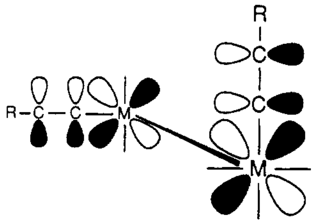

These findings suggest to us that compounds of this type that possess differentially substituted electron-donating and -withdrawing R groups should behave as push-pull metallapolyynes and that low-dimensional conjugated chains of metal dimers may be prepared from μ-η^1:η^1-diynyl ligands;[20] we are currently investigating these materials and are examining additional manifestations of conjugation in the physical properties of the complexes reported herein.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for the support of this research.

Supplementary Material Available: A listing of NMR spectroscopic data and elemental analyses for compounds **1–5** (1 page). Ordering information is given on any current masthead page.

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(19) The CCR π (and π^*) orbitals that lie perpendicular to the metal–metal bond transform as $a_2 + b_1 + e$ and hence can mix with the $b_1\delta$ and $a_2\delta^*$ orbitals. Stronger mixings (on energetic grounds) should occur among the CCR $[\pi,\pi^*]$ orbitals that lie parallel to the M_2 axis ($a_1 + b_2 + e$) and the metal–metal $e[\pi,\pi^*]$ orbitals, but we cannot judge their magnitude since we lack experimental probes of these orbitals.

(20) Dicarboxylato-bridged quadruply bonded tetranuclear complexes have recently been reported for which there is electrochemical evidence for electronic coupling: Cayton, R. H.; Chisholm, M. H. *J. Am. Chem. Soc.* **1989**, *111*, 8921–8923.

An Unprecedented Propellane-to-Spirofused Skeletal Rearrangement Upon Oxidative Demetalation of CpCo-Complexed Polycyclic Dienes: Synthesis of a Pentacyclic, Potential Precursor to Strychnine

Douglas B. Grotjahn and K. Peter C. Vollhardt*

Department of Chemistry, University of California
at Berkeley, and the Materials and Chemical Sciences
Division, Lawrence Berkeley Laboratory
Berkeley, California 94720

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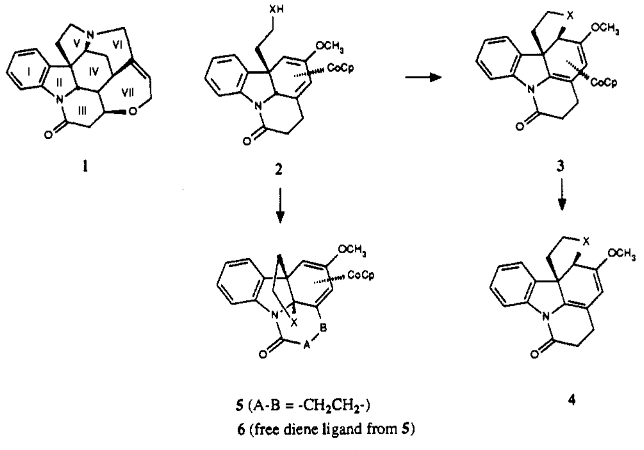
The presence of what might be envisaged to become rings I–IV of the synthetically challenging, convulsant poison strychnine (**1**)[1] in complexes of the type **2**, recently made readily available by the CpCo-mediated one-step fusion of rings III and IV to the indole nucleus,[2] led us to initiate investigations aimed at effecting the oxidative cyclization of **2** to **3**, in analogy to related ring-closures found with (diene)Fe(CO)$_3$ complexes.[3] In contrast to the chemistry of the latter, we report that compounds **2** undergo non-demetalative oxidation to the propellanes **5**, *from which the ligands can be removed intact or in the spirofused form* **4** (containing, according to IUPAC, a "non-free spiro union"), *depending upon the reaction conditions.*

Table I. Oxidative Cyclizations of Substrates **2**

substrate **2**[a]	conditions[b]	yields of products,[c] % **5**	**6**	**7**	ratio of **5**:**6**:**7**[d]
a (X = O)	A	96 (61)			
	B	93			15:1:1
	C	9	(17)	(34)	2:3:6
b (X = NH)	A	(67)		(7)	8:0:1
c (X = NC(O)CH$_3$)	A[e]				1:0:2
d (X = NCH$_2$C$_6$H$_5$)	A	93 (64)			25:1:<1
	B	84			
	D	(79)			≥20:0:0
e (X = NCH$_2$CH=CH$_2$)	A	95			25:1:0
f (X = NCH$_2$C≡CH)	A	(34)			≥10:1:0

[a] Prepared from the complexes in ref 2 by protodesilylation [(CH$_3$)$_3$N$^+$CH$_2$C$_6$H$_5$F$^-$, 1–1.2 equiv, DMSO or THF–DMSO (1:1), 80–110 °C, 1–17 h, 79–94%], followed by standard functional group manipulations of X. [b] A, aged MnO$_2$; B, Aldrich "activated" MnO$_2$; C, γ-MnO$_2$ (all three reagents 20–30 molar equiv); D, Cp$_2$Fe$^+$PF$_6^-$, [(CH$_3$)$_2$CH)]$_2$NCH$_2$CH$_3$. Reactions were performed in CH$_2$Cl$_2$, at 23 °C, for 5–30 min, except in the case of **2c**. [c] Yield of crude material; that of analytically pure material in parentheses. For **5f**, the yield applies to the overall conversion of **2a** (see footnote *a*). [d] By ^{1}H NMR of the crude reaction mixture. A zero entry means that signals for that product could not be detected. [e] In boiling solvent, 16 h.

The results of the first step are summarized in Table I[4] and merit the following comments. (1) Oxidation of model complex **2a** by the moderately active MnO$_2$,[5] particularly when aged, produces propellane **5a** in high yields, contaminated with small amounts of **6a** and **7a**.[6] Use of the more active γ-MnO$_2$[5] (all in excess) favors side-chain dehydrogenation (**7a**), as well as demetalation (**6a**), whereas BaMnO$_4$[7] affords a mixture of products (qualitative ^{1}H NMR experiment) in which **5a** and **6a** predominate. (2) Primary amine **2b** furnishes a relatively large proportion of overoxidized **7b**, the generation of which can be suppressed by alkylation of the nitrogen (substrates **2d–f**); acylation (**2c**), on the other hand, has the opposite effect, while at the same time reducing the rate of cyclization dramatically. Significantly (vide infra), the cleanest transformation is caused by ferricenium ion {Cp$_2$Fe$^+$PF$_6^-$, 2 equiv; [(CH$_3$)$_2$CH]$_2$NCH$_2$CH$_3$, 2 equiv; CH$_2$Cl$_2$, 25 °C, 10 min; **2d** → **5d**, 79%}. (3) One notes that conversion of **2** to **5** requires loss of the dienylic hydrogen located exo with respect to the CpCo fragment, in contrast to an Fe(CO)$_3$ system.[3a] (4) That the metal fragment is crucial to the success



1 **2** **3**

5 (A-B = -CH$_2$CH$_2$-)
6 (free diene ligand from **5**)
7 (A-B = -CH=CH-)

4

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(1) (a) Woodward, R. B.; Cava, M. P.; Ollis, W. D.; Hunger, A.; Daeniker, H. U.; Schenker, K. *Tetrahedron* **1963**, *19*, 247–288. (b) Creasey, W. E. In *The Chemistry of Heterocyclic Compounds. Indoles, Part Four*; Saxton, J. E., Ed.; Wiley: New York, 1983; pp 800–802. (c) Husson, H.-P. *Ibid.*, pp 293–330. (d) Smith, G. F. In *The Alkaloids*; Manske, R. F., Ed.; Academic: New York, 1965; Vol. 8, pp 591–671.

(2) Grotjahn, D. B.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 2091–2093.

(3) (a) Birch, A. J.; Chamberlain, K. B.; Thompson, D. J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1900–1903. (b) Pearson, A. J. *J. Chem. Soc., Chem. Commun.* **1980**, 488–489. (c) Pearson, A. J.; Ong, C. W. *Tetrahedron Lett.* **1980**, *21*, 2349–2350. (d) Pearson, A. J.; Chandler, M. *Ibid.* **1980**, 3933–3936. (e) Pearson, A. J.; Ong, C. W. *J. Chem. Soc., Perkins Trans. 1* **1981**, 1614–1621. (f) Pearson, A. J.; Ong, C. W. *J. Org. Chem.* **1982**, *47*, 3780–3782. (g) Pearson, A. J.; Kole, S. L.; Yoon, J. *Organometallics* **1986**, *5*, 2075–2081. (h) Knölker, H.-J.; Bauermeister, M.; Bläser, D.; Boese, R.; Pannek, J.-B. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 223–225.

(4) Unless otherwise specified, all compounds were characterized by IR, ^{1}H and ^{13}C NMR, DEPT, and combustion or high-resolution MS analyses. Structural assignments were made on the basis of well-established precedents.[2,8,11]

(5) Fatiadi, A. *Synthesis* **1976**, 65–104; **1976**, 133–167.

(6) Characterized by ^{1}H NMR spectroscopy.

(7) Fatiadi, A. *Synthesis* **1987**, 85–127.

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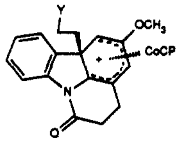
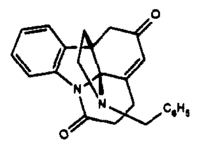
of the oxidative cyclization becomes evident through a control experiment in which the free diene ligand derived from **2d** is degraded by aged MnO_2 (CH_2Cl_2, 25 °C, 2 days) into a complex mixture of products containing only traces of **6d**. (5) It is tempting to propose that the complexes **5** (and eventually compounds **6** and **7**) arise through the intermediacy of CpCo-stabilized cations of the type **9**,[8] perhaps via **3**.[3e,9] Consistent with these notions, **9d**[6] [from **5d**: CF_3CO_2H (2.2 equiv), $CDCl_3$, <1 min] regenerates **5d** on kinetic deprotonation,[9] with regioselectivity similar to that found in analogous $Fe(CO)_3$ systems,[3,10] and **9g** (84% from **2a** via **5a**[3b–e]) results in the acetate of **2a** when attacked by hydride [$NaBH_4$, CH_3OH–THF or $(CH_3CH_2CH_2CH_2)_4NBH_4$, CH_2Cl_2)].



9d [Y = $C_6H_5CH_2NH_2^+(CF_3CO_2^-)_2$]

9g [Y = $\mathrm{O\overset{\overset{O}{\|}}{C}CH_3(PF_6)^-}$]



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Most remarkable is, however, that standard oxidative demetalation [$CuCl_2 \cdot H_2O$, 5 equiv, $(CH_3CH_2)_3N$, 2 equiv, 1,2-dimethoxyethane–H_2O, 0 °C][11] of **5d** provides not only the expected **6d** (27%) *but also the originally desired framework of spirofusion in **4d*** (51%)![12] That neither is the precursor to the other can be shown by control experiments. Thus, when reexposed to the conditions employed for their generation, **6d** slowly hydrolyzes to **10**, while **4d** is stable. Judging from these observations, it appears that an intermediate (perhaps the radical cation derived from **5** by one-electron transfer)[13] is present in the form of two equilibrating species, one bearing the propellane and the other the spirofused ligand; in such a case, selective interception of either one through manipulation of the reaction conditions might be possible. Indeed, upon switching to a non-nucleophilic medium (CH_2Cl_2), with $Cp_2Fe^+PF_6^-$ as the oxidant (1.1 equiv, 25 °C, 0.2–2 h), a mixture of **4d** and **6d** in ratios near 20:1 (yield of **4d**: 74–82%) is obtained. In 1,2-dimethoxyethane, this ratio drops to 8:1, and in CH_3CN it reverses to 1:4 (yield of **6d**: 55%). Unsaturated N-functionality does not perturb the regiochemical course of the rearrangement (**5e** → **4e**, 55%; **5f** → **4f**, 37%; ratio of **4**:**6** in the crude products ca. 20:1). The potential for direct regiocontrolled conversions of **2** is indicated by the preliminary finding that **2d** undergoes $CuCl_2$ decomplexation[11] to **4d** and **6d**, in addition to its free ligand **8**.

Clearly, the reported chemistry is of relevance not only to the systems under investigation on the way to strychnine **1**, but also more generally to the problem of biasing the equilibrium between complex structural isomers of this type in favor of a desired product.

Acknowledgment. This work was supported by NIH Grant GM22479. D.B.G. thanks the Monsanto Chemical Company for the sponsorship of an ACS Organic Division Fellowship (1986–1987).

Supplementary Material Available: Experimental, spectral, and analytical data for all new compounds (32 pages). Ordering information is given on any current masthead page.

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[8] Sternberg, E. D.; Vollhardt, K. P. C. *J. Org. Chem.* **1984**, *49*, 1564–1573.

[9] Pearson, A. J.; Ham, P.; Rees, D. C. *J. Chem. Soc., Perkin Trans. I* **1982**, 489–497.

[10] Birch, A. J.; Stephenson, G. R. *J. Organomet. Chem.* **1981**, *218*, 91–104.

[11] Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539–556.

[12] Under these conditions **5b** and **5c** gave only unrearranged **6b** (84%) and **6c** (78%), respectively.

[13] Brammer, L.; Connelly, N. G.; Edwin, J.; Geiger, W. E.; Orpen, A. G.; Sheridan, J. B. *Organometallics* **1988**, *7*, 1259–1265 and the references therein.

First Synthesis of Aromatic Compounds Carrying Two 1-Adamantyls on Adjacent Positions: 3,4-Di-1-adamantylthiophene, *o*-Di-1-adamantylbenzene, and 4,5-Di-1-adamantylpyridazine

Juzo Nakayama* and Ryuji Hasemi

Department of Chemistry, Faculty of Science
Saitama University, Urawa, Saitama 338, Japan

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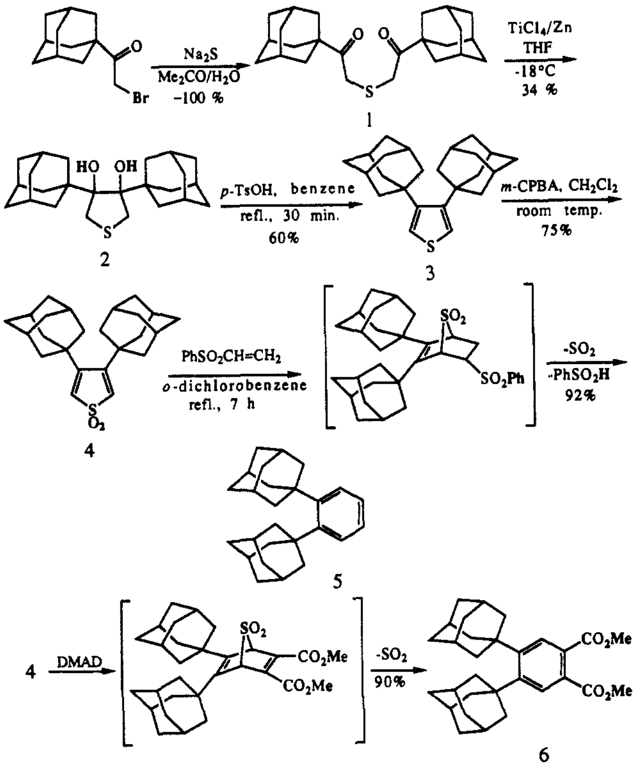
1-Adamantyl is a very bulky substituent similar to *tert*-butyl. It can be considered a kind of "tied-back" *tert*-butyl group but is far less flexible and thus might behave as a bulkier substituent than *tert*-butyl. To our knowledge, no report has appeared on the successful synthesis of five- or six-membered aromatic rings carrying two 1-adamantyl groups on adjacent positions. These would be sterically more strained than the corresponding di-*tert*-butyl-substituted compounds. Here we report the first synthesis of such molecules, 3,4-di-1-adamantylthiophene (**3**), *o*-di-1-adamantylbenzene (**5**), and 4,5-di-1-adamantylpyridazine (**8**).



Diketo sulfide **1** is easily obtainable by reaction of sodium sulfide with commercially available 1-adamantyl bromomethyl ketone (Aldrich).[1] Intramolecular pinacol reduction of **1** by a low valent titanium reagent, prepared from $TiCl_4$ and zinc powder,[2] at −18 °C for 9 h in tetrahydrofuran affords the diol **2**[3,4] in 34% yield.[5]

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[1] Nakayama, J.; Konishi, T.; Ishii, A.; Hoshino, M. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2608–2612.

[2] Mukaiyama, T.; Sato, T.; Hanna, J. *Chem. Lett.* **1973**, 1041–1044. For reviews on the carbonyl-coupling reactions using low valent titanium reagents, see: (a) McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513–1524. (b) Lenoir, D. *Synthesis* **1989**, 883–897.

[3] **2**: mp 205–220 °C dec; ^1H NMR (CD_2Cl_2) (400 MHz) δ 1.70 (s, 12 H), 2.02 (s, 6 H), 2.14 (br s, 12 H), 2.73 (d, J = 12 Hz, 2 H, thiolane ring), 3.30 (s, 2 H, OH), 3.33 (d, J = 12 Hz, 2 H, thiolane ring). The hydroxy groups of **2** are probably cis to each other.[5]

[4] Satisfactory NMR and IR spectra and combustion analyses (high-resolution mass spectra) were obtained for all new compounds.

[5] (a) Nakayama, J.; Machida, H.; Saito, R.; Hoshino, M. *Tetrahedron Lett.* **1985**, *26*, 1983–1984. (b) Nakayama, J.; Yamaoka, S.; Hoshino, M. *Ibid.* **1987**, *28*, 1799–1802. (c) Nakayama, J.; Yamaoka, S.; Hoshino, M. *Ibid.* **1988**, *29*, 1161–1164.

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