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# A New Oxidative Addition of Ruthenium(0) into an Aryl Halide Bond and Subsequent Intermolecular C−H Insertion

Helen Grounds,[†] James C. Anderson,*[,‡] Barry Hayter,[§] and Alexander J. Blake[†]

[‡]*Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, U.K.,*
[†]*Department of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD U.K., and*
[§]*AstraZeneca, Alderley Park, Macclesfield, Cheshire, SK10 4TF, U.K.*

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*Summary: An unprecedented oxidative insertion of the activated ruthenium complex "Ru(CO)(PPh$_3$)$_2$" into aryl halide bonds enables a novel preparation of stable five-coordinate 16-electron d(6) σ-aryl-Ru(II) complex Ru(CO)(p-C$_6$H$_4$Me)Br(PPh$_3$)$_2$, which has been characterized by NMR, IR, elemental analysis, and X-ray crystallography. These novel five-coordinate Ru(II) complexes were investigated as potential intermediates in the ortho-arylation of aryl ketones (α-tetralone) through C−H activation and resulted in the formation of Ru(CO)(η$^1$-C, κ$^1$-O, α-tetralone)X(PPh$_3$)$_2$ and toluene (X = Br or I).*

## Introduction

Oxidative addition of carbon halogen bonds to coordinatevely unsaturated low-valent metal complexes is a key step in many catalytic processes. Examples of the oxidative addition of aryl halides to group 10 metals are plentiful, but examples involving group 8 metals are much less common. The addition of aryl halides to ruthenium is postulated in many cross-coupling pathways, especially with the recent interest in the direct coupling of aromatic C−H bonds with aryl halides.[1] A number of ruthenium catalysts have been employed for aryl−aryl bond formation via *ortho*-metalation of a variety of aromatic compounds including [RuCl$_2$(C$_6$H$_6$)]$_2$ for aromatic imines[2] and imidazoles[3] and Ru[Cl$_2$(*p*-cymene)]$_2$ for aryl pyridines.[4,5] These reactions are generally thought to occur through directed *ortho*-metalation of the aromatic ring by ruthenium coordination to nitrogen or oxygen, followed by oxidative addition of an aryl halide to the Ru(II) metal center. Alternatively the mechanism proceeds through σ-bond metathesis, although there is limited evidence for these suggestions.[4,6]

Despite the prevalence of oxidative addition reactions using allyl and alkyl halides,[7] the Ru(0)/Ru(II) oxidative addition of aryl halides has been proposed in only a handful of cases.[8] Speculative evidence exists for this addition including the observation that activation of [RuCl$_2$(C$_6$H$_6$)]$_2$ with NaOAc in DMF-$d_7$ at 135 °C, followed by addition of iodobenzene, results in a shift of the iodobenzene peaks in the $^1$H NMR; at temperatures lower than 135 °C these signals disappear.[8a] Ru$_3$(CO)$_{12}$ has been shown to oxidatively insert into iodoarenes, but the resultant arene ligand is simultaneously σ- and π-coordinated to the ruthenium cluster.[8b] To the best of our knowledge, this cluster compound represents the only reported case of a ruthenium complex isolated from direct oxidative addition of an aryl halide.

We report here that upon activation, ruthenium complex RuH$_2$(CO)(PPh$_3$)$_3$ reacts with a number of aryl halides inserting into the aryl−halide bond. The resulting complex is a stable five-coordinate 16-electron d(6) Ru(II) complex, [Ru(CO)(*o*-C$_6$H$_4$Me)(X)(PPh$_3$)$_2$], which has been characterized by NMR, IR, elemental analysis, and X-ray crystallography. This unprecedented oxidative insertion of a Ru(0) complex enables a novel preparation of σ-arylruthenium metal derivatives. These five-coordinate Ru(II) complexes have also been investigated as potential intermediates in the *ortho*-arylation of aromatic ketones using RuH$_2$(CO)(PPh$_3$)$_3$. C−H activation of the aryl ketone was observed using our five-coordinate Ru(II) complex, resulting in the formation of Ru(CO)(η$^1$-C, κ$^1$-O, α-tetralone)Br(PPh$_3$)$_2$ and toluene (X = Br or I).

## Results and Discussion

The active catalyst (**1**, Scheme 1) was prepared from RuH$_2$(CO)(PPh$_3$)$_3$. Following the literature procedure RuH$_2$(CO)(PPh$_3$)$_3$ was synthesized from commercially available RuCl$_3$·3H$_2$O in 66% yield and isolated as an air-stable white solid.[9] Reduction of the Ru(II) complex to Ru(0) (complex **1**) was achieved by the addition of 1 equiv of styrene following the procedure of Weber and monitored by the disappearance of the peaks corresponding to the hydride protons in the

*To whom correspondence should be addressed. E-mail: j.c.anderson@ucl.ac.uk.

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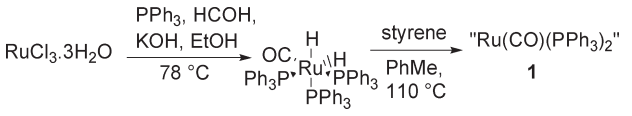
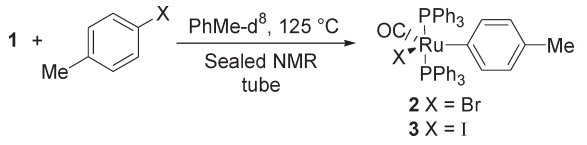
**Scheme 1. Synthesis of the Active Ru(0) Complex 1**




**Scheme 2. Synthesis of the Five-Coordinate Oxidative Addition Products RuBr(CO)(*p*-tolyl)($PPh_3$)$_2$ (2) and RuI(CO)(*p*-tolyl)-($PPh_3$)$_2$ (3)**




$^1$H NMR ($C_6D_6$ $\delta$ −8.18 and −6.35 ppm).[10] The active catalyst has been shown to be "Ru(CO)($PPh_2$)$_2$" in equilibrium with dimers and trimers.[11]

Initial oxidative addition experiments were performed in sealed Young's tap NMR tubes using PhMe-$d_8$ as the solvent. Addition of bromotoluene to a preactivated solution of "Ru(CO)($PPh_2$)$_2$" in PhMe-$d_8$ at 125 °C for 50 min, then cooling to rt, resulted in a distinctive shift of the methyl peak of the tolyl group downfield to 2.05 ppm from 1.90 ppm (Scheme 2). Conversion was estimated at 54% (**2**) and 47% (**3**) from the $^1$H NMR. These experiments were also performed on a 0.23 mmol scale using standard Schlenk techniques in toluene to give **2** and **3** in a 74% and 9% yield, respectively. Similar shifts were seen in the $^1$H NMR using tolyl triflate and *p*-methoxybromobenzene, although no product was isolated from these reactions.

Air-stable crystals of **2** precipitated from the toluene solution upon cooling and could be isolated pure by filtration without need for further purification. The vast majority of divalent ruthenium complexes are six-coordinate. The small class of five-coordinate Ru(II) complexes are often square pyramidal, generally prevented from halide-bridged dimerization by bulky phosphine ligands.[12] In addition to the shifts in the $^1$H NMR, elemental analysis and mass spectrometry supported our assignment of the resultant metal complex, and single X-ray analysis of **2** confirmed the proposed structure (Figure 1). Complex **2** crystallized as monoclinic crystals in space group *C*2/*c* (see Tables 1 and 2). Complex **2** is a distorted square pyramid with the bulky phosphorus ligands *trans* to each other and the *p*-tolyl group *trans* to the empty site, consistent with the stronger *trans* influence of the aryl group to CO, enabling the LUMO to have the highest possible energy. The crystal structure shows that the $\pi$-donor (Br) and $\pi$-acceptor (CO) ligands are *trans* to each other, benefiting from push−pull stabilization. One Ph group of the phosphine bends toward the vacant site so that the C7−P−Ru bond angle is 7° smaller than that of C1−P−Ru or C13−P−Ru. This may indicate a weak agostic interaction. Complex **3** shows very similar characterization data (see Experimental Section). These results are also in agreement with the data reported by Roper et al. for the chloro analogue of **2**, synthesized by reaction of RuHCl-(CO($PPh_3$)$_2$ with Hg(tolyl)$_2$.[13] Complexes **3** and **4** were mentioned, synthesized by halogen exchange of the chloro analogue, although no experimental details were given and only the CO IR bands were reported.

As a number of ruthenium catalysts have been employed for aryl−aryl bond formation,[2−5] we decided to investigate the role and potential use of the isolated Ru(II) oxidative addition products as intermediates in direct arylation reactions.

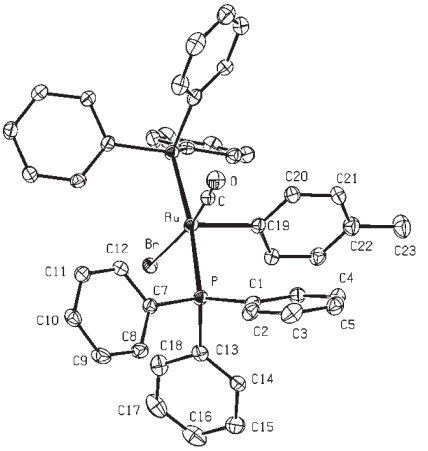



**Figure 1.** X-ray crystallography structure of RuBr(CO)(*p*-tolyl)($PPh_3$)$_2$ (**2**).

**Table 1. Selected Bond Lengths and Angles for Ru(CO)(*p*-tolyl)(Br)($PPh_3$)$_2$ (2)**

| Bond Distances (Å) | | | |
|---|---|---|---|
| Ru−Br | 2.6729(17) | Ru−C(19) | 2.032(6) |
| Ru−P | 2.3720(11) | C−O | 1.176(8) |
| Ru−C | 1.829(7) | | |
| **Bond Angles (deg)** | | | |
| C−Ru−C19 | 93.8(3) | C19−Ru−Br | 97.29(3) |
| C#1−Ru−P | 94.4(3) | P#1−Ru-Br | 85.34(4) |
| C−Ru−P | 85.1(3) | P−Ru−Br | 93.72(4) |
| C19−Ru−P | 93.71(3) | C1−P−Ru | 115.65(14) |
| P#1−Ru−P | 172.6(6) | C7−P−Ru | 109.00(14) |
| C−Ru−Br | 168.8(3) | C13−P−Ru | 118.91(14) |
| Ru−C−O | 175.9(10) | | |

**Table 2. Crystallographic Data**

| | **2** | **4** | **5** |
|---|---|---|---|
| chemical formula | $C_{44}H_{37}BrOP_2Ru$ | $C_{47}H_{39}BrO_2P_2Ru$ | $C_{47}H_{39}IO_2P_2Ru$ |
| fw | 824.66 | 878.70 | 925.69 |
| cryst syst | monoclinic | orthorhombic | orthorhombic |
| space group | *C*2/*c* | *Pna*2$_1$ | *Pna*2$_1$ |
| *a*/Å | 12.837(2) | 25.240(2) | 25.138(2) |
| *b*/Å | 13.965(2) | 9.8942(7) | 9.8971(9) |
| *c*/Å | 20.176(3) | 15.5546(11) | 15.824(2) |
| *V*/Å$^3$ | 3605(2) | 3884.4(8) | 3936(11) |
| *Z* | 4 | 4 | 4 |
| *T*/K | 150(2) | 150(2) | 150(2) |
| $\lambda$/Å | 0.71073 | 0.71073 | 0.71073 |
| $D_{Calcd.}$/Mg cm$^{-3}$ | 1.519 | 1.503 | 1.562 |
| $\mu$/cm$^{-1}$ | 16.7 | 15.5 | 13.0 |
| *R* | 0.0461 | 0.0447 | 0.0526 |
| $R_w$ | 0.117 | 0.0734 | 0.123 |

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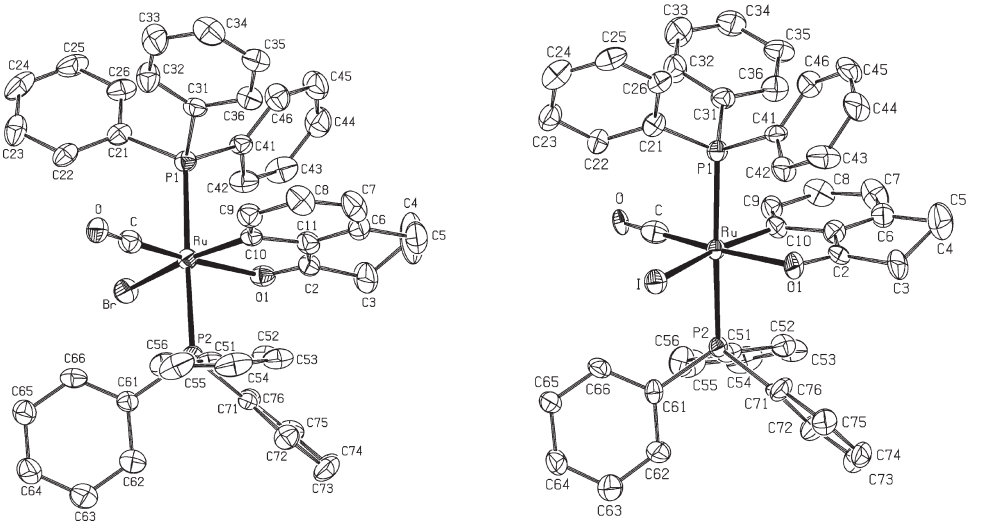
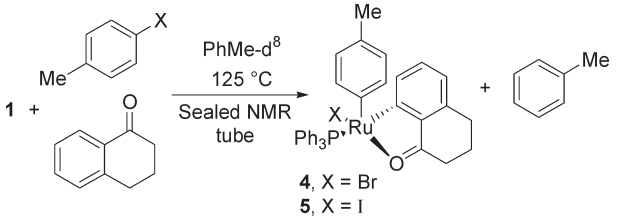


**Figure 2.** X-ray crystallography structure of RuBr(CO)(α-tetralone)($PPh_3$)$_2$ (**4**) and RuI(CO)(α-tetralone)($PPh_3$)$_2$ (**5**).

**Scheme 3. Reaction of Tetralone and Iodo/Bromotoluene with Active Ru(0) Catalyst 1**



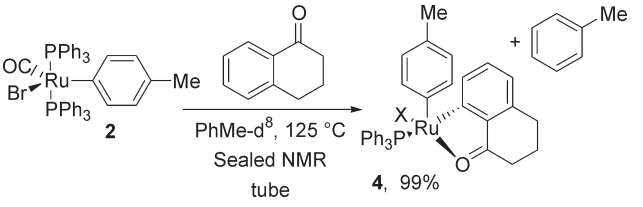

One equivalent of bromotoluene and α-tetralone were added to stoichiometric amounts of activated complex **1**. Analysis by $^1$H NMR showed the formation of both a new α-tetralone product, RuBr(CO)($\eta^1$-C, $\kappa^1$-O, α-tetralone)-($PPh_3$)$_2$, with substitution *ortho* to the ketone (**4**), and toluene (51% conversion). Complex **2** was also detected as a minor product (Scheme 3). The analogous compound was formed using iodotoluene to give RuI(CO)($\eta^1$-C, $\kappa^1$-O, α-tetralone)($PPh_3$)$_2$ (**5**) (61% conversion). The iodotoluene oxidative addition product **3** was also present, in 39% conversion. Similar shifts were seen in the H NMR using tolyl triflate, although no product was isolated from this reaction.

Analysis of the yellow orthorhombic crystals isolated from the reactions confirmed the structure of **4** and **5** as RuBr-(CO)(α-tetralone)($PPh_3$)$_2$ and RuI(CO)(α-tetralone)($PPh_3$)$_2$, respectively (Figure 2). Complexes **4** and **5** crystallized as orthorhombic crystals in space group *Pna*2$_1$ (see Tables 2 and 3). These complexes are octahedral Ru(II) with the bulky phosphorus ligands *trans* to each other. The CO stretching band appears at a lower frequency for **5** (1919 cm$^{-1}$) as opposed to that for **4** (1929 cm$^{-1}$), as I is a stronger $\pi$-donor than Br, which results in a more electron-rich metal center and hence stronger back-bonding that lowers the CO stretching frequency.[15] No direct arylation products were observed from these reactions.

**Table 3. Selected Bond Lengths and Angles for 4 and 5**

| bond distances (Å) | **4** (X = Br) | **5** (X = I) |
|---|---|---|
| Ru−C | 1.832(5) | 1.844(7) |
| Ru−C10 | 2.028(5) | 2.030(7) |
| Ru−O1 | 2.151(3) | 2.140(4) |
| Ru−P1 | 2.3739(13) | 2.3857(18) |
| Ru−P2 | 2.3791(12) | 2.3817(17) |
| Ru-X | 2.6247(6) | 2.7872(8) |
| C−O | 1.104(5) | 1.058(8) |
| O1−C2 | 1.250(5) | 1.252(9) |
| bond angles (deg) | **4** (X = Br) | **5** (X = I) |
| C−Ru−C10 | 92.9(2) | 93.6(3) |
| C−Ru−O1 | 172.36(19) | 172.4(3) |
| C10−Ru−O1 | 79.44(17) | 78.8(3) |
| C−Ru−P2 | 90.91(14) | 91.1(2) |
| C10−Ru−P2 | 88.76(12) | 89.9(2) |
| O1−Ru−P2 | 88.84(8) | 89.13(13) |
| C−Ru−P1 | 89.68(14) | 89.9(2) |
| C10−Ru−P1 | 88.97(12) | 87.9 (2) |
| O1−Ru−P1 | 90.28(8) | 89.59(13) |
| P2−Ru−P1 | 177.69(5) | 177.65(7) |
| C−Ru−X | 101.16(17) | 100.3(3) |
| C10−Ru−X | 165.87(14) | 166.0(2) |
| O1−Ru−X | 86.48(10) | 87.34(15) |
| P2−Ru−X | 92.15(3) | 91.85(5) |
| P1−Ru−X | 89.93(3) | 90.06(5) |
| O−C−Ru | 176.7(5) | 178.3(8) |
| C2−O1−Ru | 112.8(3) | 113.9(5) |
| C9−C10−Ru | 131.6(4) | 131.6(6) |
| C11−C10−Ru | 112.5(4) | 114.1(5) |

**Scheme 4. Synthesis of the Six-Coordinate C−H Activation Products from Tetralone and RuX(CO)(*p*-tolyl)($PPh_3$)$_2$ (2/3)**




To investigate the mechanism of the above reaction, the bromotoluene insertion product (**2**) was reacted directly with α-tetralone (Scheme 4). This reaction proceeded quantitatively to give **4** after just 30 min. Although a transmetalation mechanism cannot be ruled out (**2** could be in equilibrium

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with bromotoluene and activated ruthenium complex **1**), the stability of **2** to heat suggests that the ruthenium aryl halide complex inserts into the *ortho* C−H bond of α-tetralone. This could either be via electrophilic substitution or by a concerted mechanism where a [2+2] reaction occurs, forming toluene and a new Ru−C bond. In both cases toluene was produced as a byproduct.

Similar ruthenium-bound ketones, with a chloro ligand, have some precedent in the literature, although the syntheses of these complexes are not from a five-coordinate Ru(II) species.[16] The corresponding displacement of phenyl ligands from $RuCl(CO)(C_6H_6)(P^iPr_3)_2$ reacting with benzophenone imines has been reported by Esteruelas.[16] They conclude that carbon−carbon replacements occur before coordination of the nitrogen, achieving a novel $C(sp^2)/C(sp^2)$ metathesis type reaction (concerted [2+2] type reaction). This proposed mechanism supports our observations and the postulated formation of **4** and **5**.

## Conclusion

In conclusion we have reported the first example of an isolable five-coordinate Ru(II) complex derived from the oxidative addition of either an aryl bromide or iodide to a Ru(0) complex ($RuX(CO)(p\text{-tolyl})(PPh_3)_2$). The addition of a ketone to this complex results in C−H insertion to give a six-coordinate, Ru(II) complex ($RuX(CO)(\alpha\text{-tetralone})(PPh_3)_2$) and aryl-H. Despite no observed aryl−aryl bond formation, the Ru(0)/Ru(II) redox couple cannot be ruled out in the mechanism of the direct arylation of aryl halides.

## Experimental Section

**Preparation of RuBr(CO)(*p*-tolyl)($PPh_3$)$_2$ (2). NMR Scale.** Styrene (3.8 μL, 0.030 mmol) was added to a solution of $RuH_2(CO)(PPh_3)_3$ (37 mg, 0.040 mmol) in PhMe-$d_8$ (0.75 mL) under argon using a glovebox and sealed in a Young's tap NMR tube. The solution was heated to 110 °C for 1 h, in which time the solution turned dark red, and allowed to cool to rt. Bromotoluene (5 μL, 0.040 mmol) was added dropwise under a $N_2$ atmosphere and the solution heated to 130 °C for 50 min. The reaction was cooled to rt; $^1$H NMR indicated 54% conversion to **2**. Complex **2** (18 mg, 55%) was isolated directly from the reaction as red monoclinic crystals suitable for X-ray analysis.

**Preparative Scale.** The synthesis was as above, but the reaction was performed using Schlenk techniques on a 0.23 mmol scale. After the reaction was cooled to rt the solvent was removed *in vacuo* until 1 mL of solvent remained, and the solvent removed by filter cannula to give a red solid. Purification was achieved by washing the solid with PhMe to give **2** as a red solid (0.14 g, 74%); mp 228−230 °C; IR $\nu_{max}$ 1919 ($\nu_{CO}$), 1478, 1432, 1092, 1043, 1011, 795 cm$^{-1}$; $^1$H NMR $\delta$ 2.11 (3H, s, C$H_3$), 6.35 (2H, d, $J$ = 8.0, Ar$H$), 6.56 (2H, d, $J$ = 8.0, Ar$H$), 7.25−7.45 (30H, m, $PPh_3$); $^{13}$C NMR $\delta$ 20.4, 127.3, 128.4, 128.4, 128.5, 130.5, 132.6, 134.8, 134.8, 134.9, 137.6; HRMS $C_{42}H_{38}NaOP_2Ru$ calcd 745.13347, found 745.1330. Anal. Calcd for $C_{44}H_{37}RuOP_2Br$: C, 64.09; H, 4.52. Found: C, 64.44; H, 4.61.

**Preparation of RuI(CO)(*p*-tolyl)($PPh_3$)$_2$ (3). NMR Scale.** The synthesis was performed in an identical manner to that for the NMR experiment of **2** except iodotoluene (7.3 μL, 0.030 mmol) was added. $^1$H NMR indicated 47% conversion to **3**. Complex **3** (16 mg, 46%) was isolated directly from the reaction as a red solid.

**Large Scale.** The synthesis was as above, but the reaction was performed using Schlenk techniques on a 0.230 mmol scale. After the reaction was cooled to rt the solvent was removed *in vacuo* until 1 mL of solvent remained and the resultant precipitate filtered. Purification was achieved by washing the precipitate with $Et_2O$ to give **3** as a red solid (18 mg, 9%); mp 210−212 °C; IR $\nu_{max}$ 1919 ($\nu_{CO}$), 1478 ($\delta_{CH}$), 1433 ($\delta_{CH}$), 1092, 1042, 1010, 843 cm$^{-1}$; $^1$H NMR $\delta$ 2.04 (3H, s, C$H_3$), 6.25−6.31 (4H, d, Ar$H$), 7.20−7.38 (30H, m, $PPh_3$); HRMS $C_{44}H_{37}OP_2Ru$ calcd 745.1334, found 745.1330. Anal. Calcd for $C_{44}H_{37}RuOP_2I$: C, 60.63; H, 4.28. Found C, 64.85; H, 4.49.

**Preparation of RuBr(CO)($\eta^1$-C, $\kappa^1$-O, α-tetralone)($PPh_3$)$_2$ (4). NMR Scale.** The synthesis was performed in an identical manner to that for the NMR experiment of **2** except α-tetralone (4.4 μL, 0.030 mmol) was added to the solution, immediately followed by bromotoluene (4.1 μL, 0.030 mmol), under a $N_2$ atmosphere, and the solution was heated to 135 °C for 1 h. The reaction was cooled to rt; $^1$H NMR indicated 12% conversion to **2** and 51% conversion to **4** (based upon amount of toluene present). Complex **4** (16 mg, 46%) was isolated directly from the reaction as yellow orthorhombic crystals suitable for X-ray analysis.

**Method 2.** A solution of **2** (10 mg, 0.012 mmol) in PhMe-$d_8$ (0.6 mL) was treated with α-tetralone (1.60 μL, 0.012 mmol) under argon using a glovebox and sealed in a Young's tap NMR tube. The reaction mixture was heated to 135 °C for 30 min. In this time the solution changed color from red to yellow. On cooling, yellow crystals of **4** precipitated and the solution was filtered to give **4** (11 mg, >99%) as a yellow solid, the analytical data of which were identical to above: mp 126−129 °C; IR $\nu_{max}$ 1919 ($\nu_{CO}$), 1582, 1566 ($\nu_{CO}$), 1433, 1092, 773 cm$^{-1}$; $^1$H NMR $\delta$ 1.42 (2H, app quin, $J$ = 6.0, C$H_2$), 1.83 (2H, t, $J$ = 6.0, C$H_2$), 2.40 (2H, t, $J$ = 6.0, C$H_2$), 6.42 (2H, m, Ar$H$), 6.55 (1H, d, $J$ = 6.4, Ar$H$), 7.19−7.38 (30H, m, $PPh_3$); $^{13}$C NMR $\delta$ 23.7 ($CH_2$), 28.7 ($CH_2$), 36.3 ($CH_2$), 119.4 (CH), 124.8 (C), 127.5 (CH), 129.5 (CH), 131.3 (C), 131.5 (C), 131.7 (C), 134.0 (CH), 134.5 (CH), 138.9 (CH), 146.2 (C), 210.9 (C); $m/z$ (EI+) 799 (60%, $M^+$ − Br), 675 (42%, $M^+$ + Na − Br,α-tetralone); HRMS $C_{47}H_{39}O_2P_2Ru$ calcd 799.1476, found 799.1491. Anal. Calcd for $C_{47}H_{39}RuO_2P_2Br$: C, 64.24; H, 4.47. Found: C, 63.98; H, 4.52.

**Preparation of RuI(CO)($\eta^1$-C, $\kappa^1$-O, α-tetralone)($PPh_3$)$_2$ (5). NMR Scale.** The synthesis was performed in an identical manner to that for the NMR experiment of **2** except iodotoluene (3.1 μL, 0.030 mmol) was added. The reaction was cooled to rt; $^1$H NMR indicated 39% conversion to **3** and 61% conversion to **5** (based upon amount of toluene present). Complex **5** (15 mg, 41%) was isolated directly from the reaction as yellow orthorhombic crystals suitable for X-ray analysis: mp 132−137 °C; IR $\nu_{max}$ 2941 ($\nu_{CH}$), 1929 ($\nu_{CO}$), 1585, 1568 ($\nu_{CO}$), 1485, 1439, 1115, 1092, 998 cm$^{-1}$; $^1$H NMR $\delta$ 1.41 (2H, m, 6.0, C$H_2$), 1.90 (2H, t, $J$ = 6.2, C$H_2$), 2.43 (2H, t, $J$ = 6.2, C$H_2$), 6.42 (1H, d, $J$ = 7.4, Ar$H$), 6.54 (1H, t, $J$ = 7.4, Ar$H$), 6.75 (1H, d, $J$ = 7.4, Ar$H$), 7.19 − 7.38 (30H, m, $PPh_3$); $^{13}$C NMR $\delta$ 23.7 ($CH_2$), 28.6 ($CH_2$), 36.4 ($CH_2$), 117.3 (CH), 118.0 (CH), 119.6 (CH), 124.8 (C), 127.5 (CH), 129.5 (CH), 131.3 (C), 131.5 (C), 131.7 (C), 134.0 (CH), 135.3 (CH), 138.9 (CH), 146.2 (C); $m/z$ (EI+) 799 (60%, $M^+$ − I), 675 (42%, $M^+$ + Na − I,α-tetralone); HRMS $C_{47}H_{39}O_2P_2Ru$ calcd 799.1476, found 799.1491.

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**Supporting Information Available:** Crystal structure determinations, reports for **2**, **4**, and **5**; the crystallographic data are also given as CIF files. These materials are available free of charge via the Internet at http://pubs.acs.org.

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