formed in situ from Me_3N and $[Me_3O]BF_4$, to give the methylamine complex $[(\eta^5\text{-cp})Ru(NH_2Me)(Cy_2PCH_2CH_2PCy_2)]BF_4$ (eq 3). The formulation of this

$$(\eta^5\text{-cp})Ru(NH_2)(Cy_2PCH_2CH_2PCy_2) + Me_4N^+ \rightarrow [(\eta^5\text{-cp})Ru(NH_2Me)(Cy_2PCH_2CH_2PCy_2)]^+ + Me_3N \quad (3)$$

complex has been confirmed by its independent synthesis as the triflates salt from reacting a THF solution of $(\eta^5\text{-cp})RuCl(Cy_2PCH_2CH_2PCy_2)$ with silver triflate followed by methylamine.[10] An analogous synthetic procedure with *tert*-butylamine and $(\eta^5\text{-cp})RuCl(PPh_3)(P(OMe)_3)$ gives the primary amine complex $[(\eta^5\text{-cp})Ru(NH_2CMe_3)(PPh_3)(P(OMe)_3)]CF_3SO_3$, which has been characterized by X-ray crystallography.[11] An ORTEP representation of the cation is shown in Figure 2. The molecule has a "piano stool" structure with an Ru–N distance of 2.216 (2) Å, longer by 0.044 Å than is found in $[(\eta^5\text{-cp})Ru(NH_3)(PPh_3)_2]CF_3SO_3$. This elongation is due to the greater steric requirement of the *tert*-butylamine ligand.

The formation of $(\eta^5\text{-cp})Ru(NH_2)(Cy_2PCH_2CH_2PCy_2)$ demonstrates that monomeric unsubstituted amides of ruthenium(II) can be synthesized and that the complexed amide is more nucleophilic to a methyl cation than is Me_3N.[12]

Acknowledgment. We thank the Louisiana Educational Quality Support Fund, administered by the Louisiana Board of Regents, for support of this research. We thank Johnson Matthey Inc. for a loan of ruthenium trichloride.

Supplementary Material Available: Tables of positional parameters for non-H and H atoms, bond distances and angles, general displacement parameter expressions, root-mean-square amplitudes of anisotropic displacement, and torsion angles, along with crystallographic data and refinement details, for $[cpRu(NH_3)(PPh_3)_2]CF_3SO_3$ and $[cpRu(NH_2CMe_3)(PPh_3)(P(OMe)_3)]CF_3SO_3$ (45 pages); tables of observed and calculated structure factor amplitudes (111 pages). Ordering information is given on any current masthead page.

---

[10] $[(\eta^5\text{-cp})Ru(NH_2Me)(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$: ^1H NMR (C_6D_6) δ 4.35 s (C_5H_5), 2.34 t (CH_3; $^3J(HH) = 5.8$ Hz), 2.7 br (NH_2); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 85.1 s. Anal. Calcd for $C_{33}H_{54}F_3NO_3P_2RuS$: C, 51.8; H, 7.12; N, 1.83. Found: C, 51.7; H, 7.22; N, 1.70.

[11] Crystal data for $[(\eta^5\text{-cp})Ru(NH_2CMe_3)(PPh_3)(P(OMe)_3)]CF_3SO_3$: monoclinic, $P2_1/c$, $a = 10.366$ (2) Å, $b = 21.862$ (2) Å, $c = 15.371$ (2) Å, $\beta = 92.33$ (1)°, $V. = 3481$ (2) Å^3, $Z = 4$, ρ(calcd) = 1.48 cm^{-3}, μ(Mo Kα) = 6.4 cm^{-1}, λ(Mo Kα) = 0.71073 Å (graphite monochromator); 6109 unique reflections with $1° < 2\theta < 50°$ were collected, of which 4778 reflections with $I \geq 3\sigma(I)$ were used in refinement; $R = 4.1\%$, $R_w = 6.3\%$, GOF = 2.249. The complex $(\eta^5\text{-cp})RuCl(PPh_3)(P(OMe)_3)$ has been prepared from $(\eta^5\text{-cp})RuCl(PPh_3)_2$ and $P(OMe)_3$. See: Joslin, F. L.; Mague, J. T.; Roundhill, D. M. *Organometallics*, in press.

[12] A similar alkyl group transfer has been observed for $(\eta^5\text{-cp})Re(NH_2)(NO)PPh_3$. See: Dewey, M. A.; Bakke, J. M.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1349–1351.

Distinct Chemical Reactivities of Tungsten Propargyl and Allenyl Complexes: Novel C–C Bond Formation of the Allenyl Ligand and Molecular Structure of a Tungsten Complex Containing an Azametallacyclobutane Ring

Tian-Wen Tseng, Iuan-Yuan Wu, Ying-Chih Lin,* Chun-Ting Chen, Ming-Chou Chen,
Yi-Jong Tsai, Ming-Chu Chen, and Yu Wang

Department of Chemistry, National Taiwan University, Taipei, Taiwan 10764, Republic of China

Received September 26, 1990

Summary: The reactions of $Cp(CO)_3WCH{=}C{=}CH_2$ (**1**) with excess methylamine and with 1 equiv of ethanol produce the aza metallacycle complex $Cp(CO)_2WCH(CONHMe)CHMeNHMe$ (**3**) and $Cp(CO)_2W(\eta^3\text{-}CH(COOC_2H_5)CHCH_2)$ (**5**), respectively. The C–C bond formation takes place at the α-carbon of the original allenyl fragment. The reaction of $Cp(CO)_3WCH_2C{\equiv}CH$ (**2**) with amine yields $Cp(CO)_2W(\eta^3\text{-}CH_2C(CONHR)CH_2)$ (**4**), in which the amido group is attached at the β-carbon of the allyl group.

The chemistry of organometallic complexes containing one or more M–C σ-bonds has long been a subject of interest.[1] However, chemical reactivities of the transition-metal σ-allenyl complexes are less well-known,[2] due to their rarity. Recently, Wojcicki and co-workers[3] employed a substituted propargyl ligand as a template and reported the preparation of a polynuclear cluster containing a bridging allenyl ligand. We have observed the transformation of a simple propargyl ligand to an allenyl group in a mononuclear W complex.[4] We feel this body of work has revealed a new class of chemical reactions of transition-metal propargyl/allenyl complexes and hope to employ these complexes to further study their chemical re-

---

[1] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 681.

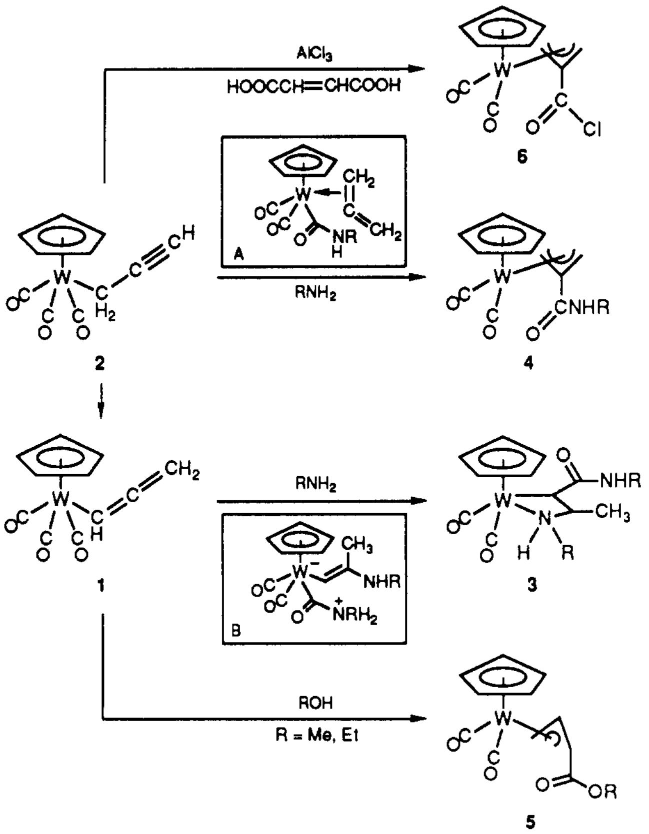
[2] Several (π-allenyl)metal complexes are known: (a) Wojcicki, A. *Adv. Organomet. Chem.* **1974**, *12*, 31. (b) Lennon, P.; Madhavarao, M.; Rosan, A.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *108*, 93. (c) Benaim, J.; Merour, J. Y.; Roustan, J. L. *Tetrahedron Lett.* **1971**, 983. (d) Casey, C. P.; Austin, E. A. *J. Am. Chem. Soc.* **1988**, *110*, 7106 and references therein. (e) Jolly, P. W.; Pettit, R. *J. Organomet. Chem.* **1968**, *12*, 491. (f) Johnson, M. D.; Mayle, C. *J. Chem. Soc. D* **1969**, 192. (g) Roustan, J.; Cadiot, P. *C.R. Seances Acad. Sci., Ser. C* **1968**, *268*, 734. (h) Kroll, J. O.; Wojcicki, A. *J. Organomet. Chem.* **1974**, *66*, 95. (i) Jacobs, T. L. *The Chemistry of the Allenes*; Landor, S. R., Ed.; Academic Press: London, 1982; Volume 2, Chapter 4.3.

[3] Young, G. H.; Wojcicki, A.; Calligaris, M.; Nardin, G.; Bresciani-Pahor, N. *J. Am. Chem. Soc.* **1989**, *111*, 6890.

[4] Keng, R. S.; Lin, Y. C. *Organometallics* **1990**, *9*, 289.

0276-7333/91/2310-0043$02.50/0

Scheme I



activities. To this end, we have investigated the reaction of amines with tungsten propargyl and the corresponding allenyl complexes. In this communication, we report the regiospecific C–C bond formation of the propargyl and allenyl ligand systems and the isolation of a four-membered aza metallacycle from the reaction of the tungsten allenyl complex with amine.

The tungsten allenyl complex $Cp(CO)_3WCH{=}C{=}CH_2$ (1) could be obtained from the rearrangement of the tungsten propargyl complex $Cp(CO)_3WCH_2C{\equiv}CH$ (2) in benzene.[4] When complex 2 is allowed to react with excess aniline, an immediate reaction occurs, producing an orange benzene-soluble complex, $Cp(CO)_2W(\eta^3\text{-}CH_2C(CONHPh)CH_2)$ (4),[5] in 80% yield. The ^1H and ^{13}C NMR spectra of 4 are consistent with an η^3-allylic group. The methylene protons of 4 appear as two broad signals at 3.34 and 1.75 ppm in the ^1H NMR spectrum, assigned as the syn and anti protons of the allylic system, respectively. When treated with excess $AlCl_3$, in the presence of excess fumaric acid, complex 2 is converted to $Cp(CO)_2W(\eta^3\text{-}CH_2C(COCl)CH_2)$ (6)[5] in 75% yield, indicating the same reactivity of the C–C bond formation at the β-position of the propargyl ligand. The structure of 6 is assigned on the basis of the spectroscopic data. In the ^1H NMR spectra, the characteristic allylic resonances at δ 3.01 and 1.12 ppm are observed.

Alkoxycarbonylation of the propargyl ligand at the β-carbon by alcohol has been observed in other metal complexes,[6] and our results on the reactivities of complex 2 are consistent with those reported by Roustan.[6] The reaction most likely proceeds via the intermediate A, containing a π-allene ligand and a carbamoyl ligand, as suggested in Scheme I. Compound 4 can, therefore, be accounted for by an apparent coupling of the carbamoyl ligand with the β-carbon of the π-coordinated allene ligand. Rearrangement of a σ-methylvinyl to an η^3-allyl ligand has been reported to proceed through a similar intermediate, namely, a metal hydrido allene compound, followed by the same type of C–H coupling at the β-position.[7]

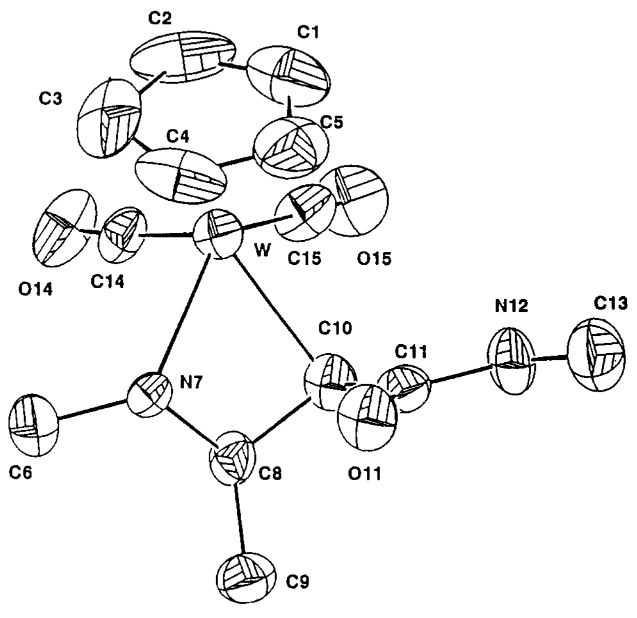


Figure 1. ORTEP diagram of $Cp(CO)_2W(CH(CONHCH_3)CH(Me)NHCH_3)$ (3), showing the atom-labeling scheme. Selected bond distances (Å) and bond angles (deg) are as follows: W–N(7), 2.224 (6); W–C(10), 2.276 (8); N(7)–C(8), 1.469 (9); C(8)–C(10), 1.524 (11); C(10)–C(11), 1.478 (12); C(8)–C(9), 1.532 (12); C(11)–O(11), 1.238 (9); C(11)–N(12), 1.342 (10); N(7)–C(6), 1.471 (11); N(12)–C(13), 1.427 (12); C(14)–W–C(15), 74.5 (3); N(7)–C(8)–C(10), 99.5 (6); N(7)–W–C(10), 61.00 (25); W–N(7)–C(8), 95.2 (4); W–C(10)–C(8), 91.6 (5); W–N(7)–C(6), 122.4 (5); W–C(10)–C(11), 110.9 (5); C(8)–C(10)–C(11), 116.3 (7); C(10)–C(11)–N(12), 117.3 (7).

In contrast to the C–C coupling at the β-position of the propargyl ligand, treatment of the allenyl complex 1 with excess methylamine that has been frozen in benzene affords a high yield of $Cp(CO)_2WCH(CONHMe)CHMeNHMe$ (3).[5] In this reaction, C–C bond formation occurs at the α-position of the allenyl ligand with the formation of an azatungstacyclobutane ring. In the ^1H NMR spectrum of 3, the coupling constant between the α-NH proton and the β-methine proton is 10.9 Hz.

The formation of 3 can be envisaged as involving two amine additions: one at the CO ligand and the other at the center (β) carbon of the allenyl ligand. The regiospecific C–C bond formation at the α-carbon of the original allenyl fragment possibly takes place either by the direct coupling of the carbamoyl group with the α-carbon or by the reductive elimination of the carbamoyl group and the allenyl fragment. Details of the conversion of 1 to 3 are not yet clear and are currently under investigation.

Reaction of 1 with stoichiometric or excess ethanol yields $Cp(CO)_2W(\eta^3\text{-}CH(COOC_2H_5)CHCH_2)$ (5).[5] The C–C bond formation again occurs at the α-position of the allenyl ligand, and only one alcohol is added to 1. In the ^1H NMR spectrum of 5, one of the coupling constants, 11.0 Hz at 2.75 ppm, falls in the range of proton coupling between

---

[5] Spectroscopic data are given in the supplementary material.

[6] (a) Roustan, J. L.; Guinot, A.; Cadiot, P. *J. Organomet. Chem.* **1980**, *194*, 357. (b) Collin, J.; Roustan, J. L.; Cadiot, P. *J. Organomet. Chem.* **1978**, *162*, 67.

[7] (a) Wolf, J.; Werner, H. *Organometallics* **1987**, *6*, 1164. (b) Allen, S. R.; Beevor, R. G.; Green, M.; Norman, N. C.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1985**, 435. (c) Boag, N. M.; Sieber, W. J.; Kampe, C. E.; Knobler, C. B.; Kaesz, H. D. *J. Organomet. Chem.* **1988**, *355*, 385. (d) Merola, J. S. *Organometallics* **1989**, *8*, 2975.

the central CH and the anti CH of an allylic group. Two other coupling constants, 7.09 and 7.65 Hz at δ 3.74 and 3.22 ppm, respectively, are assigned as the proton coupling between central and syn protons. In the ^{13}C NMR spectrum, coupling constants between W and all the allylic carbon atoms are in the range 3.8–7.1 Hz, indicating the η^3-allylic bonding mode. Since alcohol is not as strong a nucleophile as amine, addition of alcohol across the terminal double bond of the allenyl ligand does not take place. Instead, the reaction results in the formation of the allyl complex **5** with the ester group bound to the terminal carbon at the anti position of the allylic ligand.

Both complexes **3** and **4** are also identified on the basis of their single-crystal X-ray analysis.[8] The ORTEP drawing of **3** is shown in Figure 1. It is clear that the organic ligand of **3** is bonded to the metal in an η^2 fashion. The most interesting structural feature is this four-membered tungstacyclic ring, which includes the atoms W, C(10), C(8), and N(7). The C(10)–C(8) distance of 1.524 (11) Å and the C(8)–N(7) distance of 1.469 (9) Å are typical for single bonds. These distances are to be contrasted with the comparable ones in a aza manganacyclic system,[9] $\overline{(CO)_4Mn[C({=}N\text{-}p\text{-tolyl})C(=N}\text{-}p\text{-tolyl})CH_2C_6H_4\text{-}p\text{-OMe}]$, where there exists a C=N bond with C—C = 1.490 (5) Å and C=N = 1.287 (4) Å. The allyl ligand of **4** is coordinated symmetrically to the tungsten with two approximately equal C—C bonds (details given in the supplementary material). Unlike that of **3**, the distance between the central carbon and the metal, W–C(8), is 2.77 (2) Å, showing that there is now bonding.

Using tungsten propargyl and allenyl complexes, we have demonstrated the facile C–C bond formation and its regiospecific control by means of the different bonding types of the C_3 unit to the metal. Further work is in progress, and the details of the regiospecificity and stereochemistry of the C—C bond formation will be the subject of future reports.

Acknowledgment. This research has been supported by the National Science Council (NSC) of the Republic of China. The NMR instruments used were funded by the NSC Instrumentation Program.

Supplementary Material Available: Details of the structure determination for complexes **3** and **4**, including tables of crystal and data collection parameters, general temperature factor expressions (B's), positional parameters and their estimated standard deviations, and intramolecular distances and angles, spectroscopic data for complexes **3**–**6**, and an ORTEP drawing of complex **4** (10 pages); tables of observed and calculated structure factors for **3** and **4** (18 pages). Ordering information is given on any current masthead page.

---

(8) X-ray analysis of **3** and **4**. Crystal data for **4** are as follows: space group $P2_1/c$, a = 8.6963 (13) Å, b = 20.691 (4) Å, c = 9.1135 (22) Å, β = 108.81 (2)°, Z = 4. X-ray data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. A total of 2728 reflections were collected with use of the ω–2θ scanning technique between 2.0 and 49.8° in 2θ. A total of 1920 reflections with $I > 2\sigma(I)$ were used in the full-matrix least-squares refinement. The structure was solved by using heavy-atom methods with the NRCC computing package. The final values of the agreement indices were R = 0.030, R_w = 0.028, and GOF = 1.75. Crystal data for **3** are as follows: space group $C2/c$, a = 20.551 (8) Å, b = 11.100 (4) Å, c = 12.784 (3) Å, β = 94.40 (3)°, Z = 8. The final residuals refined against 1889 data for which $I > 2.0\sigma(I)$ were R = 0.031, R_w = 0.024, and GOF = 1.78.

(9) (a) Motz, P. L.; Alexander, J. J.; Ho, D. M. *Organometallics* **1989**, *8*, 2589. (b) Carney, M. J.; Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 8751. (c) Handwerker, B. M.; Garrett, K. E.; Nagle, K. L.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1990**, *9*, 1562.

X-ray Structure Analysis and Reactivity of the Zirconaazaphosphirane $\overline{Cp_2Zr(Cl)N(SiMe_3)P}(H)N(SiMe_3)_2$

Nathalie Dufour, Jean-Pierre Majoral,* Anne-Marie Caminade, and Robert Choukroun
Laboratoire de Chimie de Coordination du CNRS, UPR 8241 liée par conventions à l'Université
Paul Sabatier et à l'Institut Polytechnique de Toulouse, 205, route de Narbonne,
31077 Toulouse Cêdex, France

Yves Dromzée
Laboratoire de Chimie des Métaux de Transition, Université Pierre et Marie Curie,
75230 Paris Cêdex 05, France

Received September 17, 1990

Summary: The structure of the 18-electron complex $\overline{Cp_2Zr(Cl)N(SiMe_3)P}(H)N(SiMe_3)_2$ (**3a**) has been determined by single-crystal X-ray diffraction. Reaction of **3a** with $MeOSO_2CF_3$ and $Me_3SiOSO_2CF_3$ leads, with ring retention, to the neutral and cationic zirconium phosphorus species **9** and **10**, respectively, while ring opening with formation of a phosphorus–iron complex or phosphorus sulfide or selenide occurs when **3a** is treated with $Fe_2(CO)_9$, S_8, or Se, respectively.

It is well-known that hydrozirconation of olefins with a zirconium hydride such as Cp_2ZrHCl (**1**) places the zirconium moiety at the sterically less hindered position of the olefin chain as a whole.[1] Nevertheless, it has also been reported that hydrozirconation of styrene gives both terminal and internal products.[2] Indeed, the reactions of Cp_2ZrHCl are very much akin to the reactions of dialkylboranes. The resulting products are emerging as useful reagents and intermediates for organic synthesis.

Surprisingly, no similar work has been undertaken with unsaturated, low-coordinated, heavier main-group-element species. Such reactions might lead to new kinds of met-

---

(1) Reviews: Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333. Negishi, E.; Takamashi, T. *Synthesis* **1988**, *1*, 1. Erker, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 397.

(2) Nelson, J. E.; Bercaw, J. E.; Labinger, J. A. *Organometallics* **1989**, *8*, 2484.

0276-7333/91/2310-0045$02.50/0