the subsequent reaction of this solution with 1 equiv of Ph_3SnCl in THF at −78 °C to give a 57% yield of off-white needles of $Li[W(CO)_4\{P(i\text{-}Pr)_3\}SnPh_3]\cdot 2THF$[31] after precipitation with benzene and recrystallization from Et_2O. Counterion exchange using $[NEt_4]Br$ in ethanol gives $[NEt_4][W(CO)_4\{P(i\text{-}Pr)_3\}SnPh_3]$, which recrystallized as off-white needles of a CH_2Cl_2 solvate[32] from CH_2Cl_2.

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Registry No. $Na_2[Cr(CO)_5]$, 51233-19-3; $Na_2[Mo(CO)_5]$, 57127-94-3; $Na_2[W(CO)_5]$, 57127-91-0; $Li_2[W(CO)_5]$, 75706-82-0; $NaC_{10}H_8$, 3481-12-7; $LiC_{10}H_8$, 7308-67-0; $[Mo(CO)_5(NMe_3)]$, 15152-84-8; $[W(CO)_5(NMe_3)]$, 15228-32-7; $[Mo(CO)_5SnPh_3][NEt_4]$, 55971-56-7; $[NEt_4][W(CO)_5SnPh_3]$, 55971-72-7; $[W(CO)_5][Na(crypt)]_2$, 79199-37-4; $[Mo(CO)_5][Na(crypt)]_2$, 79135-07-2; $[W(CO)_4\{P(i\text{-}Pr)_3\}(NH_3)]$, 79199-38-5; $[W(CO)_4\{P(i\text{-}Pr_3\}]^{2-}$, 79135-08-3; $Li[W(CO)_4\{P(i\text{-}Pr)_3\}SnPh_3]$, 79135-09-4; $[NEt_4][W(CO)_4\{P(i\text{-}Pr)_3\}SnPh_3]$, 79135-11-8; $W(CO)_6$, 14040-11-0.

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[31] IR: $\nu(CO)$ (THF) 1978 (s), 1858 (vs), 1823 (s) cm^{-1}. ^1H NMR $[(CD_3)_2CO]$ δ 8.62–8.37 (m, 6 H, m-H of Ph), 8.07–7.72 (m, 9 H, o- and p-H of Ph), 3.64 (m, 8 H, OCH_2CH_2), 1.79 (m, 8 H, OCH_2CH_2), 1.12 (dd, 18 H, J = 6.4 Hz, $J_{H\text{-}P}$ = 12.8 Hz, $CH(CH_3)_2$), $CH(CH_3)_2$ obscured by solvent.

[32] Anal. Calcd for $C_{39}H_{56}NO_4PSnW\cdot 0.5CH_2Cl_2$: C, 48.46; H, 5.82. Found: C, 48.65; H, 6.12. IR: $\nu(CO)$ (CH_2Cl_2) 1975 (s), 1863 (vs), 1810 (s) cm^{-1}. ^1H NMR $[(CD_3)_2CO]$: δ 7.75–7.63 (m, 6 H, m-H of Ph), 7.17–7.01 (m, 9 H, o- and p-H of Ph), 5.58 (s, 1 H, $0.5CH_2Cl_2$); 3.32 (q, 8 H, J = 7.3 Hz, CH_2CH_3), 2.00 (septuplet, 3 H, J = 7.2 Hz, $CH(CH_3)_2$, partially obscured by solvent), 1.31 (t of t, 12 H, J = 7.3 Hz, $J_{H\text{-}N}$ = 1.6 Hz, CH_2CH_3), 1.11 (d of d, 18 H, J = 7.2 Hz, J_{HP} = 12.5 Hz, $CH(CH_3)_2$).

Synthesis and Structure of $[Ru(C_3Ph_2)(PMe_3)_2(Cp)][PF_6]$, a Cationic Diphenylallenylidene Complex

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Summary: The electron-rich complex $[RuCl(PMe_3)_2(Cp)]$ reacts with the alkynol $Ph_2C(OH)(C{\equiv}CH)$ and NH_4PF_6 to produce the novel diphenylallenylidene complex $[Ru(\eta^1\text{-}C{=}C{=}CPh_2)(PMe_3)_2(Cp)][PF_6]$. An X-ray structural determination reveals a nearly linear metallacumulene chain with a short (1.884 (5) Å) ruthenium–carbon bond.

The chemistry of transition-metal alkylidene (carbene) complexes is now well established,[1] but only recently have unsaturated alkylidenes (vinylidene complexes, $M{=}C{=}CR_2$) been explored.[2] Still more rare are examples of the cumulogs[3] of alkylidene complexes, allenylidene complexes $(M{=}C{=}C{=}CR_2)$.[4] A simple method for the preparation of cationic ruthenium allenylidene complexes is reported here, along with the structure of one of these complexes.

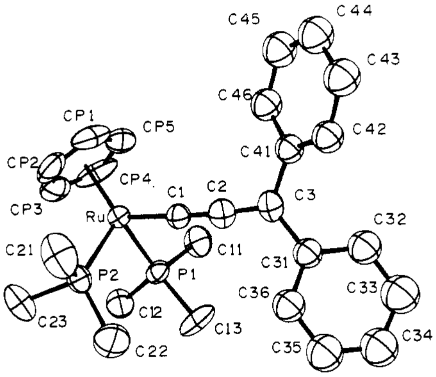

Figure 1. A perspective ORTEP diagram of the cation of $[Ru(C_3Ph_2)(PMe_3)_2(Cp)][PF_6]$ showing 50% probability ellipsoids.

Table I. Selected Bond Lengths and Angles with Errors for $[Ru(C_3Ph_2)(PMe_3)_2(CP)][PF_6]$

atoms	bond length, Å	atoms	angle, deg
Ru-C1	1.884 (5)	Ru-C1-C2	175.9 (5)
Ru-P1	2.289 (2)	C1-C2-C3	175.1 (7)
Ru-P2	2.292 (2)	C2-C3-C31	119.8 (6)
Ru-CPO[a]	1.929	C2-C3-C41	119.5 (6)
C1-C2	1.255 (8)	C31-C3-C41	120.7 (5)
C2-C3	1.329 (9)	P1-Ru-P2	94.57 (6)
C3-C31	1.462 (9)	P1-Ru-C1	87.0 (2)
C3-C41	1.511 (8)	P2-Ru-C1	92.4 (2)
		CPO[a]-Ru-C1	127.95

[a] CPO is the centroid of the cyclopentadienyl ring.

The reaction of $[RuCl(PMe_3)_2(Cp)]$[5] with the acetylenic alcohol $Ph_2C(OH)(C{\equiv}CH)$[6] and NH_4PF_6 in ethanol (25 °C, 27 h) leads to a deep orange-brown solution and a brown precipitate. Cooling, filtration, washing with water and ethanol, and drying in vacuo produces a 76% yield of a brown microcrystalline solid. Recrystallization from dichloromethane/ether yields large orange-brown crystals suitable for X-ray diffraction.

Spectroscopic characterization of the product suggests that is $[Ru(C_3Ph_2)(PMe_3)_2(Cp)][PF_6]$ (I), a cationic diphenylallenylidene complex. Strong infrared absorptions are found at 1926 and 840 cm^{-1} (in $CHCl_3$), corresponding to the asymmetric $C{=}C{=}C$ stretch of an allene system[7,8] and to the asymmetric stretch of the $[PF_6]^-$ ion,[9] respectively. The proton NMR spectra of several $[RuL(PMe_3)_2(Cp)]^+$ derivatives have suggested a direct relationship between the chemical shift of the cyclopentadienyl group and the degree of "electron richness" at the metal site.[5a] In light of this correlation, the ^1H NMR spectrum of complex I ($CDCl_3$, 90 MHz; δ 7.8–7.4 (m, Ph), 5.50 (s, Cp), 1.55 (br t, PMe_3)) suggests that the diphenyl-

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[1] Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1–122.

[2] See for example: (a) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7763–7765. (b) Adams, R. D.; Davison, A.; Selegue, J. P. *Ibid.* **1979**, *101*, 7232–7238. (c) Bruce, M. I.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1471–1485. (d) Bruce, M. I.; Swincer, A. G. *Ibid.* **1980**, *33*, 1471–1483. (e) Antonova, A. B.; Kolobova, N. E.; Petrovsky, P. V.; Lokshin, B. V.; Obezyuk, N. S. *J. Organomet. Chem.* **1977**, *137*, 55–67. (f) King, R. B.; Saran, M. S. *J. Am. Chem. Soc.* **1973**, *95*, 1811–1817, 1817–1824. (g) Boland, B. E.; Fam, S. A.; Hughes, R. P. *J. Organomet. Chem.* **1979**, *172*, C29–C32. (h) Chevrier, B.; Weiss, R.; Lange, M.; Chottard, J. C.; Mansuy, D. *J. Am. Chem. Soc.* **1981**, *103*, 2899–2901. (i) Berke, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 86–90. (j) Folting, K.; Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1979**, *18*, 3483–3486.

[3] Parmantier, M.; Galloy, J.; Van Meerssche, M.; Viehe, H. G. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 53.

[4] (a) Fischer, E. O.; Kalder, H.-J.; Frank, A.; Kohler, H.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 623–624. (b) Berke, H. *Chem. Ber.* **1980**, *113*, 1370–1376. (c) Berke, H. *J. Organomet. Chem.* **1980**, *185*, 75–78.

[5] (a) Treichel, P. M.; Komar, D. A. *Synth. React. Inorg. Met.-Org. Chem.* **1980**, *10*, 205–218. (b) Bruce, M. I.; Wong, F. S. *J. Organomet. Chem.* **1981**, *210*, C5–C8.

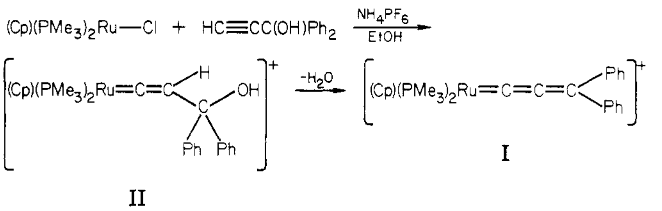
[6] Midland, M. M. *J. Org. Chem.* **1975**, *40*, 2250–2252.

[7] Silverstein, R. M.; Bassler, G. C.; Morill, T. C. "Spectrometric Identification of Organic Compounds", 3rd ed.; Wiley: New York, 1974; p 88.

[8] The value of $\nu(C{=}C)$ in the complex $[Mn(\eta^1\text{-}C_3Ph_2)(CO)_2(Cp)]$ is 1909 cm^{-1}.[4b]

[9] Corbridge, D. E. C. "Topics in Phosphorus Chemistry"; Grayson, M., Griffith, E. J., Eds.; Interscience: New York, 1969; Vol. 6, p 330.

Scheme I



allenylidene ligand is a significantly less effective π-acid than the similar phenylvinylidene (η^1-C=CHPh) ligand (δ(Cp) 5.94)[10] but that it is similar in π-acid strength to a carbonyl ligand (δ(Cp) 5.47).[5a] The $^{13}C\{^1H\}$ NMR spectrum of complex I (50 MHz, $(CD_3)_2CO$; δ_C 295.8 (s, C1), 216.0 (s, C2), 153.8 (s, C3), 145.0 (s, C_{ipso}), 131.6 (s, C_{para}), 130.4 (s, C_{ortho}), 130.0 (s, C_{meta}), 92.0 (s, Cp), 22.9 (t, $^1J_{CP}$ = 17.9 Hz, PMe_3)) clearly reflects the presence of an unsaturated alkylidene ligand. Furthermore, the simplicity of the aromatic region of the ^{13}C spectrum suggests that both phenyl groups rotate freely and that rotation of the diphenylallenylidene moiety with respect to the $[Ru(PMe_3)_2(Cp)]$ symmetry plane is rapid on the ^{13}C NMR time scale at room temperature.

Because of the paucity of structural data on metallacumulene complexes, a single-crystal X-ray diffraction study of complex I was undertaken.[11] An ORTEP plot of the $[Ru(C_3Ph_2)(PMe_3)_2(Cp)]^+$ cation is shown in Figure 1, and selected bond distances and angles are presented in Table I. The diphenylallenylidene ligand is of primary interest. The ruthenium to carbon (C1) bond is considerably shorter than a typical Ru—C single bond length of ca. 2.1 Å[12] and slightly shorter than most ruthenium to carbonyl bonds (1.92–1.93 Å).[13] The C1—C2 bond length in I is nearly as short as a carbon–carbon triple bond (1.20–1.21 Å).[14] The C2—C3 bond length is typical of an allene C(sp)—C(sp²) double bond (e.g., 1.31 Å in CH_2=C=CH_2[14b,c]). These structural parameters indicate a substantial contribution from two different mesomeric forms, Ia and Ib, $[CpL_2Ru=C=C=CPh_2]^+ \leftrightarrow [CpL_2Ru—C\equiv C—CPh_2]^+$ with the cationic charge stabilized by both the metal center and the diphenylcarbenium moiety. A similar conclusion was reached in the structural analysis of $[Cr(CO)_5\{\eta^1\text{-}C=C=C(NMe_2)Ph\}]$.[4a] The nearly linear metallacumulene moiety in I is oriented such that it lies approximately in the $[Ru(PMe_3)_2(Cp)]$ pseudomirror plane; i.e., the plane defined by C2, C3, C31, and C41 forms a dihedral angle of 10.6° with the plane defined by Ru, C1, and the centroid of the cyclopentadienyl ring. This allenylidene orientation is consistent with that predicted by Hoffmann and his co-workers to maximize π-orbital overlap in the model compound $[Fe(\eta^1\text{-}C=C=CH_2)(CO)_2(Cp)]^+$.[15]

A probable mechanism for the formation of I is indicated in Scheme I. Heterolytic dissociation of the highly polarized ruthenium–chlorine bond of $[RuCl(PMe_3)_2(Cp)]$[5,10] is followed by alkyne coordination and a 1,2-hydrogen shift to form the intermediate hydroxyvinylidene complex II.[2c,10] Although not observed in this case, such intermediates may be isolated from reactions of [FeCl(dppe)(Cp)] with alkynols.[17] Under the reaction conditions, complex II spontaneously dehydrates to form allenylidene complex I.[18]

Other reactions of $[MX(PR_3)_2(Cp)]$ (M = Fe, Ru; X = Cl, Br, I) with alkynols are under investigation. In particular, it appears that alkyl-substituted allenylidene complexes (e.g., $[Ru(C_3Me_2)(PPh_3)_2(Cp)]^+$) may be prepared similarly to I, but their chemistry is dominated by deprotonation of the alkyl groups.[17]

Acknowledgment. Thanks are due to Research Corp., Sigma Xi, and the Research Foundation and Graduate School of the University of Kentucky for financial support and to Engelhard Industries and Johnson Matthey, Inc., for generous loans of ruthenium trichloride.

Registry No. I, 79152-77-5; $[RuCl(PMe_3)_2(Cp)]$, 74558-74-0; $Ph_2C(OH)(C\equiv CH)$, 3923-52-2.

Supplementary Material Available: Listings of positional and thermal atomic parameters (Table II) and experimental and calculated structure factors (Table III) (27 pages). Ordering information is given on any current masthead page.

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(10) Treichel, P. M.; Komar, D. A. *Inorg. Chim. Acta* **1980**, *42*, 277–280.

(11) Crystal data for complex I: space group $P2_1/n$, a = 10.815 (2) Å, b = 13.602 (3) Å, c = 20.268 (2) Å, α = 103.06 (1)°, V = 2904.38 Å, Z = 4, ρ_{calcd} = 1.495 g·cm^{-3}. The structure was solved by Patterson and difference Fourier techniques and refined by full-matrix least-squares procedures: R = 0.069 and R_w = 0.085 using 4318 reflections with $F^2 \geq 3\sigma(F^2)$. The relatively high R factors are probably due to unresolvable disorder in the $[PF_6]^-$ ion.

(12) Bruce, M. I.; Gardner, R. C. F.; Howard, J. A. K.; Stone, F. G. A.; Welling, M.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1977**, 621.

(13) (a) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655. (b) Cobbledick, R. E.; Einstein, F. W. B.; Pomeroy, R. K.; Spetch, E. R. *J. Organomet. Chem.* **1980**, *195*, 77–88.

(14) (a) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, New York, 1960; pp 221–231. (b) Almenninger, A.; Bustiansen, O.; Tratteberg, M. *Acta Chem. Scand.* **1959**, *13*, 1699–1702. (c) Maki, A. G.; Toth, R. A. *J. Mol. Spectrosc.* **1965**, *17*, 136–155.

(15) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1977**, *101*, 585–591.

(16) The stable hydroxyvinylidene complex $[Mn\{\eta^1\text{-}C=CHC(OH)(CMe_3)_2\}(CO)_2(Cp)]$ undergoes dehydration in the mass spectrometer.[2i]

(17) Selegue, J. P., unpublished results.

(18) A similar dehydration reaction occurs when *trans*-$[PtHCl(PPh_3)_2]$ reacts with α-hydroxyalkynes, e.g., $Me_2C(OH)(C\equiv CH)$ yields *trans*-$[PtCl(C\equiv CCMe=CH_2)(PPh_3)_2]$. Furlani, A.; Licoccia, S.; Russo, M. V.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1980**, 1958.

Synthesis of the Elusive 1,8-Bis(trimethylsilyl)naphthalene and Its Facile Rearrangement to the 1,7 Isomer

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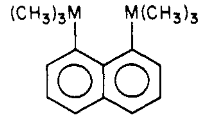
Peri-substituted naphthalenes are an important subset of the class of overcrowded molecules.[1] Most notable in this group are 1,8-di-*tert*-butylnaphthalenes (**1a**) in which



1a, M = C
b, M = Si
c, M = Ge
d, M = Sn

the steric interaction is so great that the naphthalene skeleton is severely distorted from planar geometry.[2] It

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(1) For a review of early work, see: Balasubramanian, V. *Chem. Rev.* **1966**, *66*, 567.