ether layer was dried with $MgSO_4$, and the solvent was removed under reduced pressure. The resulting oil was partitioned between hexane and acetonitrile. The solvent was removed from the acetonitrile layer under reduced pressure. Column chromatography (30% EtOAc/hexane on silica gel) yielded 62.4 mg (0.172 mmol, 73.2% yield) of **7** as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 6.85 (d, J = 16 Hz, 1 H), 6.25 (dd, J = 5, 16 Hz, 1 H), 4.40 (m, 1 H), 4.15 (q, J = 6.5 Hz, 2 H), 2.7 (m, 2 H), 2.35 (m, 5 H), 1.3 (m, 13 H); IR (film) 3430, 2920, 2845, 1730, 1685, 1635, 1590 cm^{-1}; UV λ_{EtOH} 278 nm (2.85×10^4).

Methyl 7-(5-Triflato-1-methyl-2-oxo-4-cyclopenten-1-yl)heptanoate (9). To a stirred solution of 0.226 g (1.10 mmol) of 2,6-di-*tert*-butyl-4-methylpyridine, 0.255 g (1.00 mmol) of **8**, and 10 mL of dry, distilled CH_2Cl_2 was rapidly added 0.18 mL (0.30 g, 1.10 mmol) of triflic anhydride at room temperature. The reaction mixture was then heated at reflux for 24 h. Pentane was added, and the mixture was filtered. The solvent was removed under reduced pressure. Column chromatography (30% EtOAc/hexane on silica gel) afforded 0.230 g (0.596 mmol, 59.6%) of **9** as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 6.10 (t, J = 2 Hz, 1 H), 3.70 (s, 3 H), 3.10 (d, J = 2 Hz, 2 H), 2.4 (m, 2 H), 1.7 (m, 10 H), 1.30 (s, 3 H); HRMS calcd for $C_{15}H_{22}F_3O_6S$ (M + 1) 387.1090, found 387.1099.

Methyl Ester of 8-Methylprostaglandin C_1 (10). A slurry of 0.185 g (0.479 mmol) of **9**, 0.220 g (0.528 mmol) of (*S*)-**3**, 55 mg (0.048 mmol) of tetrakis(triphenylphosphine)palladium(0), 60 mg (1.4 mmol) of lithium chloride, and 5 mL of dry, distilled THF was heated at 60 °C for 48 h. The solids were removed by filtration. The filtrate's solvent was removed under reduced pressure. The resulting oil was partitioned between hexane and acetonitrile. The solvent was removed under reduced pressure from the acetonitrile extracts. Column chromatography (30% EtOAc/hexane on silica gel) afforded 0.104 g (0.286 mmol, 59.7% yield) of **10** as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 6.10 (m, 3 H), 4.20 (m, 1 H), 3.60 (s, 3 H), 2.90 (m, 2 H), 2.30 (t, J = 7 Hz, 4 H), 1.4 (m, 23 H); HRMS calcd for $C_{22}H_{34}O_4$ (M − 2) 362.2457, found 362.2448.

Coriolic Acid (13). A 40% aqueous KOH solution (11 mL) was cooled in an acetone/ice bath, and 3.48 g (30.0 mmol) of azodicarbonamide was added with stirring. After 1 h, the solid (dipotassium azodicarboxylate) was isolated by filtration and washed with cold methanol. Acetic acid (6 mL) was added dropwise to a slurry of the dipotassium azodicarboxylate, 0.2945 g (1.001 mmol) of **11**, and 16 mL of distilled methanol. The reaction solution was stirred for 6 h and then was partitioned between water and ether. The organic layer was dried with $MgSO_4$, and the solvent was removed under reduced pressure. Column chromatography (30% EtOAc/hexane on silica gel) afforded 0.1952 g (65.85%, 0.6592 mmol) of **12** as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 6.15 (m, 2 H), 2.4 (m, 4 H), 1.4 (m, 10 H). A solution of 75.2 mg (0.254 mmol) of **12**, 0.1165 g (0.279 mmol) of (*S*)-**3**, 2.6 mg (0.0095 mmol) of bis(acetonitrile)palladium(II) chloride, and 2.5 mL of dry, distilled dimethylformamide was stirred at room temperature for 8 h. The reaction solution was partitioned between ether and water. The ether layer was dried with $MgSO_4$. The solvent was removed under reduced pressure. The resulting oil was partitioned between acetonitrile and hexane. The solvent was removed from the acetonitrile layer under reduced pressure. Column chromatography (10% methanol/CH_2Cl_2 on silica gel) afforded 56.7 mg (0.192 mmol, 75.6% yield) of a yellow oil (**13**): ^{1}H NMR ($CDCl_3$) δ 6.50 (dd, J = 11, 15 Hz; 1 H), 6.1 (bs, 1 H), 5.97 (dd, J = 11, 11 Hz; 1 H), 5.65 (dd, J = 7, 15 Hz; 1 H), 5.43 (dt, J = 7, 11 Hz; 1 H), 4.2 (m, 1 H), 2.45 (t, J = 7 Hz, 2 H), 1.8 (m, 20 H), 1.0 (t, J = 6 Hz, 3 H); $[\alpha]_D$ = +7.6° (c = 1.13, $CHCl_3$) (lit.[13b] $[\alpha]_D$ = +7.8° (c = 1.15, $CHCl_3$)).

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Alkynylation of Organometallic Systems. A New, Simple Method for the Introduction of Terminal Acetylides: Formation of Rhodium(III) and Iridium(III) σ-Acetylide Complexes[†]

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Summary: Reaction of *trans*-$(Ph_3P)_2Ir(CO)(Cl)$ and *trans*-$(Ph_3P)_2Rh(CO)(Cl)$ with $RC{\equiv}CI^+Ph{\cdot}^-OSO_2CF_3$ in toluene at room temperature gives the corresponding iridium(III) and rodium(III) σ-acetylide complexes in 89–96% isolated yields.

Transition-metal σ-acetylide or σ-alkynyl complexes, $RC{\equiv}CML_n$, are of current interest and are the subject of considerable research activity for a variety of reasons.[1,2] First, the parent acetylide, HC≡C, is isoelectronic with both CO and CN. Second, alkynes are unique among carbon ligands in the variety and modes of multisite interactions possible with transition metals. Third, their susceptibility to both electrophilic[3] and nucleophilic[4] attack allows for further transformations and ready functionalization.[5] Fourth, they are of some interest in organic and organometallic synthesis.[6] Fifth, they have implications in catalysis[7] and the preparation of novel, new materials.[8]

[†] Dedicated to the memory of John K. Stille.

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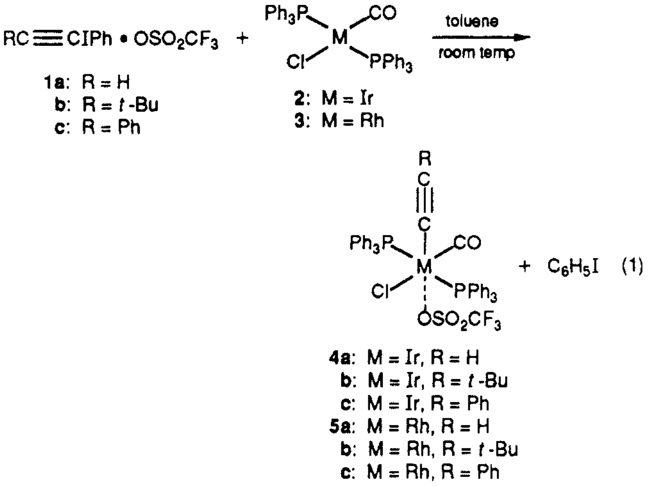
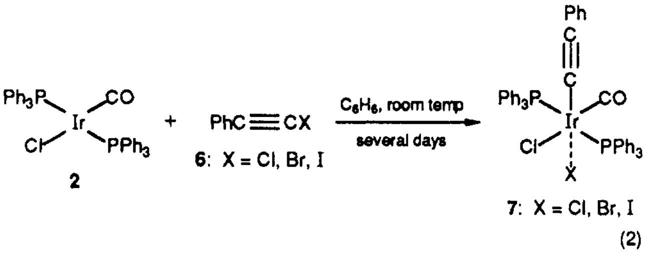
The great majority of σ-alkynyl and acetylene transition-metal cmplexes are prepared by the interaction of either a metal acetylide, RC≡CM (M = Li, Na, Mg, etc.), with a transition-metal halide, L_nMX (X = Cl, Br, I), or the neutral alkyne itself with a transition-metal complex.[1,2] The former reaction amounts to a displacement reaction with the acetylide anion acting as a nucleophile and the metal halide as the electrophilic substrate. In this note, we report a new reaction that amounts to the reversal of this traditional methodology, namely, alkynylation of organometallic systems via alkynyliodonium triflates[9] 1 where the transition-metal complex acts as nucleophile and the alkynyliodonium species as the electrophilic substrate. In other words, $RC{\equiv}CI^{+}Ph{\cdot}{}^{-}OSO_2CF_3$ serves as a synthon for "$RC{\equiv}C^{+}$".

Interaction of Vaska's complex 2 or its rhodium analogue 3 with 1 in toluene at room temperature (for 5–30 min for 2 and 1–9 h for 3) gives the corresponding σ-alkynyl complexes 4 and 5 (eq 1). Adducts 4 and 5 are isolated as stable microcrystalline solids by precipitation with hexanes and standard workup; their physical and spectral properties are summarized in Table I.



Products 4 and 5 were characterized[10] by multinuclear NMR and infrared spectroscopies. Specifically, the infrared spectra clearly showed the presence of a CO at 2080–2090 cm^{-1} for 4 and at 2106–2115 cm^{-1} for 5 highly characteristic of hexacoordinated Ir(III) and Rh(III) species, respectively. Likewise, the infrared spectra indicated the presence of a C≡C as well as the triflate. The presence of the triflate was confirmed by the characteristic fluorine signal at −75 to −78 ppm in the ^{19}F NMR spectra. The presence of the mutually *trans*-phosphines was indicated by the singlet at −9.3 ± 0.3 ppm for 4 and the Rh-coupled doublet between 17.6 and 18.8 ppm for 5 in the ^{31}P NMR spectra. Further structural confirmation was evident from the respective ^{1}H and ^{13}C NMR spectra that are completely consistent with 4 and 5. The trans arrangement of Cl and O is indicated by the characteristic band[11] at 314 ± 1 cm^{-1} for the Ir–Cl stretch for 4 in the far infrared. Hence, the structure as well as the stereochemistry of these octahedral hexacoordinate species 4 and 5 is clearly established.

A similar reaction between 2 and PHC≡CX, 6, resulting in 7 (eq 2), has been reported.[12]



However, this reaction does not seem to be general for it was only reported for the halophenylethynes 6 and for iridium. Moreover, the reaction times were several days with 6 versus a few minutes with 1, and the isolated product yields were 50–69% for 7 versus 90–93% for 4.

In conclusion, we have discovered a new way of introducing acetylenes as σ-complexed ligands into organometallic species. The parent, alkyl, as well as aryl-substituted acetylenes may be introduced by this methodology employing alkynyliodonium triflates, 1, in high isolated yields. This method amounts to an umpolung of the normal acetylene reactivity and corresponds to an alkynylation reaction in analogy with the well-established alkylation reactions using saturated substrates.

Experimental Section. General Considerations. Melting points were obtained with a Mel-Temp capillary melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Mattson Polaris FTIR spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian SC 300 spectrometer. Chemical shifts (^{1}H, ^{13}C) are reported in parts per million (ppm) downfield from tetramethylsilane (Me_4Si), ^{19}F NMR shift (ppm) are relative to $CFCl_3$, and ^{31}P NMR shifts are relative to 85% H_3PO_4.

Materials. Toluene was washed with sulfuric acid and distilled over calcium hydride prior to use. Hexane was distilled from calcium hydride prior to use. All solvents were degassed by standard freeze–thaw methods before use. NMR solvents were purified by drying over CaH_2 and then vacuum transferred. *trans*-$(Ph_3P)_2Ir(CO)(Cl)$ (2) and *trans*-$(Ph_3P)_2Rh(CO)(Cl)$ (3) were prepared by standard methods.[13]

General Procedure for the Formation of Transition-Metal σ-Acetylide Complexes: $(Ph_3P)_2Ir(CO)(Cl)(C{\equiv}CH)(OTf)$ (4a). All reactions were performed under a nitrogen atmosphere. Reactions involving rhodium were carried out with protection from the light. Vascas complex (2) (100 mg, 0.128 mmol) was dissolved in 5 mL of toluene. A suspension of phenyl(ethynyl)iodonium triflate (1a) (0.128 mmol, 48.5 mg) was added to the above solution. The yellow color from the Vascas complex disappeared within 1 min, and stirring was continued for 30 min. Hexanes (20 mL) was then added to the solution, resulting in the precipitation of the product. The crystals were filtered and washed with additional hexanes, and the product was dried overnight in vacuo, resulting in off-white crystals (110 mg, 90% yield). All properties are summarized in Table I.

$(Ph_3P)_2Ir(CO)(Cl)(C{\equiv}C{-}t\text{-}Bu)(OTf)$ (4b). This compound was prepared from Vascas complex (2) (100 mg,

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Table I. Physical and Spectral Properties of Complexes 4 and 5

compd	mp, °C	IR	^{31}P NMR	^{19}F NMR	^{13}C NMR	^{1}H NMR
4a	228–229 (dec)	3290, 3063, 2090 (CO), 2022 ($C\equiv C$), 1484, 1435, 1333, 1323, 1231, 1197, 1176, 1097, 976, 750, 708, 694	−9.5	−76.4		1.8 (1 H), 7.06–6.93 (18 H), 8.32–8.26 (12 H)
4b	215–216 (dec)	3063, 2965, 2944, 2140 ($C\equiv C$), 2083 (CO), 1484, 1435, 1320, 1231, 1199, 1162, 1095, 995, 745, 707, 692, 680, 642	−9.6	−75.7	(CO) 154.5 (^1J(CP) = 6 Hz), 134.8 (J(CP) = 5 Hz), 131.0, 128.2 (J(CP) = 13 Hz), 127.9 (J(CP) = 5 Hz), 117.0 (J(CF) = 319 Hz), (β-C) 110.9 (J(CP) = 2 Hz), (*t*-Bu) 31.7, (CH_3) 29.4, (α-C) 25.1 (J(CP) = 11.7 Hz)	1.1 (9 H), 7.4–8.2 (18 H), 8.3–8.2 (12 H)
4c	175–192 (dec)	3062, 2051 ($C\equiv C$), 2083 (CO), 1484, 1434, 1316, 1231, 1196, 1161, 1090, 989, 745, 707, 689, 641, 625	−9.0	−76.4	(CO) 154.6 (^1J(CP) = 6 Hz), 134.9 (J(CP) = 5 Hz), 131.0 (J(CP) = 0 Hz), 128.2 (J(CP) = 13 Hz), 127.9 (J(CP) = 5 Hz), 131.2, 129.0, 127.7, 126.2, (CF_3) 117.1 (J(CF) = 319 Hz), (β-C) 103.6 (^3J(CP) = 2 Hz), (α-C) 43.8 (^2J(CP) = 12 Hz)	7.1–7.2 (5 H), 7.3–7.5 (18 H), 8.0–8.1 (12 H)
5a	161–163 (dec)	3285, 3062, 2114 (CO), 2015 ($C\equiv C$) 1483, 1434, 1325, 1096, 1030, 1071, 1006, 749, 708, 693, 638, 628, 618	18.3 (^1J(Rh,P) = 82 Hz)	−78.7		2.2 (1 H), 8.0–7.9 (12 H), 7.6–7.4 (18 H)
5b	122–123 (dec)	3263, 2965, 2174, ($C\equiv C$) 2108 (CO), 1485, 1434, 1314, 1250, 1200, 1092, 1005, 745, 695	17.6 (^1J(Rh,P) = 78 Hz)	−78.4	(CO) 176.9 (^1J(RhC) = 58, ^2J(PC) = 9 Hz), 135.5 (J(CP) = 5 Hz), 133.1, 129.2 (J(CP) = 12 Hz), 129.6 (J(PC) = 5 Hz), (β-C) 120.3 (^2J(Rh,C) = 8, ^3J(PC) = 3 Hz), (α-C) 54.4 (^1J(Rh,C) = 40, ^2J(PC) = 14 Hz), (CH_3) 31.3, (*t*-Bu) 29.8	1.15 (9 H), 7.17–7.29 (18 H), 8.49–8.55 (12 H)
5c	112–114 (dec)	3063, 2144 ($C\equiv C$), 2106 (CO) 1484, 1435, 1311, 1231, 1202, 1092, 1072, 1003, 744, 692, 642	18.8 (^1J(Rh_3P) = 74 Hz)	−78.5	(CO) 176.3 (^1J(Rh,C) = 58, ^2J(PC) = 9 Hz), 135.2 (J(PC) = 5 Hz), 1330, (J(PC) = 0 Hz), 129.6 (J(PC) = 5 Hz), 129.1 (J(CP) = 11 Hz), 131.5, 128.9, 128.3, 125.7, (CF_3) 122.0 (J(CF) = 320 Hz), (β-C) 111.1 (^2J(Rh,H) = 8 Hz), (^3J(C,P) = 3 Hz), (α-C) 72.1 (^1J(Rh,C) = 41, ^2J(PC) = 14 Hz)	6.9–7.1 (23 H), 8.3–8.4 (12 H)

0.128 mmol) and phenyl (*tert*-butylethynyl)iodonium triflate (**1b**) (55.7 mg, 0.128 mmol) according to the general procedure. Stirring was maintained for 5 min followed by precipitation by hexanes, filtration, and washing with hexanes, resulting in 120 mg (93% yield) of **4b** as off-white crystals.

$(Ph_3P)_2Ir(CO)(Cl)(C\equiv C—Ph)(OTf)$ (4c). This compound was prepared from **2** (100 mg, 0.128 mmol) and **1c** (58.2 mg, 0.128 mmol). Washing with hexanes provided 119 mg (90% yield) of **4c** as off-white crystals.

$(Ph_3P)_2Rh(CO)(Cl)(C\equiv C—H)(OTf)$ (5a). This compound was prepared from **3** (100 mg, 0.1447 mmol) and **1a** (54.7 mg, 0.1447 mmol). The reaction was complete in 9 h, and the product was precipitated with hexanes (20 mL). The light-yellow product was filtered, then washed with additional hexanes, and dried in vacuo overnight, giving 144 mg (91% yield) of product.

$(Ph_3P)_2Rh(CO)(Cl)(C\equiv C—$*t*-Bu$)(OTf)$ (5b). This compound was prepared from **3** (100 mg, 0.1447 mmol) and **1b** (62.8 g, 0.1447 mmol). The reaction mixture was stirred for 2 h, and the product was precipitated with hexanes as a light-yellow powder. Filtration and washing with hexanes followed by drying in vacuo resulted in 128 mg (96% yield) of product.

$(Ph_3P)_2Rh(CO)(Cl)(C\equiv C—Ph)(OTf)$ (5c). This compound was prepared from **3** (100 mg, 0.1447 mmol) and **1c** (65.7 mg, 0.1447 mmol) according to the general procedure. After 1 h of stirring, workup gave 121 mg (89% yield) of **5c** as a yellow powder.

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