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Neutral, Cationic, and Zwitterionic Ruthenium(II) Atom Transfer Radical Addition Catalysts Supported by P,N-Substituted Indene or Indenide Ligands

Rylan J. Lundgren,[†] Matthew A. Rankin,[†] Robert McDonald,[‡] and Mark Stradiotto*,[†]

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3, and X-Ray Crystallography Laboratory, Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

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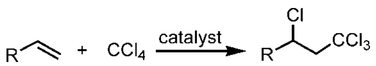
A series of Ru-based complexes supported by P,N-substituted indene or indenide ligands have been prepared and tested for activity in the atom transfer radical addition of CCl_4 to alkenes. The catalytic performance was found to be influenced by the charge and substitution pattern of the P,N ligand and other coligands, as well as the nature of the counteranion, with the best of these catalysts being effective at low catalyst loadings and under mild conditions.

Scheme 1. Generic Representation of the Catalysed ATRA of CCl_4 to Monosubstituted Olefins



The metal-catalyzed atom transfer radical addition (ATRA) of halocarbons to olefins, often referred to as the Kharasch reaction, represents an efficient and atom-economical method of C−C bond formation (Scheme 1).[1] Although several classes of metal complexes act as ATRA catalysts,[1,2] Ru-based species are among the most active for this transformation.[3] The most extensively employed Ru-based precatalyst, $RuCl_2(PPh_3)_3$,[4] has been used to promote the addition of halocarbons to various olefinic substrates and has found application in related atom transfer radical cyclizations (ATRC).[5] However, major drawbacks associated with this precatalyst include the relatively high catalyst loading (≥0.5 mol %) and temperatures (≥80 °C) that are often needed to achieve acceptable yields. In the pursuit of more effective Ru-based ATRA and ATRC catalysts, a number of ancillary ligation strategies have been evaluated, including (but not restricted to):[3] alkylidene, vinylidene, and N-heterocyclic carbene ligated structures;[6] dimeric and multinuclear phosphine/arene-type systems;[7] carborane-supported complexes;[8] η^5-cyclopentadienyl-type complexes featuring amidinate,[9] alkoxide,[10] or other coligands. In recent studies by Demonceau and co-workers,[11] divergent catalytic abilities were noted for half-sandwich Ru(phosphine) complexes supported by η^6-arene, η^5-indenyl, η^5-C_5H_5 (Cp), or η^5-C_5Me_5 (Cp*) ligands, with $Cp^*Ru(PPh_3)_2Cl$ proving capable of mediating the addition of CCl_4 to a variety of olefins at low catalyst loadings (0.33 mol % Ru) and under mild conditions. More recently, Severin and co-workers[12] observed that $[Cp^*Ru(PPh_3)_2(MeCN)]^+SO_3CF_3^-$ displayed increased catalytic activity versus $Cp^*Ru(PPh_3)_2Cl$ in ATRA chemistry, thereby suggesting that such formally cationic Cp*Ru species may offer advantages over related neutral precatalysts; indeed, this cationic complex is one of the most active Ru-based ATRA precatalysts known. Notwithstanding the diverse set of Ru complexes that have been

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* To whom correspondence should be addressed. Fax: 1-902-494-1310. Tel: 1-902-494-7190. E-mail: mark.stradiotto@dal.ca.

[†] Dalhousie University.

[‡] University of Alberta.

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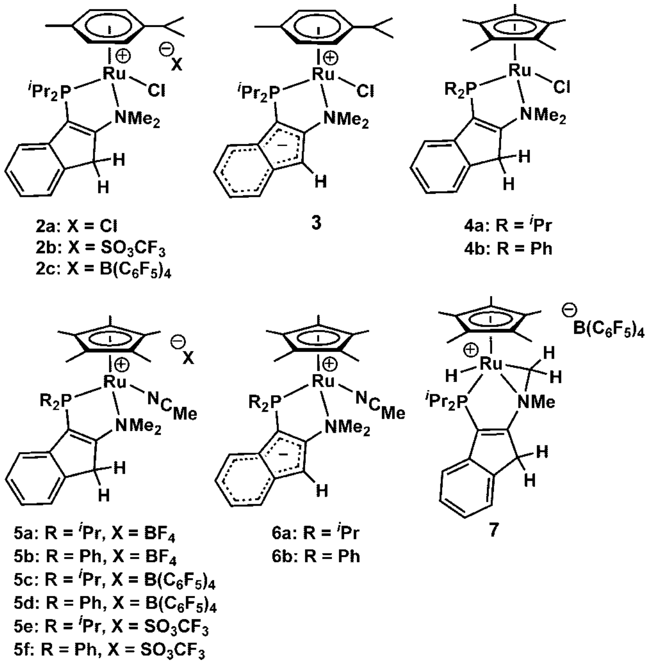
Chart 1



2a: X = Cl
2b: X = SO$_3$CF$_3$
2c: X = B(C$_6$F$_5$)$_4$

4a: R = ^{i}Pr
4b: R = Ph

5a: R = ^{i}Pr, X = BF$_4$
5b: R = Ph, X = BF$_4$
5c: R = ^{i}Pr, X = B(C$_6$F$_5$)$_4$
5d: R = Ph, X = B(C$_6$F$_5$)$_4$
5e: R = ^{i}Pr, X = SO$_3$CF$_3$
5f: R = Ph, X = SO$_3$CF$_3$

6a: R = ^{i}Pr
6b: R = Ph

shown to catalyze ATRA processes, mechanistic details of this reaction remain elusive, and definitive structure–reactivity relationships that are needed in order to guide the future development of increasingly effective catalysts have not yet been established. Consequently, "universal" Ru-based ATRA catalysts that are highly active, are long-lived, and exhibit a wide substrate scope are unknown.

Despite the established utility of P,N ligands in engendering desirable reactivity properties to platinum-group metal catalysts,[13] the application of P,N ligands in Ru-mediated ATRA has yet to be reported in the literature. In this context, and as part of our ongoing research program comparing the reactivity of structurally related neutral, cationic, and formally zwitterionic[14] metal complexes supported by P,N-substituted indene and indenide ligands,[15] we became interested in evaluating the utility of such Ru complexes in promoting the ATRA of chlorocarbons to olefins, especially in light of the interesting stoichiometric and catalytic reactivity exhibited by Ru derivatives of 1-^{i}Pr$_2$P-2-Me$_2$N-indene (**1a**).[15a,e] We disclose herein the application of previously reported neutral, cationic, and zwitterionic Ru complexes derived from **1a**, as well as several new Ru derivatives of 1-Ph$_2$P-2-Me$_2$N-indene (**1b**[16]), as precatalysts for ATRA chemistry (Chart 1). Notably, the catalytic performance exhibited by such Ru species was found to be influenced by the charge and substitution pattern of the coordinated P,N and other coligands, as well as the nature of the accompanying counteranion. The most active of the Ru complexes explored herein (**5b**) proved capable of mediating the ATRA of CCl$_4$ to a variety of olefins under mild conditions. Also described are the results of catalytic ATRA experiments employing AIBN (AIBN = azobis(isobutyronitrile)) as a cocatalyst, which enabled Ru loadings as low as 0.02 mol % to be utilized effectively.

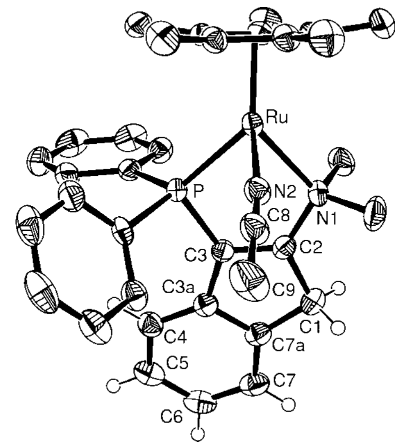


Figure 1. ORTEP diagram for **5f**, shown with 50% displacement ellipsoids and with the atomic numbering scheme depicted. Selected H atoms and the triflate counteranion have been omitted for clarity. Only one of the two crystallographically independent molecules of **5f** is shown. Selected bond lengths (Å) and angles (deg) data for **5f**: Ru–P, 2.2956(8); Ru–N1, 2.302(2); Ru–N2, 2.067(3); P–C3, 1.796(3); N1–C2, 1.454(4); C1–C2, 1.516(4); C2–C3, 1.338(4); Ru–N2–C8, 170.7(3); N2–C8–C9, 178.8(4).

Results and Discussion

In order to survey a broad set of Ru-based complexes for ATRA reactions, we sought to expand our library of catalysts based on P,N-substituted indene or indenide ligands by preparing a new set of complexes derived from 1-Ph$_2$P-2-Me$_2$N-indene (**1b**). The addition of 0.25 equiv of [Cp*RuCl]$_4$ to **1b** afforded Cp*Ru(Cl)(κ^2-1-Ph$_2$*P*-2-Me$_2$*N*-indene) in 97% isolated yield. Isomerization of this complex to **4b** (86% isolated yield, Chart 1) was achieved upon exposure to NEt$_3$ in THF. Treatment of **4b** with an appropriate chloride-abstracting agent in acetonitrile afforded the corresponding cationic complexes [Cp*Ru(MeCN)(κ^2-3-Ph$_2$*P*-2-Me$_2$*N*-indene)]$^+$X$^-$ (X = BF$_4$, **5b**, 94%; X = B(C$_6$F$_5$)$_4$, **5d**, 91%; X = SO$_3$CF$_3$, **5f**, 90%). Preparation of the zwitterionic complex **6b** was achieved in 89% isolated yield by the addition of K$_2$CO$_3$ to an acetonitrile solution of **4b**. The structures of these new complexes were assigned on the basis of NMR data and, in the case of **5f**, X-ray diffraction data (Figure 1).[17] As expected, **5f** exhibits a piano-stool geometry reminiscent of the crystallographically characterized complex **5a**.[15e]

The Ru-mediated ATRA of CCl$_4$ to styrene at 60 °C was employed as a preliminary test reaction with which to survey the catalytic abilities of the P,N-ligated complexes depicted in Chart 1. Both cationic (**2a**–**c**) and zwitterionic (**3**) compounds supported by η^6-arene ligands proved to be catalytically inactive, yielding negligible amounts of the desired addition product. Conversely, all of the Cp*Ru species surveyed exhibited

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(17) Selected crystal data for **5f**: monoclinic ($P2_1/n$); a = 18.3091(12) Å; b = 19.9442(13) Å; c = 19.2586(12) Å; β = 91.1091(9)°; V = 7031.2 (8) Å^3; Z = 8; GOF = 1.042; R1 = 0.0414; wR2 = 0.1050.

Table 1. Screening of Complexes for ATRA of CCl_4 to Styrene[a]

entry	catalyst	conversn (%)[b]	yield (%)[c]
1	**4a**	84	78
2	**4b**	91	78
3	**5a**	71	66
4	**5b**	>99	97
5	**5c**	87	75
6	**5d**	>99	95
7	**5e**	69	43
8	**5f**	>99	90
9	**6a**	93	78
10	**6b**	94	82
11	**7**	79	55

[a] Conditions: reactions performed in toluene for 4 h at 60 °C; Ru:olefin:CCl_4 = 1:300:600; [olefin] = 1.4 M. [b] Conversion determined on the basis of the styrene consumed. [c] Yield based on formation of the ATRA product as determined by GC using dodecane as an internal standard. See the Experimental Section for complete experimental details.

Table 2. ATRA of CCl_4 to Olefins Catalyzed by Ru Complexes[a]

entry	catalyst	olefin	temp (°C)	time (h)	yield (%)[b]
1	**4b**	styrene	24	5	50
2	**5d**	styrene	24	5	48
3	**5f**	styrene	24	5	95
4	**6b**	styrene	24	5	62
5	**5b**	styrene	24	5	95
6	**5b**	*p*-chlorostyrene	24	5	83
7	**5b**	α-methylstyrene	40	4	91
8	**5b**	1-hexene	40	6	37
9	**5b**	methyl methacrylate	40	4	34

[a] Conditions: reactions performed in toluene; Ru:olefin:CCl_4 = 1:300:600; [olefin] = 1.4 M. [b] Yield based on formation of the ATRA product as determined by GC using dodecane as an internal standard. See the Experimental Section for complete experimental details.

moderate (43%) to excellent (97%) yields of the addition product after 4 h when employing a catalyst-to-substrate ratio of 1:300 (Table 1). The neutral complexes **4a**,**b** and **6a**,**b** (zwitterionic) showed very similar ATRA activity, affording 78–80% of the addition product after 4 h at 60 °C. In contrast, the catalytic efficiency of the salts **5a**−**f** differed significantly, with precatalysts featuring PPh_2-based ligands consistently outperforming analogous complexes supported by P^iPr_2-based ligands. While under the conditions surveyed **5b** proved to be the most effective precatalyst in mediating the addition of CCl_4 to styrene (>99% conversion, 97% yield; Table 1, entry 4), the related acetonitrile-stabilized cations supported by 3-Ph_2P-2-Me_2N-indene (**5d**,**f**) also provided excellent results (Table 1, entries 6 and 8). Given the postulate that ATRA catalysis could be facilitated by coordinative unsaturation at Ru,[1,3] we investigated the activity of **7**, which in solution has been shown to provide access to the coordinatively unsaturated species $[Cp^*Ru(\kappa^2\text{-}3\text{-}Ph_2P\text{-}2\text{-}Me_2N\text{-indene})]^+B(C_6F_5)_4^-$ by way of reversible intramolecular C−H activation.[15e] However, the observation that **7** afforded only 55% yield after 4 h (Table 1, entry 11) and proved to be one of the least effective Cp*Ru precatalysts examined in our reactivity survey suggests that coordinated MeCN might play an important role in engendering desirable catalytic properties to $[Cp^*Ru(PPh_3)_2(MeCN)]^+SO_3CF_3^-$,[12] as well as to **5a**−**f**.

Having established the catalytic utility of Cp*Ru complexes supported by P,N-substituted indene or indenide ligands for the ATRA of CCl_4 to styrene and at 60 °C, the ability of such complexes to mediate this transformation at 24 °C was tested (Table 2); given the results of our preliminary catalytic survey (*vide supra*), only Cp*Ru complexes supported by κ^2-3-Ph_2P-2-Me_2N-indene were examined. While the catalytic productivity observed for the neutral species **4b** and **6b**, as well as the salt **5d**, at 24 °C was diminished significantly relative to experiments conducted at 60 °C, the related cationic complexes **5b,f** remained effective at lower temperatures, providing 95% yield of the desired addition product after 5 h (Table 2, entries 3 and 5). Other styrene derivatives were also employed successfully as substrates in combination with **5b**, affording the desired ATRA product in high yields (Table 2, entries 6 and 7). However, whereas the catalytic performance of **5b** with styrene-type substrates is comparable to that of $[Cp^*Ru(PPh_3)_2(MeCN)]^+SO_3CF_3^-$ reported by Severin and co-workers,[12] **5b** performed less effectively in the ATRA of CCl_4 to 1-hexene (Table 2, entry 8) and methyl methacrylate (Table 2, entry 9) under the standard conditions of 0.33 mol % **5b** at 40 °C.

Table 3. ATRA of CCl_4 to Olefins Catalyzed by Ru Complexes in the Presence of 5 mol % AIBN[a]

entry	catalyst	olefin	S:C[b]	time (h)	yield (%)[c]
1	**4b**	styrene	5000	24	89
2	**5d**	styrene	5000	24	49
3	**5f**	styrene	5000	24	88
4	**5b**	styrene	5000	24	87
5	**5b**	*p*-chlorostyrene	5000	28	90
6	**5b**	α-methylstyrene	3750	30	85
7	**5b**	1-hexene	2000	24	99
8	**5b**	methyl methacrylate	2000	24	66

[a] Conditions: reactions performed at 60 °C in toluene; olefin:CCl_4 = 1:4; 5 mol % AIBN relative to olefin; [olefin] = 1.4 M. [b] Substrate (olefin) to Ru catalyst ratio. [c] Yield based on formation of the ATRA product as determined by GC using dodecane as an internal standard. See the Experimental Section for complete experimental details.

It has been demonstrated recently that the addition of cocatalysts such as the radical initiator AIBN can result in significantly enhanced efficiency in metal-mediated ATRA,[18] presumably by facilitating the regeneration of catalytically active metal species.[19] In applying this protocol to the more effective precatalysts under scrutiny herein, we observed that the use of 5 mol % AIBN (relative to olefin) in reactions conducted at 60 °C allowed for the efficient ATRA of CCl_4 to styrene at Ru loadings of 0.02 mol % (Table 3). Under these conditions, the neutral precatalyst **4b** performed on a par with cations **5f** and **5b** in providing the desired ATRA product in ca. 88% yield after 24 h (Table 3, entries 1, 3, and 4); surprisingly, the structurally related cationic complex **5d** featuring the $B(C_6F_5)_4^-$ counteranion proved inferior to the aforementioned precatalysts (Table 3, entry 2). A catalyst mixture comprised of 5 mol % AIBN and 0.02–0.05 mol % **5b** also allowed for the efficient ATRA of CCl_4 to substituted styrenes (Table 3, entries 5 and 6), 1-hexene (Table 3, entry 7), and methyl methacrylate (Table 3, entry 8); notably, the yields achieved for the last two substrates exceeded greatly those obtained by use of AIBN-free conditions (Table 2, entries 8 and 9).

Despite the desirable catalytic performance exhibited by the Cp*Ru complexes herein for the ATRA of CCl_4 to olefins, we have not been able to extend this catalysis to the use of $CHCl_3$ as a substrate. Essentially no conversion was observed for the ATRA of $CHCl_3$ to styrene when employing the precatalysts studied in this work at the 1 mol % Ru catalyst loading level.[20] Furthermore, efforts to use 0.1 mol % **5b** as a precatalyst for this transformation in the presence of 5 mol % AIBN also

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(18) (a) Eckenhoff, W. T.; Pintauer, T. *Inorg. Chem.* **2007**, *46*, 5844. (b) Quebette, L.; Thommes, K.; Severin, K. *J. Am. Chem. Soc.* **2006**, *128*, 7440.

(19) The use of Mg in a three-fold excess relative to the olefin substrate has also been shown to enhance Ru-catalyzed ATRA: Thommes, K.; Içli, B.; Scopelliti, R.; Severin, K. *Chem. Eur. J.* **2007**, *13*, 6899.

(20) The observation of desirable performance in Ru-mediated ATRA chemistry employing CCl_4 but not $CHCl_3$ (or vice versa) is well-established.[3a,7a]

proved unproductive. The complete lack of reactivity observed when using $CHCl_3$ as a substrate cannot be explained exclusively in terms of a deactivating effect of this substrate on the Ru precatalysts employed, given that the ATRA of CCl_4 to styrene using $CHCl_3$ as the solvent still provided good yields of the desired CCl_4 addition product (**5b**:olefin = 1:300; 24 °C, 5 h, 87% yield).

Summary and Conclusions

The exploration of a diverse set of neutral, cationic, and zwitterionic Ru species derived from P,N-substituted indenes has established that, for this family of precatalysts, ATRA activity is influenced by a number of structural factors. While (*p*-cymene)Ru complexes of this type were found to be ineffective catalysts, related Cp*Ru complexes, in particular cationic species supported by 3-Ph_2P-2-Me_2N-indene, displayed high activity for the ATRA of CCl_4 to styrene under mild conditions and at low catalyst loadings. When structurally analogous salts of the type $[Cp^*Ru(MeCN)(\kappa^2\text{-}3\text{-}Ph_2P\text{-}2\text{-}Me_2N\text{-indene})]^+X^-$ were employed as ATRA precatalysts at 24 °C, a considerable counteranion effect on catalyst performance was observed. While the complexes explored herein proved inactive for the ATRA of $CHCl_3$, the use of AIBN as a cocatalyst provided enhanced catalytic performance for the ATRA of CCl_4, with moderate to excellent yields obtained for a series of unsaturated substrates at low Ru loadings (0.05–0.02 mol %). Given that the oxidation of Ru(II) to Ru(III) upon abstraction of a chlorine atom from CCl_4 represents a viable mechanistic step in such ATRA catalysis,[3] the superior performance noted for the Cp*Ru complexes in our study may be attributable to the greater ability of the anionic η^5-$C_5Me_5^-$ ligand to stabilize such Ru(III) intermediates. However, given that precise details regarding the mechanism of Ru-mediated ATRA are lacking,[3] we are unable to provide a rationale for the consistently superior performance of complexes supported by κ^2-3-Ph_2*P*-2-Me_2*N*-indene versus those featuring κ^2-3-$^iPr_2$*P*-2-Me_2*N*-indene ligation, nor are we able to comment definitively regarding the origins of the divergent catalytic performance of structurally related neutral, cationic, and zwitterionic complexes. Nonetheless, it is our hope that these findings will contribute to the rational discovery of new, more robust, and effective Ru-based ATRA catalysts.

Experimental Section

Representative synthetic procedures (for **4b**, **5f**, and **6b**) and catalytic protocols are provided below. Other experimental details pertaining to the synthesis of Cp*Ru(Cl)(κ^2-1-Ph_2*P*-2-Me_2*N*-indene), **5b**, and **5d** and the crystallographic solution and refinement of **5f** are given in the Supporting Information.

Synthesis of 4b. To a glass vial containing a magnetically stirred solution of freshly prepared Cp*Ru(Cl)(κ^2-1-Ph_2*P*-2-Me_2*N*-indene) (0.30 g, 0.49 mmol) in THF (8 mL) was added NEt_3 (3 mL). The vial was then sealed with a PTFE-lined cap, and the solution was stirred magnetically for 72 h. ^{31}P NMR data collected on an aliquot of this solution indicated clean conversion to **4b**. The THF solvent and other volatile materials were then removed in vacuo, yielding a dark red oily solid. The solid was then triturated with pentane (2 × 1.5 mL), followed by pentane washes (2 × 1.5 mL), and the product was then dried in vacuo to yield **4b** as an analytically pure orange powder (0.26 g, 0.42 mmol, 86%). Anal. Calcd for $C_{33}H_{37}PNRuCl$: C, 64.41; H, 6.07; N, 2.28. Found: C, 64.44; H, 6.00; N, 2.24. ^1H NMR (CD_2Cl_2): δ 7.87–7.81 (m, 2H, P-aryl-H's), 7.63–7.56 (m, 2H, P-aryl-H's), 7.42–7.31 (m, 7H, 6 P-aryl-H's and either C4-H or C7-H), 7.09 (apparent d of t, J = 7.0 Hz, J = 1.0 Hz, 1H, C5-H or C6-H), 7.02 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C6-H or C5-H), 6.96 (m, 1H, C7-H or C4-H), 3.47–3.35 (m, 2H, C(H_a)(H_b)), 3.22 (s, 6H, NMe_a and NMe_b), 1.52 (d, J = 1.5 Hz, 15H, C_5Me_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 176.4 (d, $^2J_{PC}$ = 22.8 Hz, *C*2), 144.0 (d, J_{PC} = 4.8 Hz, C3a or C7a), 140.8 (d, J_{PC} = 3.7 Hz, C7a or C3a), 136.2–135.6 (m, P-aryl-C and C3), 134.1 (d, J_{PC} = 12.6 Hz, P-aryl-CH's), 133.9 (d, J_{PC} = 10.1 Hz, P-aryl-CH's), 131.9 (d, $^1J_{PC}$ = 45.8 Hz, P-aryl-C), 130.1 (P-aryl-CH), 129.1 (P-aryl-CH), 128.6 (d, J_{PC} = 9.4 Hz, P-aryl-CH's), 127.5 (d, J_{PC} = 9.6 Hz, P-aryl-CH's), 126.7 (C5 or C6), 125.5 (C6 or C5), 125.1 (C4 or C7), 122.9 (C7 or C4), 81.1 (d, J = 2.4 Hz, C_5Me_5), 31.4 (d, $^3J_{PC}$ = 8.9 Hz, C1), 10.6 (C_5Me_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 43.3.

Synthesis of 5f. To a glass vial containing a magnetically stirred orange solution of **4b** (0.21 g, 0.34 mmol) in MeCN (4 mL) was added solid $AgSO_3CF_3$ (0.090 g, 0.35 mmol) all at once. The addition caused an immediate formation of a precipitate. The vial was then sealed with a PTFE-lined cap, and the solution was stirred magnetically for 2 h. ^{31}P NMR data collected on an aliquot of this crude reaction mixture indicated the quantitative formation of **5f**. The reaction mixture was then filtered through Celite, yielding a yellow solution. The solvent and other volatile materials were subsequently removed in vacuo, affording a waxy yellow solid. The solid was then treated with CH_2Cl_2 (5 mL), and the resulting mixture was filtered through Celite. After removal of CH_2Cl_2 in vacuo, the residual solid was then washed with pentane (5 × 1.5 mL) and the product was then dried in vacuo to yield **5f** as a yellow powder (0.24 g, 0.31 mmol, 90%). ^1H NMR (CD_2Cl_2): δ 7.72–7.66 (m, 2H, P-aryl-H's), 7.52–7.42 (m, 9H, 8 P-aryl-H's and either C4-H or C7-H), 7.19 (apparent d of t, J = 7.5 Hz, J = 1.0 Hz, 1H, C5-H or C6-H), 7.06 (t, $^3J_{HH}$ = 8.0 Hz, 1H, C6-H or C5-H), 6.86 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C7-H or C4-H), 3.71–3.59 (m, 2H, C(H_a)(H_b)), 3.29 (s, 3H, NMe_a), 3.09 (s, 3H, NMe_b), 1.89 (d, $^5J_{PH}$ = 2.0 Hz, 3H, CH_3CN), 1.53 (d, J = 2.0 Hz, 15H, C_5Me_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 177.5 (d, $^2J_{PC}$ = 22.4 Hz, *C*2), 144.0 (d, J_{PC} = 5.3 Hz, C3a or C7a), 139.0 (C7a or C3a), 135.1 (d, $^1J_{PC}$ = 32.3 Hz, C3), 133.4 (d, J_{PC} = 12.9 Hz, P-aryl-CH's), 132.1 (d, J_{PC} = 10.2 Hz, P-aryl-CH's), 131.5–131.2 (m, P-aryl-C and P-aryl-CH), 130.6–130.2 (m, P-aryl-C and P-aryl-CH), 129.4 (d, J_{PC} = 10.4 Hz, P-aryl-CH's), 129.1 (d, J_{PC} = 9.6 Hz, P-aryl-CH's), 127.3 (C5 or C6), 126.7 (C6 or C5), 125.9 (CH_3CN), 125.6 (C4 or C7), 123.1 (C7 or C4), 85.6 (C_5Me_5), 60.7 (NMe_a), 53.6 (NMe_b), 31.3 (d, $^3J_{PC}$ = 9.4 Hz, C1), 10.3 (C_5Me_5), 4.3 (CH_3CN). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 43.1. A crystal of **5f** suitable for single-crystal X-ray diffraction analysis was grown from a mixture of diethyl ether and CH_2Cl_2 at −37 °C.

Synthesis of 6b. To a glass vial containing a magnetically stirred orange solution of **4b** (0.23 g, 0.37 mmol) in MeCN (7 mL) was added solid anhydrous K_2CO_3 (0.10 g, 0.74 mmol) all at once. The vial was then sealed with a PTFE-lined cap, and the solution was stirred magnetically for 48 h. During this time period, the reaction mixture gradually lightened from an orange suspension into a yellow-orange suspension. The reaction mixture was filtered through Celite to yield a yellow-orange solution, and ^{31}P NMR data collected on an aliquot of this crude reaction mixture indicated the quantitative formation of **6b**. The mixture was dried in vacuo, and the residue was then triturated with pentane (2 × 1.5 mL). The remaining product was then dried in vacuo to yield **6b** as an analytically pure yellow powder (0.20 g, 0.33 mmol, 89%). Anal. Calcd for $C_{35}H_{39}PN_2Ru$: C, 67.81; H, 6.35; N, 4.52. Found: C, 67.92; H, 6.66; N, 4.05. ^1H NMR (CD_3CN): δ 7.76–7.29 (m, 10H, P-aryl-H's), 7.17 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C4-H or C7-H), 6.75 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C7-H or C4-H), 6.52 (m, 1H, C5-H or C6-H), 6.38 (m, 1H, C6-H or C5-H), 5.99 (d, J = 4.5 Hz, 1H, C1-H), 3.34 (broad s, 3H, NMe_a), 3.22 (broad s, 3H, NMe_b), 1.51 (d, J = 1.5 Hz, 15H, C_5Me_5). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 138.5 (m, C3a or C7a), 127.9 (C7a or C3a), 133.4–133.6 (m, P-aryl-CH's), 129.8–129.6 (m, P-aryl-CH's), 129.0–128.4 (m, P-aryl-CH's), 120.3 (C4 or C7), 119.1 (C7 or C4), 116.2 (C5 or C6), 115.5 (C6 or C5), 87.3 (d, $^3J_{PC}$ = 11.3 Hz, C1), 84.2 (C_5Me$_5$), 66.0 (NMe$_a$), 55.3 (NMe$_b$), 10.6 (C$_5$$Me_5$). ^{31}P{^{1}H} NMR (CD$_3$CN): δ 33.7.

Representative Protocol for Atom Transfer Radical Addition Experiments. In a typical Ru-catalyzed atom transfer radical addition (ATRA) experiment (Table 2, entry 6), a stock solution of **5b** was prepared in THF (8.9 mg; 0.0126 mmol in 3.000 mL) and the required amount (1097 μL; 0.0046 mmol) was added to a glass reaction vial. The solvent within the vial was removed in vacuo, and to the residue was added 1.000 mL of a substrate stock solution containing *p*-chlorostyrene (371 μL), CCl$_4$ (590 μL), and dodecane (188 μL) in toluene (1050 μL) (Ru:olefin:CCl$_4$ = 1:300:600; [olefin] = 1.4 M). The mixture was stirred at 24 °C, and the progress of the reaction was monitored using GC-FID methods by passing a small aliquot of the reaction mixture solution through a short plug of silica. Yields of the desired ATRA product were determined from GC-FID data by using dodecane as an internal standard. In a representative experiment employing AIBN as a cocatalyst (Table 3, entry 5), a stock solution of **5b** was prepared in THF (8.9 mg; 0.0126 mmol in 3.000 mL); the required amount (132 μL; 0.00055 mmol) was added to a Schlenk flask, and the solvent was removed in vacuo. In a separate glass container, AIBN (93 mg; 0.57 mmol) was added to a 8.200 mL toluene stock solution of the substrates (1382 μL of *p*-chlorostyrene, 4395 μL of CCl$_4$) with dodecane (643 μL) added as an internal standard; 2.000 mL of this solution was then added to the Schlenk flask containing **5b** (Ru:AIBN:olefin:CCl$_4$ = 1:250:5000:2000; [olefin] = 1.4 M). The Schlenk flask was then placed in a temperature-controlled oil bath set at 60 °C. The progress of the reaction was monitored using GC-FID methods as described above. For all experiments, the identity of the ATRA product was confirmed by comparison of ^{1}H NMR data obtained from the isolated product with values reported in the literature. All reported catalytic results represent the average of a minimum of two trials. Published control experiments confirm the inability of 5.0 mol % AIBN (in the absence of Ru) to mediate the ATRA of CCl$_4$ to styrene under the conditions employed herein.[18b]

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Supporting Information Available: Text giving experimental details as well as a CIF file giving single-crystal X-ray diffraction data for **5f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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