H}_3 \rightleftarrows \text{(COD)IrRu(PPh}_3)_3\text{H} + \text{H}_2 \quad (2)$$

processes, the possible existence of an equilibrium between 1, free H$_2$, and a dehydrogenated species was investigated. To probe for the presence of this equilibrium, 1 was reacted with hydrogen acceptors.

When 1 is reacted at 25 °C with 5 equiv of 3,3-dimethyl-1-butene for 24 h, the new species 2 is formed in 25% yield as established by $^{31}$P{$^1$H} NMR spectroscopy. This new species can be generated in greater than 95% yield in about 6 h by performing the reaction at 60 °C. To verify that 2 was indeed a product derived from the dehydrogenation of 1, an isolated sample of 2 was placed under 1 atm of H$_2$ at room temperature. In 2 h, both $^{31}$P{$^1$H} and $^1$H NMR spectroscopy showed that 1 had been cleanly regenerated. Other H$_2$ acceptors have been found to accomplish the same dehydrogenation of 1. The reaction was complete in 8 h at 60 °C when 5 equiv of ethylene was

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[15] Donahue, J. *The Structure of the Elements*; Wiley: New York, 1974.

[16] (a) Wilcyzski, R.; Fordyce, W. A.; Halpern, J. *J. Am. Chem. Soc.* **1983**, *105*, 2066. (b) The isotopic shifts of all hydride resonances were ~0.05 ppm (downfield) and thus quite comparable to those in: Luo, X.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 4813. (c) Werner, H.; Gotzig, J. *J. Organomet. Chem.* **1985**, *284*, 73.

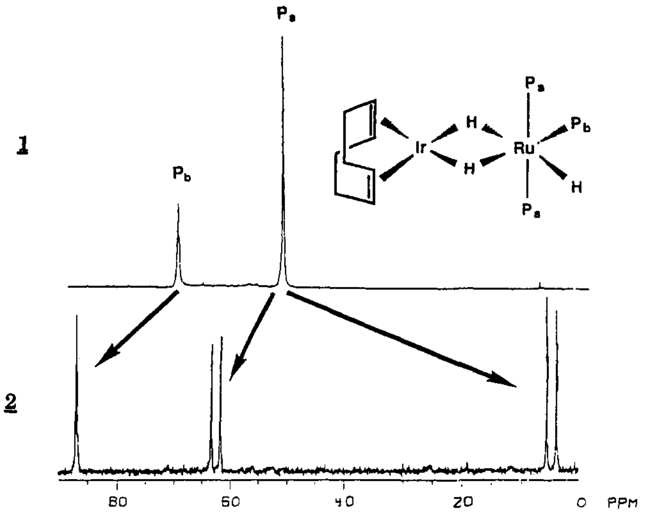

**Figure 3.** 146-MHz $^{31}P\{^1H\}$ NMR spectra (25 °C, $C_6D_6$) of 1 and 2 showing related phosphorus signals.

used; examination of this reaction mixture (in $C_6D_6$) by $^1H$ NMR methods revealed the production of ethane. Five equivalents of 2-butyne effects the transformation somewhat faster, with the reaction being complete after 4 h at 60 °C. An analysis of the volatiles from this reaction revealed a mixture of *cis*- and *trans*-2-butenes as the major organic products, along with a trace of butane. To further verify the existence of the equilibrium of interest and to confirm that the added hydrogen acceptor was acting merely as an $H_2$ "sponge" and not itself inducing $H_2$ loss, the transformation of 1 to 2 was attempted without the addition of an organic hydrogen acceptor. Indeed, bubbling $N_2$ at 25 °C through a toluene solution of 1 results in a 30% conversion to 2 after 3 h. These results also prove that the organic hydrogen acceptor is not itself incorporated into 2. Furthermore, these experiments provide compelling evidence that 1 is in equilibrium with an $H_2$-dissociated species in solution at room temperature. The rate of conversion of 1 to 2 (elevated temperature with an $H_2$ acceptor or a lengthy $N_2$ purge) is considerably slower than the conversion of 2 to 1 (25 °C, 1 atm of $H_2$, <2 h). Therefore, the equilibrium in eq 2 lies quite far to the left.

**Spectroscopic Investigations of Compound 2.** Because 1 and 2 represented a rare case[8] of two heterobimetallic compounds related by reversible loss and addition of $H_2$, it became quite important to determine the structure of 2. Since crystals of 2 grown from benzene, benzene/pentane, $CH_2Cl_2/Et_2O$, $CH_2Cl_2$/pentane, and $CH_2Cl_2$/acetone were all found to be twinned, this structure must be deduced from spectral studies.

The $^{31}P\{^1H\}$ NMR spectrum of 2 (Figure 3) shows an AMX spin system consisting of three doublets of doublets at δ 86.8 ($J$ = 24, 32 Hz), δ 62.0 ($J$ = 24, 242 Hz), and δ 4.7 ($J$ = 32, 242 Hz). The presence of three signals in a ratio of 1:1:1 indicates the absence of the mirror plane of symmetry that made the trans phosphines of 1 equivalent. The presence of a large coupling constant (242 Hz) suggests[16c] that two of the phosphines are arranged in a trans orientation. Consistent with this, the magnitude of the two other coupling constants (24, 32 Hz) are typical of two-bond cis P–P coupling; the *mer* arrangement of phosphines on Ru found in 1 has therefore been retained in 2. These also show that phosphine transfer to iridium has not occurred. Also worthy of mention is the dramatic upfield change in chemical shift (δ 52.0 to 4.7) that one of the formerly equivalent trans phosphines has undergone.

The hydride region $^1H$ NMR spectrum of 2 shows signals at δ −3.4 and −7.0. Selective phosphorus decoupling studies reveal that the relatively sharp signal at δ −3.4 couples to one phosphorus with $J$ = 4.4 Hz and to the other two with an accidentally degenerate $J$ value of 8.8 Hz. The magnitude of the coupling constants suggests that this hydride is not terminal on Ru or trans to a phosphine. Furthermore, the magnitudes of these coupling constants closely match those of bridging $H_a$ in 1, suggesting that this particular hydride of 2 may be bridging. The signal at −7.0 ppm shows three coupling constants with approximately the same $J$ value of 17 Hz. This value suggests that this hydride is not terminal on Ir or trans to a phosphine. The lack of symmetry in this molecule is further evident from the presence of 12 chemical shifts for the COD protons.

Since trihydride 1 and dihydride 2 have been shown to be related by reversible loss or addition of 1 mol of $H_2$, some carbon-bound hydrogen must be involved in the formation of 2. This implicates either the COD protons or the protons of the phosphine phenyl rings. Precedence for hydrogen activation on both of these ligands in related systems can be found in the literature. Clarke et al.[17] have observed hydrogen abstraction from COD in the reaction of $[Ir(COD)Cl]_2$ with hexafluoro-2-butyne, resulting in the formation of an allyl. $RuH_3(PPh_3)_3^-$ has been shown[16a] to incorporate deuterium into the ortho phenyl positions when placed under $D_2$. Since 1, under $D_2$ for extended periods, also incorporates deuterium into phenyl sites, the latter of these two options initially appeared to be the more attractive choice. A study of the $^{13}C\{^1H\}$ NMR spectra of 1 and 2 was initiated in an effort to independently distinguish between these possibilities.

As a result of the mirror symmetry of 1, its COD carbons appear as four $^{13}C\{^1H\}$ singlets, two in the aliphatic region and two in the olefinic region. The absence of symmetry results in eight distinct $^{13}C$ signals for the COD carbons of 2. Four of these carbons appear in the aliphatic region (30.7–32.8 ppm), and the remaining four appear in the olefinic region (δ 55.6, 67.3, 67.8, 68.3). The first of these olefinic carbon chemical shifts in 2 has moved substantially upfield (to 55.6 ppm) in comparison to that of 1, and this point will be addressed later. However, the important conclusion to be drawn from these spectra is that 2 contains four aliphatic carbons. The formation of an allyl by hydrogen abstraction from the COD would require that 2 possess only three aliphatic carbons, and the possibility that the formation of 2 involves hydrogen abstraction from the COD can therefore be discounted. Hydrogen abstraction from a phosphine phenyl ring will now be addressed.

Figure 4 shows the phenyl region of the $^{13}C\{^1H\}$ NMR spectra of 1 and 2. Immediately evident is the increased complexity of the phenyl region of 2 as compared to that of mirror-symmetric 1. Also significant in the spectrum of 2 is the presence of several low-intensity carbon resonances which requires inequivalence *among* the three rings of one triphenylphosphine. Especially noteworthy among these low-intensity signals is that found at δ 154. The position of this chemical shift, located 13 ppm downfield of the most downfield signal of 1, compares quite well to $^{13}C$ chemical shifts found for the ipso carbon of a metal-/σ-phenyl compound.[18] The complexity of the fine structure of this signal indicates coupling to more than one other spin-active nucleus, presumably phosphorus. On the basis of the extreme downfield chemical shift of this signal

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(17) Clarke, D. A.; Kemmitt, R. P. W.; Russell, D. R.; Tucker, P. A. *J. Organomet. Chem.* **1975**, *93*, C37.

(18) (a) Omae, I. *Chem. Rev.* **1979**, *79*, 287. (b) Saunders, D. R.; Stephenson, M.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1985**, 2473.

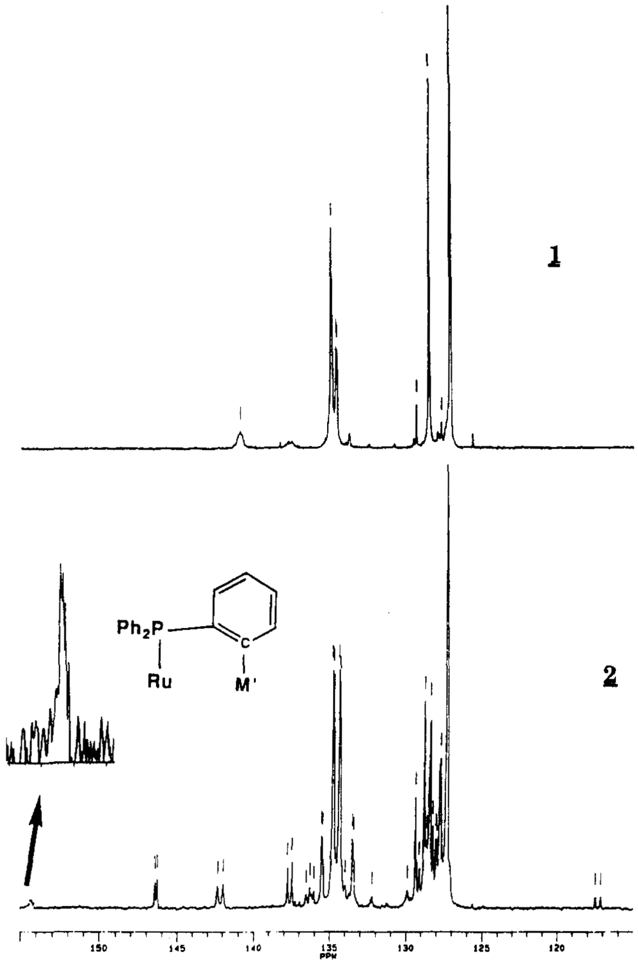
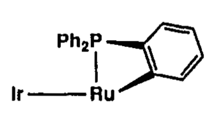


**Figure 4.** 125-MHz $^{13}C\{^1H\}$ NMR spectra of the phenyl carbons of 1 and 2 in $CD_2Cl_2$ at 25 °C.

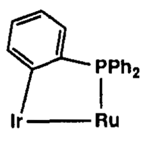
as well as the presence of coupling to more than one phosphorus, this signal is assigned to a carbon that has undergone ortho metalation.

Further experimental evidence for ortho metalation has been obtained from reactivity studies on 1-$d_{21}$. When 1-$d_{21}$ (which shows no hydride signals in the $^1$H NMR spectrum) is converted to the deuterated isotopomer of 2, hydride signals are still absent in the $^1$H NMR spectrum. However, a sample of this material shows the expected two upfield signals for metal-bound deuterides in the $^2$H NMR spectrum. This result further suggests that the COD hydrogens are not involved in the transformation of 1 to 2. Also worthy of mention is a noticeable (~20%) decrease in reaction rate when 1-$d_{21}$ is dehydrogenated. This observation suggests that an X–D bond (X = Ir, Ru, C) is broken in the rate-determining step of this transformation.

The spectroscopic and experimental observations previously discussed support the conclusion that 2 is derived from a process involving ortho metalation and $H_2$ loss from 1. However, we must now address whether M–C bond formation occurs at ruthenium (B) or at iridium (C).



B



C

Several examples of Ru$^{II}$ complexes containing an orthometalated triphenylphosphine are known.[19] It is also feasible that $PPh_3$ can ortho metalate across a Ru–Ir distance of 2.62 Å in 1, since this reaction has been observed in a dirhodium system involving a metal–metal distance of 2.55 Å.[20]

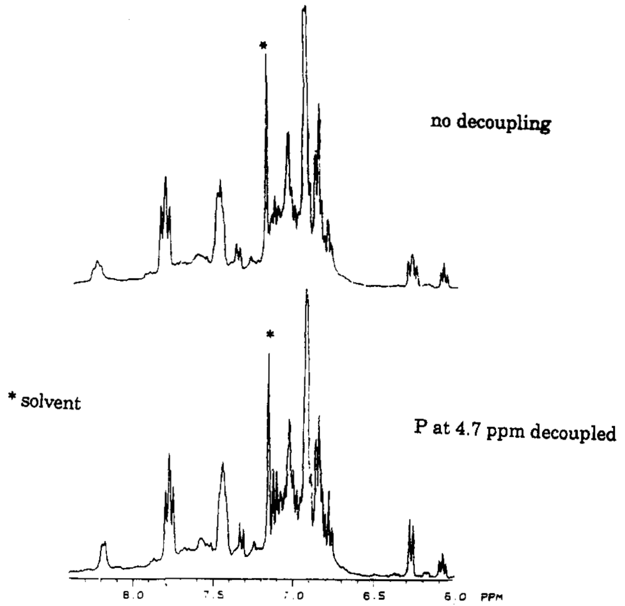


**Figure 5.** 360-MHz $^1$H NMR spectra of the phenyl region of 2 showing the results of selectively decoupling the $^{31}$P signal at δ 4.7.

A potentially useful difference between a product formed upon ortho metalation at iridium and at ruthenium is the size of the resulting ring. A four- or five-membered ring will be formed, depending on which metal undergoes ortho metalation. A downfield change in $^{31}$P NMR chemical shift with respect to the ring-free species occurs when a phosphorus is incorporated into a five-membered ring.[21] An upfield change occurs when a phosphorus atom is incorporated into a four-membered ring. This empirical relationship is quite general and is independent of the identity of the metal in the ring. However, to apply this criterion, a definitive assignment of the $^{31}P\{^1H\}$ NMR spectrum of 2 is essential.

Shown in Figure 3 are the $^{31}P\{^1H\}$ NMR spectra of 1 and 2. As previously discussed, 2 retains the meridional arrangement of phosphines around ruthenium. The $J$(P–P′) values allow association of each of the three signals in 2 to its corresponding parent in 1, as depicted by the arrows in Figure 3. Since two signals (δ 86.8, 62.0) have moved downfield with respect to their parent signals in 1 and one signal (δ 4.7) has moved upfield, a cursory examination of the $^{31}$P NMR spectrum of 2 in comparison to that of 1 is not sufficient for unambiguous assignment of the orthometalated phosphine resonance. However, since it is evident that the signal at δ 4.7 has undergone the most dramatic change in chemical environment relative to its parent in 1, preliminary assignment of this signal to the ortho-metalated phosphine was the most attractive option. This proposal can be made more certain by a study of the selectively $^{31}$P-decoupled $^1$H NMR spectrum of 2.

The $^1$H NMR spectrum of the phenyl region of 2 contains three signals of low intensity: a triplet at δ 6.07, a triplet at δ 6.26, and a poorly resolved triplet at δ 8.18 (Figure 5). Because of their low intensity and separation

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(19) (a) Cole-Hamilton, D. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 797. (b) Pez, R. P.; Grey, R. A.; Corsi, J. *J. Am. Chem. Soc.* **1981**, *103*, 7528.

(20) Barder, R. J.; Tetrick, S. M.; Walton, R. A.; Cotton, F. A.; Powell, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 4090.

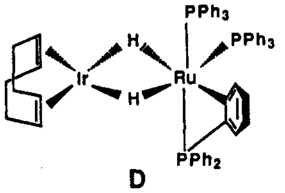
(21) Garrou, P. *Chem. Rev.* **1981**, *81*, 229.

from the majority of the phenyl protons, these signals are undoubtedly due to protons on the metalated phosphine. No change in the three signals of interest occurs upon irradiation of the $^{31}P$ signals at either 62.0 or 86.8 ppm. However, when the signal at 4.7 ppm is decoupled, the proton resonance at 8.18 ppm collapses to a poorly resolved doublet and the triplet at 6.26 ppm also collapses to a doublet (Figure 5). These observations confirm the assignment of the signal at $\delta$ 4.7 in the $^{31}P\{^1H\}$ NMR spectrum of 2 as the phosphine that has undergone ortho metalation. This assignment also serves to explain the loss of the mirror plane of symmetry that was present in 1, since one of the formerly equivalent trans phosphines has undergone ortho metalation. This would not be true if the unique phosphine of 1 had undergone ortho metalation.

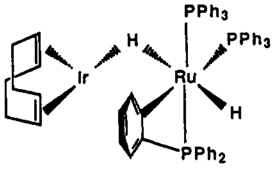
The determination of which phosphorus chemical shift is due to the metalated phosphine now allows the application of Garrou's $^{31}P$ chemical shift correlations.[21] The upfield shift from $\delta$ 52.0 in 1 in $\delta$ 4.7 in 2 for the phosphorus of interest correlates with the formation of a four-membered ring, thus indicating that ortho metalation occurs with formation of a Ru–C bond. These results provide a foundation for more detailed speculation concerning the structure of 2.

## Discussion

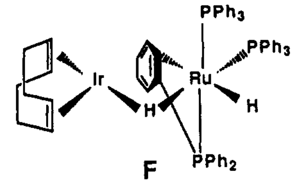
We now consider structures D–F for 2. All three have the necessary *mer* arrangement of phosphines around ruthenium, with one of the trans phosphines having undergone ortho metalation to the ruthenium. $^1H$ NMR measurements indicate that 2 possesses two hydrides. Structures D–F all have the necessary one (or more) bridging hydrides. The magnitude of the phosphorus coupling constants suggests that neither of the two hydrides is trans to a phosphine. This excludes structures D and F. Structure E lacks a second bridging ligand, yet it constrains the metalated phenyl ring to be near iridium. We propose that these two features are related: structure E must be further refined so that some portion of the $\pi$-density of the metalated phenyl ring donates to the neighboring iridium, as shown in G. This proposal has the additional advantage that it puts *only one* of the olefinic COD carbons under the influence of the $\pi$-system of the phenyl ring, where a ring-current effect will operate on the chemical shift of that carbon. This provides a natural explanation for the previously mentioned dramatic alteration of one olefinic $^{13}C$ NMR signal in 2 compared to that in 1.



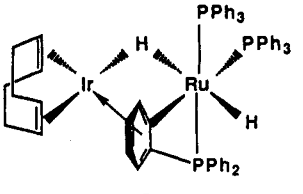
D



E



F



G

Table IV. Ru–P–$C_{ipso}$ Bond Angles (deg) for Compound 1

| Ru–$P_{trans}$–$C_{ipso}$ | Ru–$P_{trans}$–$C_{ipso}$ | Ru–$P_{unique}$–$C_{ipso}$ |
|---|---|---|
| | Molecule A | |
| 116.9 (4) | 106.2 (4) | 113.3 (3) |
| 120.8 (4) | 125.5 (4) | 115.2 (4) |
| 112.8 (3) | 109.4 (3) | 122.6 (3) |
| | Molecule B | |
| 118.9 (4) | 119.2 (4) | 111.1 (3) |
| 122.5 (4) | 124.8 (3) | 114.7 (3) |
| 108.3 (3) | 108.6 (3) | 123.4 (3) |

**Steric Strain in Compound 1.** In order to better understand the forces promoting ortho metalation, the solid-state structure of 1 was examined in more detail. Figure 1 reveals that one phenyl ring orients the ortho C–H bond on C(49) toward ruthenium in *both* of the independent molecules present in the unit cell of 1. Furthermore (Figure 2), all other pairs of phenyl rings show a greater disparity in their respective positions. These observations suggest that the orientation of this particular ring is dictated by *intramolecular* forces. This intramolecular effect is also manifest in the Ru–P–$C_{ipso}$ bond angles. As shown in Table IV, each of the two independent molecules contains at least one Ru–$P_{trans}$–$C_{ipso}$ angle that is noticeably smaller than the corresponding Ru–$P_{unique}$–$C_{ipso}$ angles. We propose that all of these effects are due to steric repulsion among the three large phosphines and that such ground-state repulsion in 1 promotes ortho metalation.[22] Finally, this reaction would immediately produce the structure (E) deduced for 2, with completion of the phenyl $\pi$ to Ir donation anticipated in the structure of 1.

In retrospect, the unusual temperature dependence of the $^1H$ NMR signal of the ortho protons on the trans phosphine phenyl rings of 1 is now more understandable. As previously discussed, this variable-temperature behavior must involve hindered rotation of the phenyl rings in light of the temperature-invariant $^{31}P\{^1H\}$ NMR spectrum. Since 1 has been shown to undergo ortho metalation at the very sites that show the unusual temperature-dependent spectroscopic behavior, it is likely that these two processes are somehow related. One plausible explanation is that steric effects of the Ir(COD) fragment cause hindered rotation around the Ru–P and P–C bonds and, in doing so, facilitate ortho metalation. Such an explanation is consistent with the fact that the ortho positions of the unique phosphine (which is more remote from the Ir(COD) unit) do not exhibit any temperature-dependent spectroscopic behavior. This is reflected in the average value for the Ir–Ru–$P_{trans}$ angle of 91.7° vs the Ir–Ru–$P_{unique}$ angle of 129.6° seen in the solid-state structure of 1. It is also possible that the iridium in 1 may weakly accept electron density from the phenyl rings of the trans phosphines and thereby hinder rotation and force an ortho hydrogen bond closer to ruthenium.

A few significant questions remain: (1) What is the driving force for the isomerization of the kinetic product into 1? (2) Why is it slow enough to be observable, given that most[23] migratory processes involving hydrides are quite fast? The answer to the first question involves a

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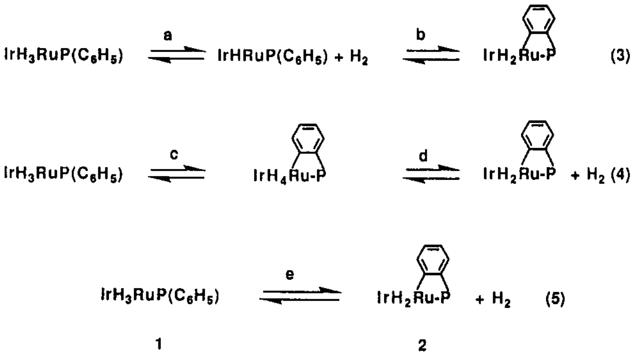
[22] A reviewer has suggested that this is due to an agostic interaction. Since the metal is saturated, we find no support for this proposal.

[23] Hydride migration in certain other heterobimetallic compounds has been reported to be slow. See for example: Ben Lanrab, H.; Chaudret, B.; Delavaux, B.; Dahan, F.; Poilblanc, R. *New J. Chem.* 1988, *12*, 436.

Scheme II



balance of steric and electronic effects. $RuH_3(PPh_3)_3^-$ exhibits a *fac* stereochemistry to avoid the unfavorable trans positioning of two strongly trans-directing hydride ligands of a *mer* isomer; this is dominant over the unfavorable steric effect resulting from crowding three triphenylphosphines into an all-cis *fac* arrangement. That is, electronic effects dictate the stereochemistry of this starting material. In addition, the *fac* isomer is especially suited to ion-pair with $Li^+$. As expected, the kinetic product results from the trapping of this rigid *fac* moiety. In the thermodynamic (*mer*) isomer, the unfavorable electronic effect of two hydride ligands in a trans orientation is reduced because one hydride is now bridging the two metal centers. This reduction of unfavorable electronic effects now allows steric effects to dominate. With regard to the second question, the rate of this process is probably influenced more by the fact that the isomerization involves the change from a $d^6$ *fac* octahedron to a $d^6$ *mer* octahedron. The majority of fast hydride migratory processes involve coordination numbers greater than 6. Thus, the dominant factor which controls the rate of this isomerization is the stereochemical rigidity of the $d^6$ octahedron, even in the presence of hydride ligands.

**Mechanism of Conversion of 1 to 2.** Two distinct events occur in this transformation: reductive elimination of $H_2$ and oxidative addition of an aromatic C–H bond. Three possibilities exist for the order in which these events could occur: (1) Reductive elimination of $H_2$ precedes oxidative addition of the C–H bond. (2) Oxidative addition of the C–H bond precedes reductive elimination of $H_2$. (3) The two events occur simultaneously in a concerted process. These three possibilities are illustrated schematically in Scheme II (unaltered ligands have been deleted for simplicity). These mechanisms can be distinguished by a more detailed analysis of the results of the 1 + $D_2$ exchange experiment together with an additional exchange study involving 2 + $D_2$. As previously mentioned, when 1 is placed under $D_2$, what is initially observed in the $^2H$ NMR spectrum is deuterium incorporation into all three metal-bound sites. Subsequently, a signal appears in the phenyl region. Because deuterium appears in the metal-bound sites before any phenyl sites, mechanism 4 shown in Scheme II is unlikely. Since deuterium enters this system in equilibrium d to form a tetrahydride intermediate, the subsequent C–H bond-forming reductive elimination should occur with a significant amount of C–D bond formation. Likewise, if the concerted mechanism 5 were occurring (i.e., direct attack of $H_2$ on the Ru–C bond), the $^2H$ NMR spectrum should also show deuterium incorporation into the phenyl sites concomitant with incorporation into the metal-bound sites. The mechanism shown as eq 3 in Scheme II is most consistent with the observed results since, in this process, $D_2$ enters the system in equilibrium a without the necessity to deuterate carbon (equilibrium b); the ortho-metalated species is achieved through a separate kinetic process. This is also consistent with the isotope effect observed when 1-$d_{21}$ is dehydrogenated. To obtain further insight into the nature of this transformation, an isolated sample of 2 was placed under 2 equiv of $D_2$ and monitored by $^2H$ NMR spectroscopy. Again, what is first visible (within minutes) are signals for the three metal-bound sites of 1. Much later (18 h), a signal begins to grow in the phenyl region. This further suggests that the mechanism in eq 4 is not applicable, since it predicts that deuterium should appear in the metal-bound sites and the phenyl sites at approximately the same rate. Assuming that the mechanism shown as eq 5 involves direct attack on the Ru–C bond by $H_2$ or $D_2$, this mechanism also predicts that deuterium should be incorporated at approximately the same rate in both the metal-bound sites and the phenyl sites. Therefore, these experimental results indicate that the transformation between 1 and 2 is best presented by the mechanism in eq 3.

As previously mentioned, another interesting characteristic of this system is that it represents one of only a handful of examples of heterobimetallic systems that interact reversibly with $H_2$. However, in contrast to other such known systems, what is especially unusual about this particular system is that the reversible interaction with $H_2$ is accomplished *with no net change in metal oxidation states between the hydrogenated form* (1) *and the dehydrogenated form* (2). Therefore, the thermodynamically higher energy bimetallic species in this system (2) still has accessible to it the widest range of possible oxidation states.

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**Supplementary Material Available:** Listings of full crystallographic details and anisotropic thermal parameters for 1 and additional NMR spectra for 1 and 2 (6 pages); a listing of observed and calculated structure factors for 1 (35 pages). Ordering information is given on any current masthead page.