Control of Nucleophilic Regiochemistry by the Diene Conformation; Development of Synthetic Application for Unstable 2-Carboxylated 1,3-Dienes

Ming-Huei Cheng,[a] Yuung-Hsing Ho,[a] Gene-Hsian Lee,[b] Shie-Ming Peng[b] and Rai-Shung Liu*[a]

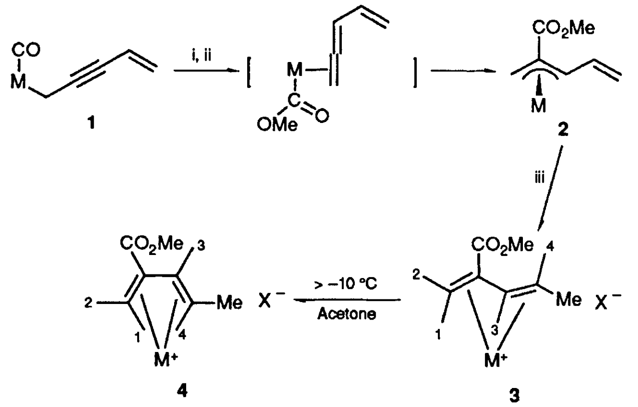
[a] *Department of Chemistry, National Tsinghua University, Hsinchu, Taiwan 30043, Republic of China*
[b] *Department of Chemistry, National Taiwan University, Taipei 10764, Republic of China*

Tungsten-η^4-carboxylated-1,3-diene cations in both s-*trans* and s-*cis* forms have been prepared and the influence of the diene conformation on its nucleophilic regiochemistry is demonstrated; the synthetic utility of these diene complexes is reported, and the crystal structure of one product has been determined.

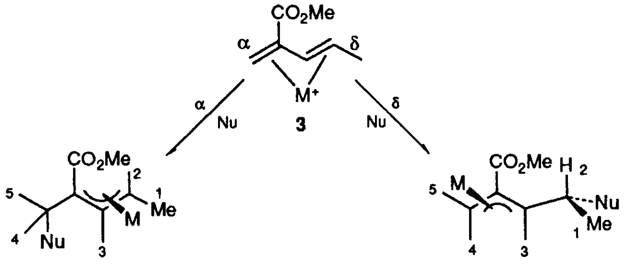
The synthetic utility of 2-carboxylated-1,3-dienes, is severely limited by remarkably facile dimerization.[1] One way to circumvent this problem is to complex such an unstable monomer with a suitable metal fragment as found for (η^4-cyclobutadiene)Fe(CO)$_3$,[2] (trimethylene)PdL$_2$[3] and (η^5-pentadienyl)Fe(CO)$_3$$^+$.[4] In connection with this, we here report the synthesis and nucleophilic chemistry of isolable tungsten η^4-carboxylated-1,3-diene cations in both the s-*trans*[5] and s-*cis* forms. Although nucleophilic addition to metal–diene complexes is a valuable route in organic synthesis, all reported chemistry so far involves the η^4-*cis*-diene form, as for [(C$_4$H$_6$)Fe(CO)$_3$][6] and [(C$_5$H$_5$)Mo(CO)$_2$(η^4-cyclohexadiene)]$^+$.[7] The synthetic application of s-*trans*-diene complexes *via* nucleophilic pathways remains virtually unknown.

The complex **2** was readily prepared by acidification of **1** with anhydrous CF$_3$SO$_3$H, followed by addition of MeOH. Its formation is believed to proceed *via* intramolecular insertion of an η^1-methoxycarbonyl group into the coordinated η^2-vinylallene ligand, which is presumably the reaction intermediate. Further treatment of **2** with CF$_3$SO$_3$H (1.2 equiv.) in cold ether (−78 °C, 2 h) generated an air-sensitive orange precipitate, the s-*trans*-2-methoxycarbonyl-*trans*-penta-1,3-diene cation **3**, which has been isolated in pure form and fully characterized. The s-*trans*-diene conformation is assigned from comparison of its four diene proton NMR resonances† with those for reported molybdenum s-*trans*[5] and s-*cis*-diene[8] cations; the magnitude of $J_{3,4}$ = 12.6 Hz is indicative of a *trans*-coupling. As expected, above −10 °C, this cation undergoes irreversible conformational isomerism to the more stable s-*cis* form **4**.

It is feasible to form various C–X bonds (X = O, N, S or C) with the s-*trans*-diene **3**; in its solid form in diethyl ether at −40 °C it shows high reactivity towards diverse nucleophiles (Scheme 2). The nucleophiles may add at the α- and δ-carbon atoms of the diene ligand, corresponding to Michael and non-Michael reactions. Hard bases, *e.g.* alcohols and amines including the bulky diisopropylamine and benzylamine, add highly regio- and stereo-selectively at the δ-carbon to produce allyl complexes as a single diastereoisomer; the nucleophiles presumably approach the ligand opposite the (C$_5$H$_5$)W(CO)$_2$ fragment. Confirmation of this stereochemistry relied on an X-ray structure determination of a γ-lactone **23** derived from **5** (*vide infra*).‡ Less hard bases like thiols slightly prefer a non-Michael reaction pathway with δ/α = 1.5. Lithium carbonanions such as MeLi, PhLi and PhCCLi are ineffective in C–C bond formation, but this can be achieved with organocuprates, alkylating preferentially at the α-carbon (α/δ > 2). The two η^3-allyl complexes for **11–15** (α/δ) may be separated by column chromatography on silica. The results in Scheme 2 clearly indicate that the regioselectivity is determined mainly by the electronic nature of the nucleophiles, and not their steric size.



Scheme 1 M = (C$_5$H$_5$)W(CO)$_2$, X = CF$_3$SO$_3$. *Reagents and conditions*: i, CF$_3$SO$_3$H (98%, 1.2 equiv.), diethyl ether, −78 °C; ii, MeOH (2.0 equiv.), −78 °C; iii, CF$_3$SO$_3$H (98%, 1.2 equiv.), diethyl ether, −78 °C



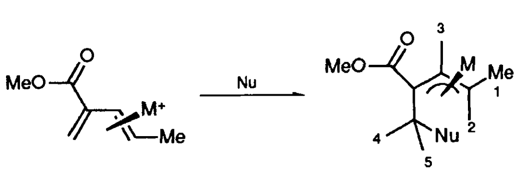
Nucleophile	Product	Yield (%)	Product
H$_2$O	δ	89	**5**
MeOH	δ	91	**6**
NaNH$_2$	δ	63	**7**
Me$_2$CHNH$_2$	δ	84	**8**
(Me$_2$CH)$_2$NH	δ	69	**9**
PhCH$_2$NH$_2$	δ	65	**10**
EtSH	δ : α 72 : 28	74	**11**
PhSH	δ : α 68 : 32	62	**12**
Me$_2$CuLi	δ : α 32 : 68	54	**13**
Ph$_2$CuLi	δ : α 36 : 64	53	**14**
(PhCC)Cu	δ : α 34 : 66	50	**15**

Scheme 2 M = (C$_5$H$_5$)W(CO)$_2$, yields were estimated from the amount of **2** used in the reaction

---

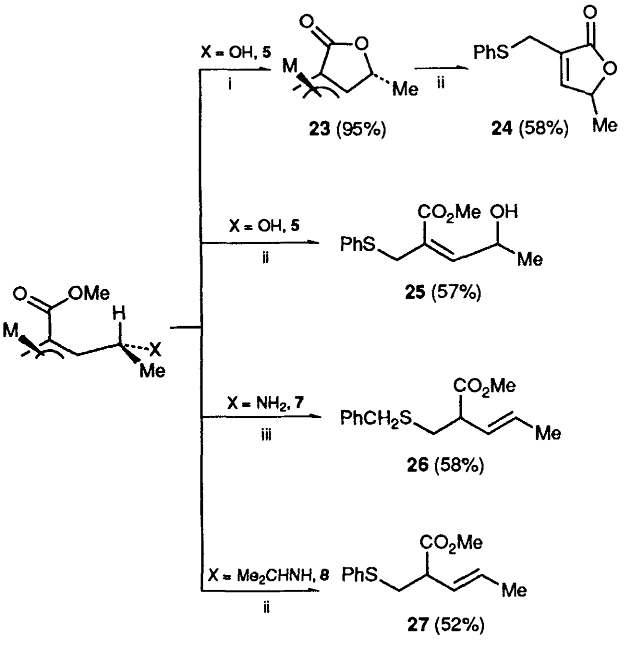
† *Selected spectroscopic data* for **3**: IR(Nujol) ν(CO)/cm^{-1} 2062s, 2014s and 1718s cm^{-1}; ^{1}H NMR (CD$_3$COCD$_3$, −40 °C): δ 2.08 (d, 3H, Me), 3.67 (s, 3H, OMe), 3.82 (s, 1H, H^1), 4.31 (s, 1H, H^2), 4.54 (d, 1H, H^3), 6.23 (dt, 1H, H^4), 6.27 (s, 5H, C$_5$H$_5$), J_{34} 12.6, $J_{4,\text{Me}}$ 6.2 Hz; ^{13}C NMR (CD$_3$COCD$_3$ −40 °C): 19.6 (Me), 45.5 (CH^{1}H^2), 52.7 (OMe), 77.8 (CH^3), 82.3 (*C*-CO$_2$Me), 95.9 (C$_5$H$_5$), 99.2 (CH^4), 169.3 (*C*O$_2$Me), 201.4, 216.5 (2 W–CO); for **4**: IR(Nujol) ν(CO)/cm^{-1}: 2065s, 2015s and 1718s cm^{-1}; ^{1}H NMR (CD$_3$COCD$_3$ −60 °C): 1.78 (br s, 1H, H^1), 1.91 (d, 3H, Me), 3.01 (br s, 1H, H^2), 3.46 (m, 1H, H^4) and 3.81 (s, 3H, OMe), 6.60 (d, 1H, H^3), J_{12} 1.5, $J_{3,4}$ 10.6, $J_{4,\text{Me}}$ 6.2 Hz; ^{13}C NMR (CD$_3$COCD$_3$, −60 °C): 18.9 (Me), 48.9 (CH^{1}H^2), 53.4 (OMe), 68.5 (*C*-CO$_2$Me), 66.8 (CH^4), 89.8 (CH^3), 93.4 (C$_5$H$_5$), 169.1 (*C*O$_2$Me), 199.3, 202.4 (2 W–CO).

‡ Complex **23** crystallizes in the monoclinic space group, $P2_1/c$, a = 8.884(2), b = 11.072(2), c = 12.789(4) Å, β = 100.71(2)°, V = 1235.9(5)A^3, Z = 4, final R = 0.023, R_w = 0.021 for 1331 reflections with $I > 2\sigma(I)$ out of 1607 unique reflections; 164 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

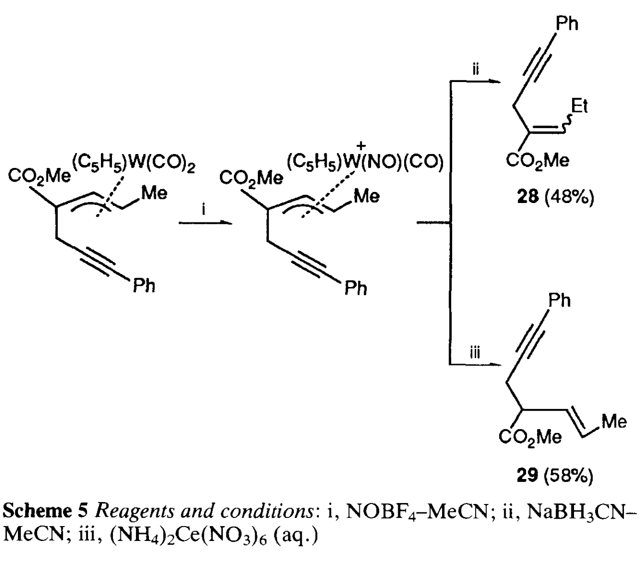


Nucleophile	Yield(%)	Product
NaOH	46	**16**
MeONa	47	**17**
Me_2CHNH_2	49	**18**
$PhCH_2NH_2$	41	**19**
EtSH	56	**20**
Me_2CuLi	50	**21**
(PhCC)Cu	48	**22**

Scheme 3 M = $(C_5H_5)W(CO)_2$



Scheme 4 M = $(C_5H_5)W(CO)_2$. *Reagents and conditions*: i, NaH–tetrahydrofuran (THF), 23 °C; ii, $NOBF_4$–MeCN, PhSNa, $(NH_4)_2Ce(NO_3)_6$ (aq.); iii, $NOBF_4$–MeCN; $PhCH_2SNa$, $(NH_4)_2Ce(NO_3)_6$ (aq.)



Scheme 5 *Reagents and conditions*: i, $NOBF_4$–MeCN; ii, $NaBH_3CN$–MeCN; iii, $(NH_4)_2Ce(NO_3)_6$ (aq.)

Scheme 3 summarizes the results for nucleophilic addition on the s-*cis*-diene cation **4** by various nucleophiles. Regardless of the nature of the nucleophile, hydroxide, methoxide, thiols, amines and organocuprates, all unambiguously add to the α-carbon to afford only one diastereoisomer. Complexes **20–22** differ structurally from the related complexes **11**, **13** and **15** distinguishable by ^1H NMR spectroscopy.§

Schemes 2 and 3 reflect the influence of the diene conformation on its nucleophilic regiochemistry. This unusual feature is valuable in synthetic organic chemistry. Outlined in Scheme 4, the γ-lactone **23** was quantitatively generated through deprotonation of **5** by NaH–THF. The X-ray structure of **23** has been determined‡ which clarifies the stereochemistry given in Scheme 4. Treatment of **23** with $NOBF_4$ generated an electrophilic NO-cation which then reacted with benzenethiolate to give, after Ce^{IV}-oxidation, the furanone **24**.¶ The pentenoate **25** was produced from **5** in a similar manner. The analogous 1,3-difunctionalized product was not found for **7** and **8** which under similar conditions proceeded in an unusual hydrodenitrogenation pathway to produce the pentenoates **26** and **27** respectively.

To demonstrate the synthetic utility of the allyls derived from **4**, we have treated the NO-cation of **22** with $NaBH_3CN$ to give, after Ce^{IV} oxidation, 2-methoxycarbonyl-1-phenylhept-4-en-1-yne **28** (Scheme 5). Direct aqueous Ce^{IV} oxidation of this NO-cation produces 4-methoxycarbonyl-1-phenylhept-5-ene-1-yne **29**. A model to establish 1,2- and 1,4-difunctionalization of its monomer is thus furnished.

Received, 22nd January 1991; Com. 1/00330E

References

1 J. M. McIntosh and R. A. Sieler, *J. Org. Chem.*, 1978, **43**, 4431; T. Tsuanetsugu, T. Fueno and J. Furukawa, *Makromol. Chem.*, 1968, **112**, 220; O. Goldberg and A. J. Dreiding, *Helv. Chim. Acta*, 1976, **59**, 1904.
2 R. Pettit, J. C. Barobak and L. Watts, *J. Am. Chem. Soc.*, 1966, **88**, 1328; J. D. Fitzpatrick, L. Watts, G. F. Emerson and R. Pettit, *J. Am. Chem. Soc.*, 1969, **87**, 3254.
3 B. M. Trost, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 1; B. M. Trost, *Chem. Soc. Rev.*, 1982, **11**, 141.
4 A. Pearson, *Acc. Chem. Res.*, 1980, **13**, 463; *Pure Appl. Chem.*, 1983, **55**, 1767.
5 Reports of preparation of metal-s-*trans*-diene cations: see S. A. Benuynes, M. Green and M. J. Grimshire, *Organometallics*, 1989, **8**, 2268; W.-J. Vong, S.-M. Peng, and R.-S. Liu, *Organometallics*, 1990, **9**, 2187; *J. Chem. Soc., Chem. Commun.*, 1990, 1285.
6 M. F. Semmelhack, and H. T. M. Lee, *J. Am. Chem. Soc.*, 1984, **106**, 2715; M. F. Semmelhack, J. W. Herndon and J. P. Springer, *J. Am. Chem. Soc.*, 1983, **105**, 2497.
7 J. W. Faller, H. H. Murray, D. L. White and K. H. Chao, *Organometallics*, 1983, **2**, 400.
8 J. W. Faller and A. M. Rosan, *J. Am. Chem. Soc.*, 1977, **99**, 4858; R. D. Adams, D. M. Chodosh, J. W. Faller and A. M. Rosan, *J. Am. Chem. Soc.*, 1979, **101**, 2570.

---

§ *Spectroscopic data* for **11δ**: ^1H NMR (300 MHz, $CDCl_3$): δ 1.18 (s, 1H, H^4), 1.23 (t, 3H, Me), 1.35 (d, 3H, H^1), 2.15 (d, 1H, H^3), 2.64 (q, 2H, CH_2), 2.96 (s, 1H, H^5), 3.67 (s, OMe), 4.27 (dq, 1H, H^2) and 5.30 (s, 5H, C_5H_5), $J_{1,2}$ 6.8, $J_{2,3}$ 10.6, $J_{CH2,Me}$ 7.5 Hz.

11α: ^1H NMR (300 MHz, $CDCl_3$): δ 1.25 (t, 3H, Me), 1.84 (d, 3H, H^1), 2.47 (d, 1H, H^4), 2.64 (m, 1H, H^2), 2.64 (q, 2H, CH_2), 3.54 (s, OMe), 3.59 (d, 1H, H^5), 4.07 (d, 1H, H^3) and 5.44 (s, 5H, C_5H_5), $J_{1,2}$ 6.38, $J_{2,3}$ 10.0, $J_{4,5}$ 13.1, $J_{CH2,Me}$ 7.35 Hz.

For **20**: ^1H-NMR (300 MHz, $CDCl_3$): δ 1.14 (t, 3H, Me), 1.40 (d, 1H, H^4), 1.87 (d, 3H, H^1), 2.41 (q, 2H, CH_2), 2.46 (m, 1H, H^2), 3.37 (d, 1H, H^5), 3.69 (s, OMe), 4.65 (d, 1H, H^3) and 5.35 (s, 5H, C_5H_5), $J_{1,2}$ 6.3, $J_{2,3}$ 10.1, $J_{4,5}$ 14.1, $J_{CH2,Me}$ 7.2 Hz.

21: ^1H NMR (300 MHz, $CDCl_3$): δ 0.13 (m, 1H, H^4), 0.78 (t, 3H, Me), 1.89 (d, 3H, H^1), 2.26 (m, 1H, H^5), 2.44 (m, 1H, H^2), 3.68 (s, OMe), 4.60 (d, 1H, H^3), 5.35 (s, 5H, C_5H_5), $J_{1,2}$ 6.4, $J_{2,3}$ 10.0, $J_{4,5}$ 14.5, $J_{4,Me}$ 7.2, $J_{5,Me}$ 7.0 Hz.

Satisfactory elemental analyses were obtained for all new complexes.

¶ *Spectroscopic data* for **24**: ^1H NMR (300 MHz, $CDCl_3$): δ 1.29 (d, *J* 6.81 Hz, 3H), 3.69 (s, 2H), 4.93 (qd, *J* 6.8 and 1.6 Hz, 1H), 6.96 (d, *J* 1.6 Hz, 1H) and 7.20–7.32 (m, 5H, Ph).

25: ^1H NMR (300 MHz, $CDCl_3$): δ 1.07 (d, *J* 6.7 Hz, 3H), 3.09 (d, *J* 12.8 Hz, 1H), 3.30 (d, *J* 12.8 Hz, 1H), 3.60 (dq, *J* 11.1 and 6.7 Hz, 1H), 3.73 (s, 3H, OMe) and 6.57 (d, *J* 11.1 Hz, 1H) and 7.15–7.40 (m, 5H, Ph).