respectively; $\delta(CH_2)$ is observed at 1420 cm^{-1}; $\delta(CH)$ and CH wags are evident at 1310, 1015, and 585 cm^{-1}; and the remaining modes at 1190 and 940 cm^{-1} are attributable to CH$_2$ twists or wags.[10]

For exposures sufficient to saturate the monolayer at 110 K (>2 × 10^{-6} Torr s), followed by momentary annealing at 180 K to desorb any condensed allyl chloride, the HREEL spectrum of Figure 1b results. A very strong band at 220 cm^{-1} attributable to ν(Ag–Cl) appears, indicating clearly that atomically adsorbed chlorine is present and that dissociation of the allyl chloride has occurred. Consistent with this conclusion, the remaining features can be reconciled convincingly with the presence of π-allyl, η^3-C$_3$H$_5$, as shown schematically with spectrum b. Note particularly by comparison to spectrum a that a discernible feature for ν(C=C) near 1620 cm^{-1} is absent, and that the bands from about 500 to 1500 cm^{-1} are significantly altered. These changes are expected for a species containing C–C bonds of both sp^2 and sp^3 hybridization transforming to one in which all C–C bonds are equivalent, as would be the case for η^3-C$_3$H$_5$. All features in spectrum b compare well with the IR spectrum of the inorganic compound $(\eta^3$-C$_3$H$_5)$Fe(CO)$_2$NO[11] and can be assigned as follows: ν_{as}(CH$_2$) $\approx$ 3050 cm^{-1}; ν_s(CH$_2$) $\approx$ 3000 cm^{-1}; ν_{as}(C–C–C) and δ(CH$_2$) $\approx$ 1450 cm^{-1} (not resolved); π(CH) and δ(CH) $\approx$ 1240 cm^{-1} (not resolved); ρ(CH$_2$) $\approx$ 1025 cm^{-1}; ν_s(C–C–C) $\approx$ 965 cm^{-1}; ρ(CH$_2$) $\approx$ 750 and 675 cm^{-1}; and δ(C–C–C) $\approx$ 600 cm^{-1}. We assign the feature at 415 cm^{-1} to ν[Ag–(η^3-C$_3$H$_5$)], the frustrated translation of π-allyl perpendicular to the surface; its frequency falls within the range observed for ν[M–(η^3-C$_3$H$_5$)] in various inorganic compounds.[11,12]

When the surface is heated further, significant changes in the vibrational spectrum of the adsorbed layer begin near 280 K and are complete by 300 K, resulting in the HREEL spectrum of Figure 1c. Most notably the feature at 415 cm^{-1} due to ν[Ag–(η^3-C$_3$H$_5$)] disappears, a ν(C=C) mode appears at 1620 cm^{-1}, and the band in the CH stretching region broadens, indicating the return of a mixture of olefinic and aliphatic CH vibrations. We identify this species as 1,5-hexadiene, formed by the dimerization of η^3-C$_3$H$_5$'s and bound to the surface through π-donor interactions at both C=C bonds, as depicted with spectrum c. This conclusion is substantiated by temperature-programmed desorption measurements, which show the signature cracking fragments of 1,5-hexadiene (m/e = 41, 54, 67 amu) desorbing near 310 K, suggesting that the heat of adsorption of 1,5-hexadiene on the chlorinated Ag(110) surface is approximately 20 kcal/mol.[13] This reaction consumes η^3-C$_3$H$_5$ completely, leaving only adsorbed chlorine. Further confirmation is provided by spectrum d, which was measured after exposure of the chlorinated but otherwise clean surface to 2 × 10^{-6} Torr s of 1,5-hexadiene at 120 K. Spectra c and d agree almost perfectly, the only distinctions being the higher absolute intensity in spectrum d, due to higher coverage, and the absence of the weak features near 500 and 740 cm^{-1}, which are probably present but not resolved.

In summary, we have successfully isolated and identified the reactive intermediate η^3-C$_3$H$_5$ on Ag(110) by adsorption and thermally activated dissociation of allyl chloride. This synthesis approach is the starting point for mechanistic investigations of its interaction with adsorbed OH and atomic oxygen, to be reported later.[10] Furthermore, we have observed the dimerization of η^3-C$_3$H$_5$'s on Ag(110) to yield 1,5-hexadiene, which is the only reaction we are aware of that couples hydrocarbon fragments on silver in vacuum by C–C bond formation.

(11) Paliani, G.; Poletti, A.; Cardaci, G.; Murgia, S. M.; Cataliotti, R. *J. Organomet. Chem.* **1973**, *60*, 157–164.

(12) Andrews, D. C.; Davidson, G. *J. Organomet. Chem.* **1973**, *55*, 383–393.

(13) Redhead, P. A. *Vacuum* **1962**, *12*, 203–211.

Single-Step Preparation of Rigid-Rod, Cationic, Bimetallic, σ-Diyne Complexes: L$_5$M$^+$C≡C(C$_6$H$_4$)C≡CM$^+$L$_5$·2TfO$^-$, M = Ir, Rh†

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There is considerable current interest in bimetallic complexes, either bridged or connected by an organic group, due to their possibly unique role in catalytic processes.[1] Particularly interesting are the rigid, acetylide-connected complexes[2-5] **1–3**, due not only to potential catalytic activity but also to their role in new, nonlinear optical materials.[6,7]

$$L_nMC{\equiv}CML_n \qquad L_nMC{\equiv}CC{\equiv}CML_n$$
$$\mathbf{1} \qquad\qquad\qquad \mathbf{2}$$
$$L_nMC{\equiv}C(C_6H_4)C{\equiv}CML_n$$
$$\mathbf{3}$$
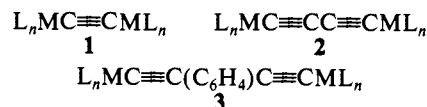
To date these complexes have been prepared via traditional acetylide, RC≡C$^-$, chemistry.[2-5] In this communication, we wish to report a single-step, high-yield preparation of **2** and **3** involving alkynyl(phenyl)iodonium species[8] as precursors. Recently, we established that alkynyl(phenyl)iodonium triflates **4** serve as synthons for electrophilic acetylene, "RC≡C$^+$", and allow the high-yield formation of σ-acetylide complexes via "alkynylation" and umpolung of the normal acetylene reactivity.[9]

$$RC{\equiv}CI^+Ph{\cdot}^-OSO_2CF_3$$
$$\mathbf{4}$$
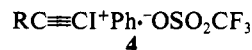
Interaction of Vaska's complex **7** or its rhodium analog **8** with the bis[(phenyl)iodonium] diyne triflates[10] **5** and **6**, respectively, in CH$_3$CN at room temperature affords the corresponding cationic, bimetallic, diyne complexes **9** and **10**, respectively (Scheme I). Likewise, reaction of iodonium triflate[11] **11** with **7** affords complex **12**. Complexes **9** and **10** are isolated as stable microcrystalline, yellow solids[12] by precipitation with ether and standard workup; their physical and spectral properties are summarized in Table I. Likewise, **12** is a semistable, pale brown, microcrystalline solid that decomposes upon standing at room temperature, or over

(1) Bullock, R. M.; Casey, C. P. *Acc. Chem. Res.* **1987**, *20*, 167. Wang, S.; Fackler, J. P. *Organometallics* **1990**, *9*, 111. Antonelli, D. M.; Cowie, M. *Ibid.* **1990**, *9*, 1818. Bruno, G.; Lo Schiavo, S.; Rotondo, E.; Arena, C. G.; Faraone, F. *Ibid.* **1989**, *8*, 886. Mackenzie, P. B.; Coots, R. J.; Grubbs, R. H. *Ibid.* **1989**, *8*, 8.

(2) Koutsantonis, G. A.; Selegue, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 2316.

(3) Davies, S. J.; Johnson, B. F. G.; Khan, M. S.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1991**, 187. Fyfe, H. B.; Mlekuz, M.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *Ibid.* **1991**, 188.

(4) St. Clair, M.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1991**, *10*, 525.

(5) Lo Sterzo, C. *Organometallics* **1990**, *9*, 3185.

(6) For recent reviews on nonlinear optical materials in general see: *Organic Materials for Non-Linear Optics*; Hahn, R. A., Bloor, D., Eds.; The Royal Society of Chemistry: London, 1989; Spec. Publ. *No.* 69. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: Orlando, FL, 1987; Vols. 1 and 2. Marder, T. B.; Lesley, G.; Yuan, Z.; Fyfe, H. B.; Chow, P.; Stringer, G.; Jobe, I. R.; Taylor, N. J.; Williams, I. D.; Kurtz, S. K. In *Materials for Nonlinear Optics: Chemical Perspectives*; Stucky, G. D., Marder, S. R., Sohn, J., Eds.; ACS Symposium Series 445; American Chemical Society: Washington, D.C., 1991.

(7) Calabrese, J. C.; Cheng, L. T.; Green, J. C.; Marder, S. R.; Tam, W. *J. Am. Chem. Soc.* **1991**, *113*, 7227. Guha, S.; Frazier, C. C.; Porter, P. L.; Kang, K.; Finberg, S. E. *Optics Lett.* **1989**, *14*, 952. Frazier, C. C.; Guha, S.; Chen, W. P.; Cockerham, M. P.; Porter, P. L.; Chauchard, E. A.; Lee, C. H. *Polymer* **1987**, *28*, 553.

(8) Stang, P. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 274.

(9) Stang, P. J.; Crittell, C. M. *Organometallics* **1990**, *9*, 3191.

(10) Stang, P. J.; Tykwinski, R.; Zhdankin, V. V. *J. Org. Chem.* **1992**, *57*, 1861.

(11) Stang, P. J.; Zhdankin, V. V. *J. Am. Chem. Soc.* **1990**, *112*, 6437.

(12) Complexes **9a**, **9b**, and **10** gave satisfactory C, H, and S elemental analyses, whereas **12** was insufficiently stable to obtain elemental analysis.

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Table I. Physical and Spectral Properties of Complexes **9a,b, 10,** and **12**

compd	yield, %	mp, °C	IR[c]	^{1}H NMR[d]	^{13}C NMR[d]	^{31}P NMR[e]	^{19}F NMR[f]
9a[a]	85	199–201, dec	3058, 2156 (C≡C), 2100 (CO), 1264, 1152, 1032	7.9–8.0 (24 H), 7.5–7.6 (36 H), 6.82 (4 H), 1.66 (6 H)	155.9 (CO, $^2J_{CP}$ = 6 Hz), 135.4 ($^2J_{CP}$ = 5 Hz), 133.3, 131.9, 129.8 ($^3J_{CP}$ = 5 Hz), 128.1 ($^1J_{CP}$ = 30 Hz), 125.3, 121.6, 108.7 (C-β), 56.3 (C-α, $^2J_{CP}$ = 12 Hz), 3.8 (CH$_3$CN)	−9.85	−79.1
9b[a]	73	105–106, dec	3061, 2147 (C≡C), 2122 (CO), 1267, 1154, 1031	7.9–8.0 (24 H), 7.5–7.6 (12 H), 7.4–7.5 (24 H), 6.78 (4 H)	g	19.74 ($^1J_{Rh,P}$ = 72.3 Hz)	−78.8
10[a]	65	165–168, dec	3062, 2124 (C≡C), 2093 (CO), 1224, 1154, 1031	7.8–7.9 (24 H), 7.2–7.4 (36 H), 7.0 (4 H), 1.64 (6 H)	155.3 (CO, $^2J_{CP}$ = 7 Hz), 136.6, 135.3 ($^2J_{CP}$ = 5 Hz), 133.0, 129.7 ($^3J_{CP}$ = 5 Hz), 127.6 ($^1J_{CP}$ = 30 Hz), 127.4, 122.2, 122.1 (OTf, $^1J_{CF}$ = 321 Hz), 109.1 (β-C, $^3J_{CP}$ = 4 Hz), 60.3 (α-C, $^2J_{CP}$ = 12 Hz), 3.6 (CH$_3$CN)	−9.50	−78.5
12[b]	69	105–107, dec	3064, 2183 (C≡C), 2102 (CO), 1436, 1263, 1154, 1031	7.9–8.0 (24 H), 7.4–7.5 (36 H), 1.6 (6 H)	152.8 (CO, $^2J_{CP}$ = 7 Hz), 134.7 ($^2J_{CP}$ = 5 Hz), 131.8, 128.6 ($^3J_{CP}$ = 5 Hz), 127.1 ($^1J_{CP}$ = 30 Hz), 120.9 (OTf, $^1J_{CF}$ = 320 Hz), 119.8, 95.6 (β-C), 46.9 (α-C, $^2J_{CP}$ = 12 Hz), 3.0 (CH$_3$CN)	−12.29	−79.3

[a] CD$_3$CN NMR solution. [b] CDCl$_3$ NMR solution. [c] CCl$_4$ thin film. [d] Relative to tetramethylsilane internal standard. [e] Relative to 85% H$_3$PO$_4$ external standard. [f] Relative to CFCl$_3$ external standard. [g] **9b** is insufficiently soluble and not stable in solution to obtain a ^{13}C spectrum.

Scheme I
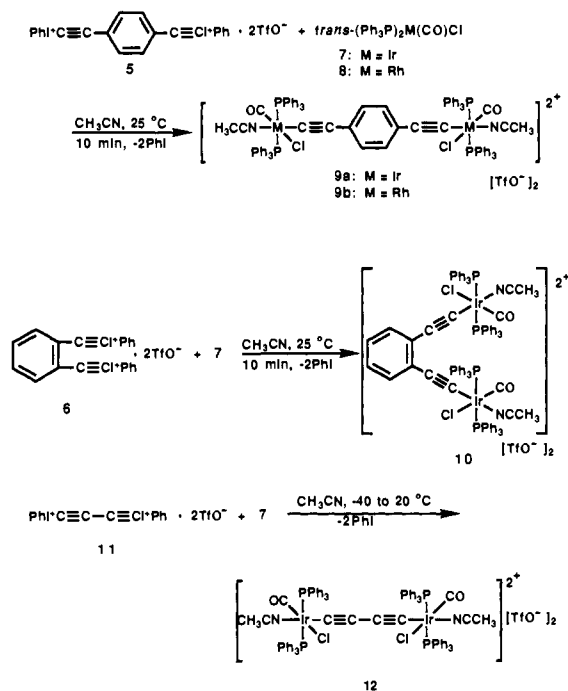
several hours in solution, but may be kept as a solid in a refrigerator. Reaction of **6** and **8** gave an impure oil as the product (~90% pure), which could not be isolated as a pure solid, whereas interaction of **11** with **8** gave only polymeric material. Products **9, 10,** and **12** were characterized by multinuclear NMR and infrared spectroscopies. Specifically, the IR spectra clearly demonstrate a C≡O stretch at 2093–2102 cm^{-1} for **9, 10,** and **12** and at 2122 cm^{-1} for **9b**, which is highly characteristic for hexacoordinated Ir(III) and Rh(III) species, respectively. Moreover, the IR data indicate the presence of the C≡C bond between 2124 and 2183 cm^{-1} and bands characteristic for the anionic triflate at 1263–1267 and 1031–1032 cm^{-1}. The presence of the OTf counterion was confirmed by the characteristic ^{19}F signal at −78 to −79 ppm. The existence of the mutually *trans* phosphines was indicated by the singlet at −9.85, −9.50, and −12.3 ppm for **9a, 10,** and **12**, respectively, and the Rh-coupled doublet at 19.7 ppm for **9b** in the ^{31}P NMR spectrum. Further structural proof was provided by the ^{1}H and ^{13}C spectra that are completely consistent with the proposed structures. Particularly useful is the

α-acetylenic carbon signal at 47–56 ppm with a carbon–phosphorus coupling of 12 Hz and the β signal at 96–109 ppm in the ^{13}C NMR spectra of **9a, 10,** and **12**.

In conclusion, we have discovered a new way of preparing rigid-rod-like, cationic, bimetallic, σ-diyne complexes in a high-yield, single-step reaction using appropriate bisiodonium diyne ditriflate precursors.[10,11] This method corresponds to an alkynylation reaction using the organometallic species as a nucleophile and the alkynyliodonium salt as the alkynylating agent and represents a reversal of the traditional acetylide, RC≡C⁻, chemistry. The use of other organometallic nucleophiles as well as other polyalkynyliodonium species is under active investigation and will be the subject of future reports.

C$_{60}$ as a Radical Sponge

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Facile additions of alkyl radicals and hydrogen atoms to C$_{60}$ are observed to occur in a mass spectrometer ion source. These reactions have not been reported previously even though mass spectrometry played an important role in the discovery of the novel C$_{60}$ allotrope of carbon[1,2], and numerous mass spectrometric studies have since been reported for the various fullerenes,[3–20] including

(1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.

(2) Rohlfing, E. A.; Cox, D. M.; Kaldor, A. J. *J. Chem. Phys.* **1984**, *81*, 3322.

(3) Cox, D. M.; Behal, S.; Disko, M.; Gorun, S. M.; Greaney, M.; Hsu, C. S.; Kolin, E. B.; Miller, J.; Robins, J.; Robins, W.; Sherwood, R. D.; Tindall, P. *J. Am. Chem. Soc.* **1991**, *113*, 2940.

(4) McElvany, S. W.; Callahan, J. H. *J. Phys. Chem.* **1991**, *95*, 6186.

(5) Wood, J. M.; Kahr, B. Hoke, S. H., II; Dejarme, L.; Cooks, R. G.; Ben-Amotz, D. *J. Am. Chem. Soc.* **1991**, *113*, 5907.

(6) Taylor, R.; Hare, J. P.; Abdul-Sada, A. K.; Kroto, H. W. *J. Chem. Soc. Chem. Commun.* **1990**, 1423.