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Reactivity studies of square planar platinum, iridium, and rhodium triflate complexes with alkynols

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Abstract

The reactions of *trans*-Pt(OTf)(CH_3)(PPh_3)$_2$, *trans*-Ir(OTf)(CO)(PPh_3)$_2$, and *trans*-Rh(OTf)(CO)(PPh_3)$_2$ with 3-butyn-1-ol and 4-pentyn-2-ol have been investigated.

Transition metal complexes containing a coordinated triflate ligand have assumed an increasingly important role in mechanistic and synthetic endeavors [1]. In our previous studies, we have demonstrated the versatility of newly prepared triflate complexes, *trans*-M(OTf)(CO)(PR_3)$_2$ (M = Ir, Rh), as precursors to a number of products in substitution reactions, including water complexes of rhodium and iridium [2a], cyclopropenone complexes of rhodium [2b], and novel heterobimetallic Ir–Pt complexes [2c,d]. In order to further develop the synthetic potential of these triflate compounds, we extended our investigation to include reactions which led to the formation of carbene complexes. Organometallic complexes containing metal–carbon double bonds exhibit unique and diverse reactivity and structural properties [3]. The important role of transition metal–carbene complexes in olefin metathesis [4], alkene and alkyne polymerization [5], and as synthetic intermediates [6], has attracted considerable attention and is of current research interest. The very recent report by O'Connor *et al.* [3a] on iridium carbene complexes prepared from iridium complexes containing labile ligands with 3-butyn-1-ol and 4-pentyn-2-ol prompted us to test the reactivity of platinum, iridium, and rhodium triflate complexes by utilizing these alkynols which are frequently employed as carbene precursors.

The starting material *trans*-Pt(OTf)(CH_3)(PPh_3)$_2$ (1) was prepared by the reaction of *trans*-Pt(I)(CH_3)(PPh_3)$_2$ [7] with 1.0 equiv. of AgOTf in benzene at

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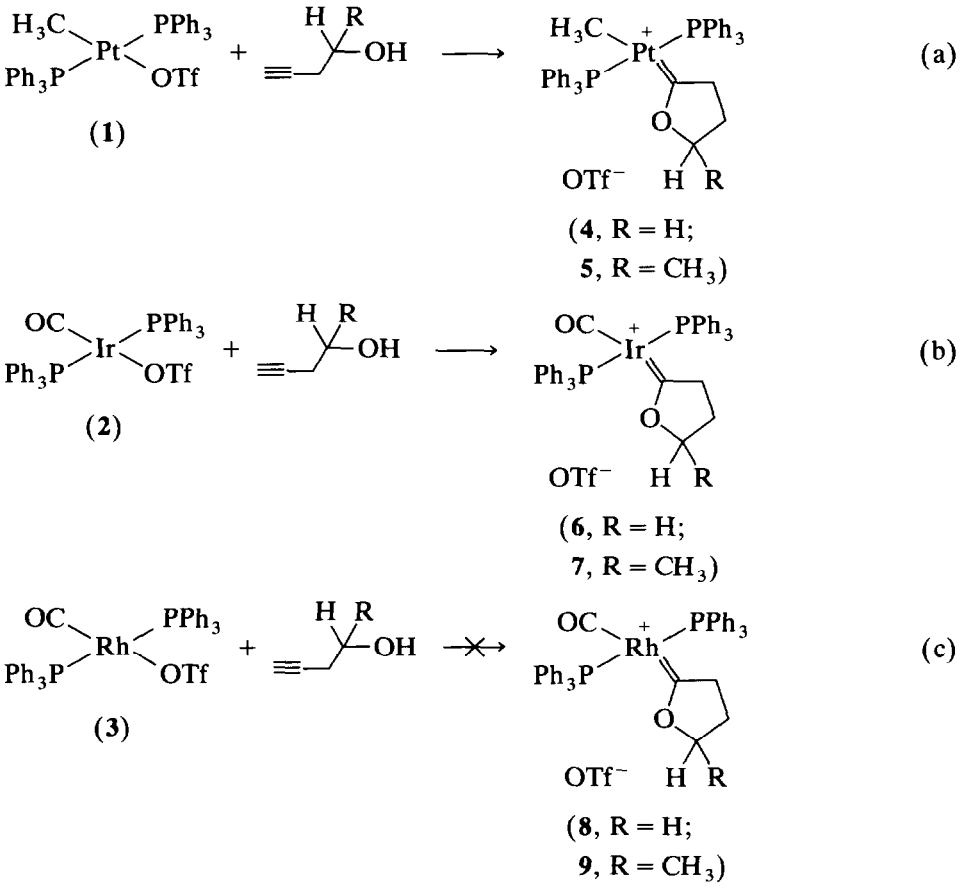
room temperature for 2 h, workup gave **1** in 91% isolated yield as a white solid. Complex **1** was characterized by NMR (^{1}H, ^{31}P{^{1}H}, ^{19}F) spectroscopy and by



Scheme 1.

microanalysis. Reaction of **1** with 1.0 equiv. of 3-butyn-1-ol in $CDCl_3$ was monitored by ^{31}P{^{1}H} and ^{1}H NMR at room temperature. The platinum carbene complex *trans*-[Pt(=C(CH$_2$)$_3$O)(CH$_3$)(PPh$_3$)$_2$]$^+$[OTf]$^-$ (**4**) cleanly formed within 3 h (Scheme 1a). In a preparative scale experiment, **4** was isolated in 86% yield as a white microcrystalline solid. In analogy to the above reaction, the interaction of platinum triflate complex **1** with 1.0 equiv. of 4-pentyn-2-ol resulted in a 86% isolated yield of the corresponding methyl-substituted carbene complex *trans*-[Pt(=C(CH$_2$)$_2$CH(CH$_3$)O)(CH$_3$)(PPh$_3$)$_2$]$^+$[OTf]$^-$ (**5**) (Scheme 1a). Complexes **4** and **5** are characterized by IR and NMR (^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, ^{19}F) spectroscopy, and by microanalysis. In the ^{13}C{^{1}H} NMR spectra the carbene–carbon resonances appear as triplets with ^{195}Pt satellites at 305.87 ppm (J(C–P) = 8.6 Hz, J(C–Pt) = 790 Hz) for **4** and 304.59 ppm (J(C–P) = 8.4 Hz, J(C–Pt) = 790 Hz) for **5**. These remarkably downfield shifts are uniquely characteristic of carbene–carbon resonances for complexes of this type [3,8]. Platinum carbene complexes which are similar to **4** and **5** have been synthesized. Chisholm and Clark [3i] reported the preparation of *trans*-[Pt(=C(CH$_2$)$_3$O)(CH$_3$)(L)$_2$]$^+$[PF$_6$]$^-$ (L = P(Me)$_2$Ph, As(Me)$_3$)

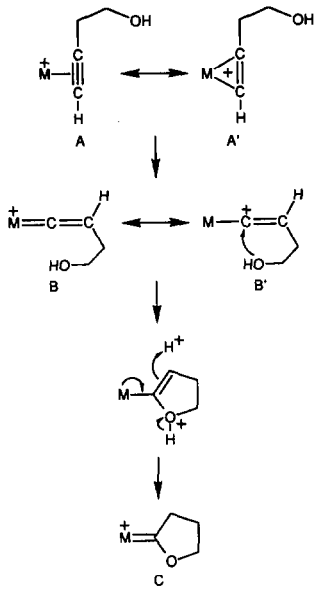
from the reaction of *trans*-Pt(Cl)(CH_3)L_2, $AgPF_6$, and 3-butyn-1-ol. However, the isolated yield of products is better in the present procedure. Other commonly used leaving groups in ligand substitution reactions include ClO_4^-, BF_4^-, and BPh_4^-. Intermediate complexes containing these leaving groups lack the thermal or photochemical stability exhibited by triflate and therefore they must be used *in situ*. It is clearly advantageous to employ an isolated, fully characterized compound, rather than a species generated *in situ* in most reactions.

Next, the reactions of **2** with alkynols were attempted under conditions identical to those for complex **1**. Reaction of *trans*-Ir(OTf)(CO)(PPh_3)$_2$ (**2**) [9*] with 1.0 equiv. of 3-butyn-1-ol in $CDCl_3$ was monitored by ^1H and $^{31}P\{^1H\}$ NMR at room temperature. After 7 h at room temperature, the $^{31}P\{^1H\}$ NMR spectrum showed a major singlet resonance appearing at 19.20 ppm accompanied by a number of low intensity resonances. With the anticipation that the resonance at 19.20 ppm in the $^{31}P\{^1H\}$ NMR spectrum was from the desired iridium carbene complex **6** (Scheme 1b), the ^1H NMR experiment for the same sample was then obtained. The ^1H NMR spectrum shows that the reaction did afford the anticipated carbene complex **6** as the major product and displays an apparently first-order pattern of two triplets and a quintet resonance characteristic of a 2-oxacyclopentylidene ligand at δ 4.13 (t, $J = 8.0$ Hz, OCH_2), δ 2.15 (t, $J = 8.0$ Hz, Ir=CCH_2), and δ 0.97 (quintet, $J = 8.0$ Hz, Ir=$CCCH_2$). Likewise, when iridium triflate complex **2** was treated with 1.0 equiv. of 4-pentyn-2-ol in $CDCl_3$, spectroscopic evidence for the formation of the corresponding methyl-substituted carbene complex **7** was observed (Scheme 1b). However, numerous other minor products were also formed.

In the preparative experiments, numerous reaction conditions were tried such as changing reaction solvents from $CHCl_3$ to acetone and benzene and utilizing 2.0 equiv. of alkynols. Many attempts to completely isolate pure **6** and **7** from the crude reaction mixture by recrystallization ($CHCl_3/Et_2O$, CH_2Cl_2/Et_2O, CH_2Cl_2/hexanes, CH_2Cl_2/Et_2O/hexanes) were unsuccessful. Thus, complexes **6** and **7** were isolated as yellow-orange crude solids in 53 and 72% yield, respectively. Clark and Manzer [8i] reported that they were unable to isolate carbene complexes from the reaction of square planar *trans*-Ir(Cl)(CO)($PMePh_2$)$_2$, $AgPF_6$, and terminal acetylenes, although they successfully prepared the iridium 2-oxocyclopentylidene complex [Ir(=C(CH_2)$_3$O)(CH_3)(Cl)(CO)($PMePh_2$)$_2$]$^+$[PF_6]$^-$ from the reaction of Ir(I)(CH_3)(Cl)(CO)($PMePh_2$)$_2$, $AgPF_6$, and 3-butyn-1-ol.

Efforts were directed next at the reaction of *trans*-Rh(OTf)(CO)(PPh_3)$_2$ (**3**) [10] with alkynols. In a representative experiment, reaction of complex **3** with 1.0 equiv. of 3-butyn-1-ol in $CDCl_3$ was monitored by $^{31}P\{^1H\}$ and ^1H NMR at room temperature. The $^{31}P\{^1H\}$ NMR spectrum showed that the resonance due to the starting material (28.31 ppm, d, J(P–Rh) = 124.4 Hz) was rapidly replaced by a new signal at 28.09 ppm (d, J(P–Rh) = 123.9 Hz). However, the ^1H NMR spectrum for the same sample showed several unresolved broad multiplet resonances in the range δ 5.23–0.74 in addition to the aromatic proton resonances at δ 7.80–7.30 for the triphenylphosphine groups. No evidence was observed for the generation of the anticipated rhodium carbene complexes **8** and **9** in the reactions, as shown in Scheme 1c. These results demonstrate that reactions of platinum and iridium

* Reference number with asterisk indicates a note in the list of references.



Scheme 2.

complexes **1** and **2** with alkynols gave the anticipated carbene complexes and led to isolation of the corresponding products, as opposed to the reactions of rhodium analogue **3** which afforded unidentifiable materials. This difference in the products obtained from rhodium triflate complex **3** may be attributed to the possibility that rhodium may catalyse side reactions more effectively than platinum and iridium or it may be due to the fact that the third row transition metals make stronger metal–ligand bonds than the first and second row transition metals [11]. In fact, to our knowledge no ynol derived square planar Rh complexes analogous to the Pt and Ir congeners are known.

As has been extensively discussed [8], the formation of 2-oxacyclopentylidene ligands from alkynols can be rationalized by initial coordination of the alkyne to the metal center to give a cationic, acetylenic π-complex (A, A′) which undergoes rearrangement to generate a vinylidene intermediate (B) which alternatively can be considered as a metal-stabilized vinyl carbonium ion (B′). Subsequent intramolecular nucleophilic attack by the hydroxyl functionality at the vinylidene carbon forms the cyclic carbene ligand (C) (Scheme 2). In addition, the generality of the carbonium ion concept for carbene formation from terminal acetylenes assists us in rationalizing why complex **1** gives products of higher yield and purity compared to complex **2**. Both **1** and **2** are the third row transition metal complexes, but the triflate ligand in **1** should be more labile than the triflate ligand in **2** towards substitution reactions. This is due to the high *trans* influence of the *trans*-methyl group in **1** compared to the *trans*-carbonyl group in **2**. Therefore, the addition of alkynes to **1** should be more facile than to **2**. Furthermore, the resulting cationic, acetylenic π-complex and the vinylidene-platinum intermediate should be more stable than those of the carbonyl iridium analogue due to the electron-donating ability of the methyl group in **1** as compared to the carbonyl ligand in **2**.

In summary, although the chemistry of the rhodium triflate complex differs substantially from that of its iridium and platinum analogues, this study has provided another application of coordinated triflate complexes as precursors to transition metal carbene products.

Experimental section

General

All reactions were conducted under a dry nitrogen atmosphere using Schlenk techniques, unless otherwise noted. IR spectra were recorded on a Mattson Polaris FTIR spectrometer. All NMR spectra were recorded on a Varian XL-300 spectrometer. ^1H NMR spectra were recorded at 300 MHz, and all chemical shifts are reported in ppm relative to internal tetramethylsilane (Me_4Si) or the proton resonance resulting from incomplete deuteration of the NMR solvent: $CDCl_3$ (7.24 ppm) or CD_3NO_2 (4.33 ppm). ^{13}C NMR spectra were recorded at 75 MHz, and all chemical shifts are reported in ppm relative to the carbon of the deuterated NMR solvent: $CDCl_3$ (77.0 ppm) or CD_3NO_2 (62.8 ppm). ^{31}P NMR spectra were recorded at 121 MHz, and all chemical shifts are reported in ppm relative to external 85% H_3PO_4 at 0.0 ppm. ^{19}F NMR spectra were recorded at 282 MHz, and all chemical shifts are reported upfield relative to external $CFCl_3$ at 0.0 ppm. Elemental analyses were conducted by Atlantic Microlab, Inc., of Norcross, Georgia. Melting points were determined in evacuated capillaries and were not corrected.

Silver triflate (Aldrich) was recrystallized from diethyl ether and vacuum dried. 3-Butyn-1-ol (Aldrich) and 4-pentyn-2-ol (Aldrich) were used as received. Solvents were purified as follows: CH_2Cl_2, $CHCl_3$, benzene, and hexanes were purified by literature procedures [12] and were distilled from CaH_2; ether was purified by literature procedures [12] and was distilled from Na/benzophenone; CD_3NO_2 was distilled from CaH_2; $CDCl_3$ was vacuum transferred from CaH_2. All solvents were freeze-thaw-pump degassed three times before use.

Preparation of trans-*Pt(OTf)(CH$_3$)(PPh$_3$)$_2$ (1).*

A Schlenk flask was charged with *trans*-Pt(I)$(CH_3)(PPh_3)_2$ (0.459 g, 0.533 mmol), AgOTf (0.137 g, 0.533 mmol), and a magnetic stirring bar and was capped with a rubber septum. Freshly distilled, degassed benzene (*ca.* 80 mL) was added via cannula. The reaction mixture was stirred at room temperature for 2 h and then was filtered under nitrogen. Solvent removal under vacuum afforded **1** (0.430 g, 0.487 mmol) in 91% yield; m.p. 160–163°C dec. ^1H NMR (δ, CD_3NO_2): 7.82–7.68; 7.67–7.52 (m, 6 C_6H_5); 0.68 (t with ^{195}Pt satellites, J(H–P) = 7.1 Hz, J(H–Pt) = 89 Hz, CH_3). $^{31}P\{^1H\}$ NMR (ppm, CD_3NO_2): 31.14 (s with ^{195}Pt satellites, J(P–Pt) = 3140 Hz). ^{19}F NMR (ppm, CD_3NO_2): −78.57 (s). Anal. Found: C, 51.38; H, 3.82. $C_{38}H_{33}F_3P_2PtO_3S$ calc.: C, 51.64; H, 3.76%.

Preparation of trans-*[Pt(=$\overline{C(CH_2)_3O}$)(CH$_3$)(PPh$_3$)$_2$]$^+$[OTf]$^-$ (4)*

A Schlenk flask was charged with *trans*-Pt(OTf)$(CH_3)(PPh_3)_2$ (**1**) (0.123 g, 0.139 mmol), $CHCl_3$ (5.0 mL), and a magnetic stirring bar and was capped with a rubber septum. To this supension was added 3-butyn-1-ol (10.5 μL, 0.139 mmol) by syringe. The reaction was allowed to stir at room temperature for 3 h under

nitrogen. Diethyl ether (*ca.* 18 mL) was added with stirring to effect precipitation. The solid was collected, washed with ether, and dried under vacuum to give **4** (0.113 g, 0.119 mmol, 86%) as a white, microcrystalline solid; m.p. 169–171°C dec. IR (cm^{-1}, KBr): ν(OTf) 1272 s, 1223 m, 1149 s, 1031 s. ^1H NMR (δ, $CDCl_3$): 7.58–7.44 (m, 6 C_6H_5); 4.18 (t, $J = 8.0$ Hz, OCH_2); 2.11 (t, $J = 8.0$ Hz, Pt=CCH_2); 0.94 (quintet, $J = 8.1$ Hz, Pt=$CCCH_2$), −0.09 (t with ^{195}Pt satellites, J(H–P) = 8.1 Hz, J(H–Pt) = 47.8 Hz, $PtCH_3$). $^{13}C\{^1H\}$ NMR (ppm, $CDCl_3$): 305.87 (t with ^{195}Pt satellites, J(C–P) = 8.6 Hz, J(C–Pt) = 790 Hz, Pt=C); aryl carbons at 133.71 (t, J(C–P) = 5.8 Hz); 131.45 (s); 128.81 (t, J(C–P) = 28.4 Hz); 128.78 (t, J(C–P) = 5.3 Hz); 120.82 (q, J(C–F) = 320.8 Hz, CF_3SO_3); 88.65 (t, $J = 25.0$ Hz, OCH_2); 56.34 (t, $J = 40.0$ Hz, =CCH_2); 18.34 (t, $J = 8.2$ Hz, =CCH_2CH_2); −4.43 (t with ^{195}Pt satellites, J(C–P) = 7.3 Hz, J(C–Pt) = 388 Hz, $PtCH_3$). $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$): 23.01 (s with ^{195}Pt satellites, J(P–Pt) = 2895 Hz). ^{19}F NMR (ppm, $CDCl_3$): −78.13 (s). Anal. Found: C, 52.61; H, 3.99. $C_{42}H_{39}F_3O_4P_2PtS$ calc.: C, 52.98; H, 4.12%.

Preparation of trans-*[Pt(=$\overline{C(CH_2)_2CH(CH_3)O}$)$(CH_3)(PPh_3)_2$]$^+$[OTf]$^-$ (5)*

This compound was prepared from *trans*-Pt(OTf)$(CH_3)(PPh_3)_2$ (**1**) (0.140 g, 0.158 mmol), 4-pentyn-2-ol (15.0 μL, 0.159 mmol), and $CHCl_3$ (5.0 mL) by a procedure identical to that given for **4**. Workup gave **5** as a white, microcrystalline solid (0.132 g, 0.136 mmol, 86%); m.p. 169–170°C dec. IR (cm^{-1}, KBr): ν(OTf) 1272 s, 1224 m, 1149 s, 1031 s. ^1H NMR (δ, $CDCl_3$): 7.60–7.43 (m, 6 C_6H_5); protons on carbene ligand at 4.09 (m), 2.76 (m), 1.82 (m), 1.46 (m), 0.31 (m); 0.99 (d, $J = 6.4$ Hz, $CHCH_3$); −0.15 (t with ^{195}Pt satellites, J(H–P) = 8.1 Hz, J(H–Pt) = 47.3 Hz, $PtCH_3$). $^{13}C\{^1H\}$ NMR (ppm, $CDCl_3$): 304.59 (t with ^{195}Pt satellites, J(C–P) = 8.4 Hz, J(C–Pt) = 790 Hz, Pt=C); aryl carbons at 134.00 (t, J(C–P) = 6.1 Hz); 131.59 (s); 129.12 (t, J(C–P) = 29.3 Hz); 128.99 (t, J(C–P) = 5.2 Hz); 121.03 (q, J(C–F) = 321.5 Hz, CF_3SO_3); 100.32 (t, $J = 24.3$ Hz, OCH_2); 57.36 (t, $J = 39.4$ Hz, =CCH_2); 26.21 (t, $J = 8.0$ Hz, =CCH_2CH_2); 19.52 (s, $OCHCH_3$), −4.07 (t with ^{195}Pt satellites, J(C–P) = 8.5 Hz, J(C–Pt) = 387 Hz, $PtCH_3$). $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$): 23.42 (s with ^{195}Pt satellites, J(P–Pt) = 2908 Hz). ^{19}F NMR (ppm, $CDCl_3$): −78.09 (s). Anal. Found: C, 53.15; H, 4.25. $C_{43}H_{41}F_3O_4P_2PtS$ calc.: C, 53.36; H, 4.27%.

Preparation of trans-*[Ir(=$\overline{C(CH_2)_3O}$)(CO)$(PPh_3)_2$]$^+$[OTf]$^-$ (6)*

(A) NMR-monitored experiment. A 5-mm NMR tube was charged with *trans*-Ir(OTf)(CO)$(PPh_3)_2$ (**2**) (0.026 g, 0.029 mmol) and was capped with a rubber septum. A needle, connected to a vacuum line, was inserted through the rubber septum. The NMR tube was degassed under vacuum and then was saturated with nitrogen. $CDCl_3$ (0.7 mL) was injected by syringe followed by 3-butyn-1-ol (2.2 μL, 0.029 mmol). The NMR tube was removed from the vacuum line and was shaken vigorously to effect dissolution. The mixture was kept at room temperature, and the reaction was periodically monitored by $^{31}P\{^1H\}$ NMR spectroscopy.

(B) Preparative-scale experiment. A Schlenk flask was charged with *trans*-Ir(OTf)(CO)$(PPh_3)_2$ (**2**) (0.130 g, 0.145 mmol), $CHCl_3$ (5.0 mL), and a magnetic stirring bar and was capped with a rubber septum. To this yellow solution was added 3-butyn-1-ol (11.0 μL, 0.145 mmol) by syringe. The reaction mixture was stirred at room temperature for 9 h under nitrogen and then filtered. All attempts at isolating the desired product from the crude reaction mixture by recrystalliza-

tion ($CHCl_3/Et_2O$, CH_2Cl_2/Et_2O, CH_2Cl_2/hexanes, CH_2Cl_2/Et_2O/hexanes) were unsuccessful. Thus, **6** was isolated as an orange-yellow crude solid (0.074 g, 0.077 mmol, 53%). Data on **6**: ^1H NMR (δ, $CDCl_3$): 7.75–7.40 (m, 6 C_6H_5); 4.13 (t, $J = 8.0$ Hz, OCH_2); 2.15 (t, $J = 8.0$ Hz, Ir=CCH_2); 0.97 (quintet, $J = 8.0$ Hz, Ir=$CCCH_2$). $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$): 19.20 (s).

Preparation of trans-*[Ir(=C(CH$_2$)$_2$CH(CH$_3$)O)(CO)(PPh$_3$)$_2$]$^+$[OTf]$^-$ (7)*

(A) NMR-monitored experiment. The sample was prepared in a 5-mm NMR tube from *trans*-Ir(OTf)(CO)$(PPh_3)_2$ (**2**) (0.027 g, 0.030 mmol), $CDCl_3$ (0.7 mL), and 4-pentyn-2-ol (2.8 μL, 0.030 mmol) by a procedure identical to that given above. The mixture was kept at room temperature, and the reaction was periodically monitored by $^{31}P\{^1H\}$ NMR spectroscopy.

(B) Preparative-scale experiment. Compound **7** was synthesized by a procedure identical to that given for **6** utilizing *trans*-Ir(OTf)(CO)$(PPh_3)_2$ (**2**) (0.250 g, 0.280 mmol), 4-pentyn-2-ol (26.4 μL, 0.280 mmol), and $CHCl_3$ (7.0 mL). All attempts at isolating the desired product from the crude reaction mixture by recrystallization as described above for **6** were unsuccessful. Thus, **7** was isolated as an orange-yellow crude solid (0.197 g, 0.201 mmol, 72%). Data on **7**: ^1H NMR (δ, $CDCl_3$): 7.73–7.35 (m, 6 C_6H_5); protons on carbene ligand at 4.13 (m), 2.71 (m), 1.76 (m), 1.49 (m), 0.26 (m); 0.87 (d, $J = 6.4$ Hz, $CHCH_3$). $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$): 18.85 (s).

Reaction of trans-*Rh(OTf)(CO)(PPh$_3$)$_2$ with 3-butyn-1-ol and 4-pentyn-2-ol*

The following experiment is representative. The sample was prepared in a 5-mm NMR tube from *trans*-Rh(OTf)(CO)$(PPh_3)_2$ (**3**) (0.023 g, 0.029 mmol), 3-butyn-1-ol (2.2 μL, 0.029 mmol), and $CDCl_3$ (0.7 mL) by a procedure identical to that given above. The mixture was kept at room temperature, and the reaction was periodically monitored by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum showed that the resonance due to the starting material (28.31 ppm, d, J(P–Rh) = 124.4 Hz) was rapidly replaced by a new signal at 28.09 ppm (d, J(P–Rh) = 123.9 Hz). However, the ^1H NMR spectrum for the same sample showed several unresolved broad multiplet resonances in the range δ 5.23–0.74 in addition to the aromatic proton resonances at δ 7.80–7.30 for the triphenylphosphine groups.

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