we were interested in comparing its parallel polarization EPR spectrum with that of the biological system. Examination of complex **1** in frozen CH_3CN at low temperature reveals a signal at $g_{eff} \sim 6$ with a peak-to-peak width of 700 G, shown in Figure 2, that bears a strong resemblance to the S_1-state MnOEC parallel polarization EPR spectrum.[4] This result lends support to the idea that the manganese aggregate in photosystem II has an electronic structure similar to the "dimer-of-dimers" compound **1**. Furthermore, on the basis of this spectral similarity we favor the oxidation state assignment of Mn(III,IV,III,IV) for the MnOEC S_1 state. This is in agreement with the conclusions of Klein, Sauer, and co-workers which were based on X-ray absorption edge and preedge studies.[7b]

Acknowledgment. We are grateful to Dr. Melvin P. Klein and Melissa Grush for assistance with the parallel polarization mode EPR measurement and for sharing their results prior to publication. Klein and co-workers provided the spectrum of spinach MnOEC used in Figure 2. We thank Phillip Matsunaga for assistance with collection of the variable-temperature magnetic susceptibility data. This work was supported by Grant No. GM382751 from the National Institute of General Medical Sciences. W.H.A. was the recipient of a Searle Scholars Award (1986-1989) and a Presidential Young Investigator Award from the National Science Foundation (1988-1993, CHE-8857455).

Supplementary Material Available: Fully labeled ORTEP drawing, atomic positional and thermal parameters, and intramolecular distances and angles for compound **1** (11 pages). Ordering information is given on any current masthead page.

(14) de Paula, J. C.; Beck, W. F.; Brudvig, G. W. *J. Am. Chem. Soc.* **1986**, *108*, 4002-4009.

Monomeric Group VI (M = Mo, W) Methylidyne Complexes and Their Dimerization to Nonclassical Vinylidene-Bridged $Tp'(CO)_2M(\mu\text{-}CCH_2)M(CO)_2Tp'$ Products

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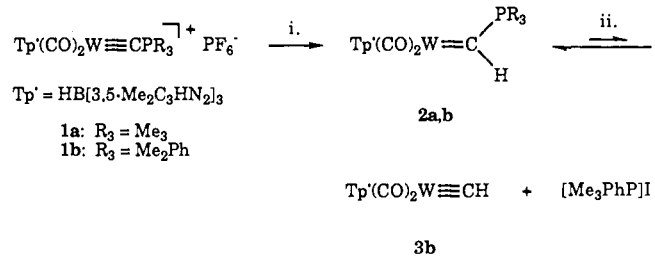
Received February 4, 1991

There are few reports of monomeric complexes bearing a simple CH carbyne ligand.[1] We now report the generation of hydridocarbyne complexes $Tp'(CO)_2M{\equiv}CH$ (**3a**, M = Mo; **3b**, M = W; Tp' = $HB[3,5\text{-}Me_2C_3HN_2]_3$, hydridotris(3,5-dimethylpyrazolyl)borate) and their dimerization to give unique vinylidene-bridged dinuclear products.

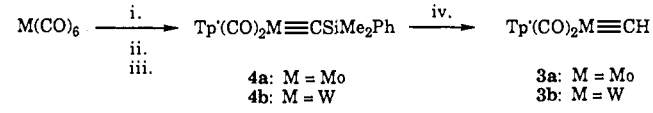
In a previous communication[2a] we reported that the cationic phosphonium carbyne complex **1a**, $[Tp'(CO)_2W{\equiv}CPMe_3][PF_6]$, was susceptible to nucleophilic attack at C_α to generate a neutral carbene complex, $Tp'(CO)_2W{=}C(H)(PMe_3)$ (Scheme I). Addition of MeI to the (dimethylphenyl)phosphonium carbene **2b**[2b,3] has permitted isolation of milligram amounts of hydridocarbyne **3b** as a bright yellow solid with $[Me_3PhP]I$ formed as a byproduct.

Scheme I[a]



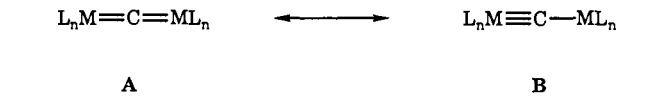
[a] (i) $KHB(O\text{-}i\text{-}Pr)_3$, MeCN, −23 °C; (ii) MeI, MeCN.

Scheme II[a]



[a] (i) $Me_2PhSiLi$, 10:1 Et_2O/THF, 0 °C; (ii) $(F_3CC(O))_2O$, −78 °C; (iii) KTp'/MeOH, −78 °C → 20 °C, 6 h; (iv) Bu_4NF, THF, 0 °C.

Scheme III



Alternatively, we have developed a more efficient route to **3a,b** involving fluoride-induced desilylation of the new silylcarbynes **4a,b**.

Following Mayr's multistep Fischer carbyne synthesis,[4] we have incorporated the bulky Tp' ligand in the coordination sphere which allows us to isolate analytically pure samples of silylcarbynes **4a,b** in low yield following alumina chromatography (Scheme II). Salient ^{13}C NMR low-field singlets identify the η^1-silylcarbyne moiety bound to molybdenum or tungsten (**4a**, δ = 360.4 ppm; **4b**, δ = 339.0 ppm, $^1J_{W-C}$ = 160 Hz; ^{183}W 14.3% abundance, $I = {}^1/_2$).[5]

Silylcarbynes **4a,b** were smoothly desilylated in THF at −78 °C with Bu_4NF[6,7] to quantitatively generate hydridocarbynes $Tp'(CO)_2M{\equiv}CH$ (**3a,b**) as monitored by IR spectroscopy. For tungsten derivative **3b** we have isolated the product as an analytically pure bright yellow powder in 30% yield; the corresponding molybdenum complex **3a** undergoes a secondary reaction upon warming to 20 °C to form a new dimeric complex **5a** identified by a four-band carbonyl stretching pattern in its IR spectrum (vide infra).

Tungsten hydridocarbyne **3b** has been fully characterized by IR, ^1H and ^{13}C NMR spectroscopy, elemental analysis, and a vapor phase osmometry molecular weight determination.[8] Its

(1) (a) Sharp, P. R.; Holmes, S. J.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 965. (b) Churchill, M. R.; Rheingold, A. L.; Wasserman, H. *J. Inorg. Chem.* **1981**, *20*, 3392. (c) Holmes, S. J.; Clark, D. N.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 6322. (d) Holmes, S. J.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *Organometallics* **1984**, *3*, 476. (e) Chisholm, M. H.; Folting, K.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6794.

(2) (a) Bruce, A. E.; Gamble, A. S.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1987**, *6*, 1350. (b) Jamison, G. M.; White, P. S.; Templeton, J. L. *Organometallics*, accepted for publication.

(3) **2b**: IR (MeCN) 1864, 1742 cm^{-1} (ν_{CO}); ^1H NMR (CD_2Cl_2) δ 13.32 (d, $^2J_{P-H}$ = 16 Hz, W=C(*H*)(PMe_2Ph)).

(4) (a) McDermott, G. A.; Dorries, A. M.; Mayr, A. *Organometallics* **1987**, *6*, 925. (b) Mayr, A.; McDermott, G. A.; Dorries, A. M. *Organometallics* **1985**, *4*, 608.

(5) (a) Kim, H. P.; Angelici, R. J. *Adv. Organomet. Chem.* **1987**, *27*, 51. (b) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988. (c) Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schrock, R. R.; Schubert, U.; Weiss, K. *Carbyne Complexes*; Verlag Chemie: Weinheim, 1988.

(6) Used as purchased from Aldrich Chemical Co., Inc., as a 1.0 M solution in THF containing ≈5 wt % H_2O.

(7) (a) Wong, A.; Kang, P. C. W.; Tagge, C. D.; Leon, D. R. *Organometallics* **1990**, *9*, 1992. (b) Furin, G. G.; Vyazankina, U. A.; Gostevsky, B. A.; Vyazankin, N. S. *Tetrahedron* **1988**, *44*, 2675 and references cited therein. (c) Roser, J.; Eberbach, W. *Synth. Commun.* **1986**, *16*, 983. (d) Cheng, J. C.-Y.; Hacksell, U.; Daves, G. D., Jr. *J. Org. Chem.* **1985**, *50*, 2778.

(8) **3b**: IR (hexanes) ν_{CO} = 1992, 1903 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 8.22 (s, $^2J_{W-H}$ = 83 Hz, W≡C*H*), 5.94, 5.81 (s, 2:1 H, Tp' C*H*), 2.54, 2.40, 2.37, 2.33 (s, 6:3:6:3 H, Tp' C-C*H*$_3$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 280.6 ($^1J_{W-C}$ = 192 Hz, $^1J_{C-H}$ = 142 Hz, W≡*C*H), 224.5 ($^1J_{W-C}$ = 169 Hz, W(*C*O)), 152.5, 151.6, 145.9, 145.1 (1:2:1:2, Tp' *C*CH$_3$), 106.7, 106.4 (1:2, Tp' *C*H), 16.6, 14.9, 12.5 (2:1:3, Tp' *C*CH$_3$); MW calcd for $C_{18}H_{23}BN_6O_2W$ 550, found 552 (three-point VPO determination in CH_2Cl_2). Anal. Calcd for $C_{18}H_{23}BN_6O_2W$: C, 39.30; H, 4.21; N, 15.28. Found: C, 39.39; H, 4.06; N, 14.92.

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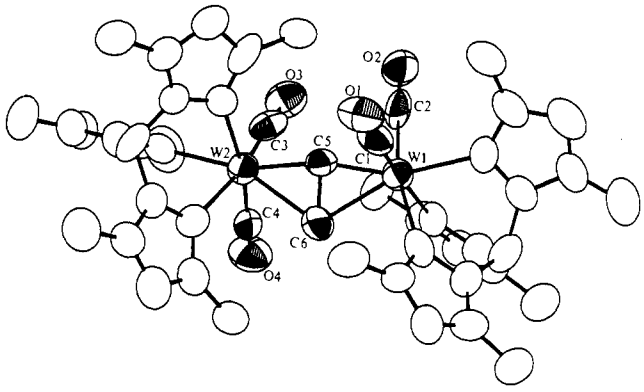
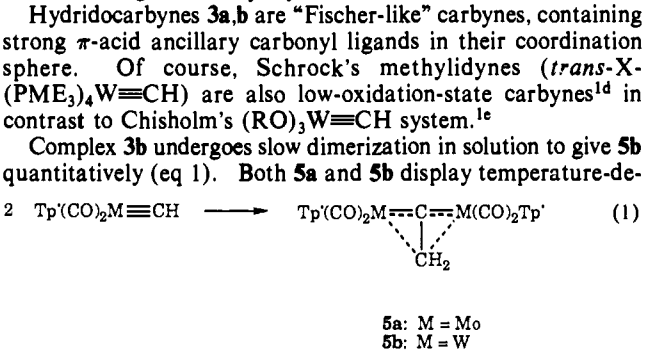


Figure 1. An ORTEP representation of the vinylidene-bridged dimeric complex **5b**. Selected bond distances (angstroms), bond angles (degrees), and torsion angles (degrees): W(1)–W(2) 3.96 (1), W(1)–C(5) 2.00 (2), W(2)–C(5) 1.98 (2), W(1)–C(6) 2.36 (2), W(2)–C(6) 2.34 (2), C(5)–C(6) 1.51 (2); W(1)–C(5)–W(2) 166.6 (9), W(1)–C(6)–W(2) 114.5 (8), W(1)–C(5)–C(6) 83 (1), W(2)–C(5)–C(6) 83 (1), W(1)–C(6)–C(5) 57.4 (9), W(2)–C(6)–C(5) 57.1 (9); C(6)–W(2)–C(5)–W(1) 0.4 (5).

downfield singlet in the ^{1}H NMR spectrum (δ = 8.22 ppm, $^2J_{W-H}$ = 83 Hz) and proton-coupled ^{13}C NMR downfield doublet (δ = 280.6 ppm, $^1J_{C-H}$ = 142 Hz, $^1J_{W-C}$ = 192 Hz) unambiguously identify the η^1-CH ligand. The magnitudes of these coupling constants are noteworthy. The terminal CH has a one-bond $^1J_{C-H}$ roughly 100 Hz smaller than is typical for terminal alkynes;[9] the implication is that the metal–carbon triple bond requires substantial s character at carbon, depleting s character available for the σ electron pair of the C–H bond. Note that this coupling constant value of 142 Hz suggests vinyl-type acid/base behavior rather than acetylene-like behavior. The value of the two-bond $^2J_{W-H}$ is also surprising and is large relative to one-bond values of 30–60 Hz for close relatives of $CpW(CO)_3H$[10] and 5–10 Hz for complexes related to $Tp'W(CO)_3H$.[11] The magnitudes of both coupling constants, however, are in agreement with those reported for other tungsten methylidynes.[1d]

Hydridocarbynes **3a,b** are "Fischer-like" carbynes, containing strong π-acid ancillary carbonyl ligands in their coordination sphere. Of course, Schrock's methylidynes (*trans*-X-$(PME_3)_4W{\equiv}CH$) are also low-oxidation-state carbynes[1d] in contrast to Chisholm's $(RO)_3W{\equiv}CH$ system.[1e]

Complex **3b** undergoes slow dimerization in solution to give **5b** quantitatively (eq 1). Both **5a** and **5b** display temperature-de-



pendent behavior in their ^{1}H and ^{13}C NMR spectra.[12] At 20 °C the bridging methylene protons appear as a broad singlet, which integrates for two protons (δ = 2.34 ppm in **5a** and δ = 2.20 ppm in **5b**). The bridging carbide carbon appears as a low-field singlet (δ = 346.7 ppm in **5a**; δ = 304.4 ppm, $^1J_{W-C}$ = 45 Hz in **5b**). These chemical shift values, in conjunction with the low magnitude of the spin coupling to ^{183}W (in **5b**), are compatible with a vinylidene-like carbide center (A),[13] as opposed to a metallamethylidyne carbon (B) (Scheme III).[5,14] The bridging methylene carbon resonates as an upfield triplet (δ = 7.2 ppm, $^1J_{C-H}$ = 162 Hz in **5a**; δ = −3.3 ppm, $^1J_{C-H}$ = 162 Hz in **5b**) in the gated-decoupled ^{13}C NMR spectra, in agreement with previous characterizations of μ_2-methylene complexes lacking metal–metal bonding.[15] The proton signal near 2 ppm correlates with the carbon of the bridging methylene moiety in 2-D HETCOR experiments.

The molecular structure of **5b** has been determined by X-ray crystallographic analysis (Figure 1).[16] The most interesting geometrical feature of the structure is the W_2C_2 core. A short C5–C6 interatomic distance of 1.51 (2) Å indicates a C5–C6 single bond. The W1–C5–W2 frame is slightly bent, with a bond angle of 166.6 (9)°. Both W1–C5 (2.00 (2) Å) and W2–C5 (1.98 (2) Å) bond distances are consistent with W=C double bonds.[17] The W1–C6–W2 bond angle of 114.5 (8)° indicates a distorted tetrahedral geometry at the bridging methylene C6.[18] The W1–C6 and W2–C6 bond lengths (2.36 (2) Å, 2.34 (2) Å, respectively) are probably best described as elongated W–C single bonds.[19] This vinylidene-like connectivity of the CCH_2 bridge contrasts with the common (μ-HCCH) bridging mode found in $Cp_2W_2(CO)_4(\mu\text{-}C_2H_2)$[20] and related bridging acetylene complexes.[21] Given that C6 is five-coordinate, a nonclassical bonding description is appropriate for the planar W_2C_2 core. Presumably three-center bonding descriptions involving both metals apply to the C6 σ-system and to the C5 π-system. Investigations into the nature of the W_2C_2 bonding interactions as well as the reactivity of

(9) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981.

(10) (a) Davison, A.; McCleverty, J. A.; Wilkinson, G. *J. Chem. Soc.* **1963**, 1133. (b) Faller, J. W.; Anderson, A. S.; Chen, C. C. *J. Chem. Soc., Chem. Commun.* **1969**, 719. (c) Keppie, S. A.; Lappert, M. F. *J. Chem. Soc. A* **1971**, 3216.

(11) Caffyn, A. J. M.; Feng, S. G.; Dierdorf, A.; Gamble, A. S.; Eldredge, P. A.; Vossen, M. R.; White, P. S.; Templeton, J. L. *Organometallics*, accepted for publication.

(12) (a) **5a**: IR (KBr) 1993, 1931, 1902, 1849 cm^{-1} (ν_{CO}); ^{1}H NMR (CD_2Cl_2) at 20 °C δ 5.88, 5.75 (s, 4:2 H Tp′ C*H*), 2.42, 2.40, 2.25 (s, Tp′ CC*H*$_3$), 2.34 (br, 2 H, (Mo(μ-C*H*$_2$)Mo); ^{13}C{^{1}H} NMR (CD_2Cl_2) at 20 °C δ 346.8 (Mo(μ-*C*)Mo), 232.0 br, Mo(*C*O), 153.3, 152.6, 145.8 (1:2:3, Tp′ *C*CH$_3$), 107.4, 107.1 (2:1, Tp′ *C*H), 15.5, 15.3, 13.2, 13.1 (2:1:1:2, Tp′ *C*CH$_3$), 7.5 (Mo(μ-*C*H$_2$)Mo). Anal. Calcd for $C_{36}H_{46}B_2N_{12}O_4Mo_2$: C, 46.77; H, 5.02; N, 18.18. Found: C, 46.88; H, 5.03; N, 17.96. (b) **5b**: IR (KBr) 1977, 1916, 1876, 1825 cm^{-1} (ν_{CO}); ^{1}H NMR (CD_2Cl_2) at 20 °C δ 5.90 (br, 4 H, Tp′ C*H*), 5.77 (s, 2 H, Tp′ C*H*), 2.64, 2.46, 2.40, 2.25, 2.19 (Tp′ CC*H*$_3$), 2.20 (br, 2 H, (W(μ-C*H*$_2$)W); ^{13}C{^{1}H} NMR (CD_2Cl_2) at 20 °C δ 304.4 ($^1J_{W-C}$ = 45 Hz, W(μ-*C*)W), 232.8, 225.2 (br, W(*C*O)), 154.2, 153.2, 145.5 (Tp′*C*CH$_3$), 107.4, 107.1 (Tp′ *C*H), 15.7, 12.9, 12.8 (Tp′ *C*CH$_3$), −3.3 (W(μ-*C*H$_2$)W). Anal. Calcd for $C_{36}H_{46}B_2N_{12}O_4W_2$: C, 39.30; H, 4.21; N, 15.28. Found: C, 39.26; H, 4.16; N, 15.04.

(13) (a) Chaona, S.; Lalor, F. J.; Ferguson, G.; Hunt, M. M. *J. Chem. Soc., Chem. Commun.* **1988**, 1606. (b) Brower, D. C.; Stoll, M.; Templeton, J. L. *Organometallics* **1989**, *8*, 2786. (c) Etienne, M.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1991**, *113*, 2324.

(14) (a) Latesky, S. L.; Selegue, J. P. *J. Am. Chem. Soc.* **1987**, *109*, 4731. (b) Beck, W.; Knauer, W.; Robl, C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 318.

(15) (a) Herrmann, W. A. *Pure Appl. Chem.* **1982**, *54*, 65. (b) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159.

(16) Crystals of **5b** containing 0.5 molecules of CH_2Cl_2 per asymmetric unit were obtained by slow diffusion of a layered dichloromethane/hexanes solution: $C_{36.50}H_{47}B_2ClO_4N_{12}W_2$; M = 1142.62, monoclinic, $P2_1/n$, a = 12.567 (3) Å, b = 17.207 (3) Å, c = 20.673 (4) Å, β = 100.40 (2)°; V = 4397 (2) Å^3, Z = 4, ρ_{calcd} = 1.723 g cm^{-3}, μ_{calcd} 55.1 cm^{-1}. Data were collected on a Rigaku AFC6S automated diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.709 30 Å) using an $\omega/2\theta$ scan ($2\theta_{max}$ = 45°), resulting in 5738 unique reflections, of which 3909 were observed ($I > 2.5\sigma(I)$). The structure was solved by Patterson methods and an empirical absorption correction applied using DIFABS (Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158). Refinement by full-matrix least squares gave residuals of R = 0.059, R_w = 0.080 for 528 parameters. Hydrogen atoms were included in calculated positions with thermal parameters derived from the atom to which they were bonded. All computations were performed by using the NRCVAX suite of programs: Gabe, E. J.; LePage, Y.; Charland, J.-P.; Lee, F.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

(17) Dotz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1983.

(18) Herrmann notes that most bridging methylene complexes have acute internal angles at the bridging carbon.[15] However, this angle is dependent upon the metal–metal interatomic distance. The interstitial carbide (C5) in **5b** dictates a W1–W2 separation of 3.959 (1) Å. Thus, no W1–W2 bonding occurs in **5b**, and an obtuse internal angle at C6 is logical.

(19) (a) Hursthouse, M. B.; Jones, R. A.; Abdul Malik, K. M.; Wilkinson, G. *J. Am. Chem. Soc.* **1979**, *101*, 4128. (b) Tooze, R. P.; Pericles, S.; Motevalli, M.; Hursthouse, M. B.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1985**, 1139. (c) Burkhardt, E. R.; Donney, J. J.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 2022. (d) Liu, A. H.; Murray, R. C.; Dewan, J. C.; Santasiero, B. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 4282. (e) Waymouth, R. W.; Potter, K. S.; Schaefer, W. P.; Grubbs, R. H. *Organometallics* **1990**, *9*, 2843 and references cited therein.

(20) Ginley, D. S.; Bock, C. R.; Wrighton, M. S.; Fischer, B.; Tipton, D. L.; Bau, R. *J. Organomet. Chem.* **1978**, *157*, 41.

(21) (a) Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858. (b) Bott, S. G.; Clark, D. L.; Green, M. L. H.; Mountford, P. *J. Chem. Soc., Chem. Commun.* **1989**, 418.

hydridocarbyne **3b** and the "dimers" **5a** and **5b** are underway.

Acknowledgment. We thank the United States Department of Energy, Division of Chemical Sciences (Grant No. 85ER13430), for financial support.

Supplementary Material Available: Details of syntheses and full analytical and spectral data for compounds **2b**, **3b**, **4a,b** and **5a,b**, complete tables of crystal data, positional and thermal parameters, bond distances and bond angles, a drawing of **5b** with the complete numbering scheme, and an expansion of the gated-decoupled ^{13}C NMR methylidyne signal of **3b** (23 pages); listing of calculated and observed structure factors for **5b** (20 pages). Ordering information is given on any current masthead page.

(Thiepine)iron Tricarbonyl: Stabilization of Thermally Labile Parent Thiepine by Transition-Metal Complexation†

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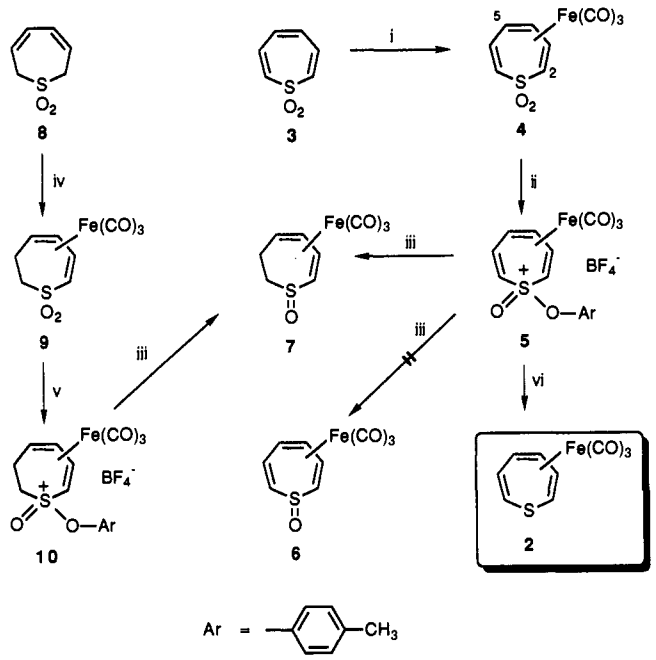
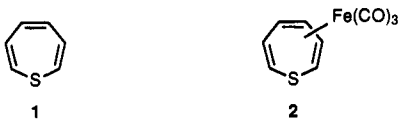
Despite the successful synthesis of several monocyclic thiepine derivatives stabilized by bulky groups at both the 2- and 7-positions,[1] the parent thiepine (**1**) has eluded synthesis.[2] This is mainly due to the pronounced thermal instability of **1**. Ready loss of sulfur from **1** presumably occurs by valence isomerization of **1** to the corresponding thianorcaradiene followed by irreversible cheletropic loss of sulfur.[3] On the other hand, the ability of transition metals to stabilize labile species by complexation[4] has allowed isolation of kinetically unstable conjugated molecules such as cyclobutadiene,[5] pentalene,[6] and norcaradiene.[7] Actually, in the field of thiepines, a transition-metal complexation strategy

Scheme I[a]



[a]Synthesis of **2**. Reagents and conditions: (i) 1.5 equiv of $Fe_2(CO)_9$, THF, 50 °C, 12 h, 99%; (ii) 1.5 equiv of p-$CH_3C_6H_4N_2^+$ BF_4^-, 95 °C, 5 min under sonication, 21%; (iii) 4.0 equiv of LAH, 1:2:1 DME-THF-ether, -100 °C, 1 h, 24%; (iv) 4.0 equiv of $Fe_2(CO)_9$, benzene, 75 °C, 48 h, 67%; (v) 2.0 equiv of p-$CH_3C_6H_4N_2^+$ BF_4^-, 95 °C, 10 min under sonication, 10%; (vi) 15.0 equiv of SmI_2, THF, 0 °C, 38%.

has recently been utilized to synthesize and isolate thermally unstable 1-benzothiepine 1-oxide by us.[8] Herein we disclose the first synthesis and characterization of (thiepine)iron tricarbonyl (**2**), which demonstrates the possibility of detection of thiepine **1**.



Our synthetic route to (thiepine)iron tricarbonyl (**2**) involves unique methodology for the reduction of sulfone to sulfide. The reaction of stable thiepine 1,1-dioxide (**3**)[9] with 1.5 equiv of $Fe_2(CO)_9$ in THF at 50 °C for 12 h furnished the iron tricarbonyl complex **4**,[10] yellow needles, mp 169-170 °C dec, in 99% yield. The η^4-complexation in **4** was confirmed on the basis of its ^1H and ^{13}C NMR spectra which exhibited substantially high field chemical shifts for 2- (δ_H = 3.73, δ_C = 67.4) and 5-positions (δ_H = 3.13, δ_C = 50.8).

Recently, the conversion of sulfones into sulfoxides has been reported by a two-stage procedure involving initial reaction of a sulfone with an arenediazonium tetrafluoroborate to form an aryloxysulfoxonium salt[11] and subsequent reaction of this either with $NaBH_4$-Al_2O_3[12] or with phenylmethanethiol.[13] Reaction of finely pulverized **4** with p-toluenediazonium tetrafluoroborate without solvent at 95 °C for 5 min under sonication afforded a 1:1 mixture of stereoisomers of the p-tolyloxysulfoxonium salts **5a**[10] and **5b**[10] which could, though tedious, be separated[14] by

† Dedicated to Professor Ronald Breslow on the occasion of his 60th birthday.

(1) (a) Hoffman, J., Jr.; Schlessinger, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 5263-5265. (b) Nishino, K.; Yano, S.; Kohashi, Y.; Yamamoto, K.; Murata, I. *J. Am. Chem. Soc.* **1979**, *101*, 5059-5061. (c) Murata, I.; Nishino, K.; Yano, S.; Kohashi, Y.; Yamamoto, K. *Croat. Chem. Acta* **1980**, *53*, 615-623. (d) Yamamoto, K.; Yamazaki, S.; Kohashi, Y.; Murata, I.; Kai, Y.; Kanehisa, N.; Miki, K.; Kasai, N. *Tetrahedron Lett.* **1982**, *23*, 3195-3198. (e) Yamamoto, K.; Yamazaki, S.; Kohashi, Y.; Matsukawa, A.; Murata, I. *Chem. Lett.* **1982**, 1843-1846. (f) Yamamoto, K.; Matsukawa, A.; Murata, I. *Chem. Lett.* **1985**, 1119-1122.

(2) Parent thiepine is considered to be an extremely thermally unstable molecule, since 2,7-di-*tert*-butylthiepine[1b,c] is quite stable whereas the corresponding 2,7-diisopropylthiepine could not be detected even at -78 °C. See: Yano, S.; Nishino, K.; Nakasuji, K.; Murata, I. *Chem. Lett.* **1978**, 723-726.

(3) See, for example: Murata, I.; Nakasuji, K. *Top. Curr. Chem.* **1981**, *97*, 33-70.

(4) See, for example: Pearson, A. J. *Metallo-organic Chemistry*; John Wiley and Sons: New York, 1985; p 61.

(5) (a) Emerson, G. F.; Watts, L.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 131-133. (b) Amiet, R. G.; Reeves, P. C.; Pettit, R. *J. Chem. Soc., Chem. Commun.* **1967**, 1208. (c) Amiet, R. G.; Pettit, R. *J. Am. Chem. Soc.* **1968**, *90*, 1059-1060. (d) Rosenblum, M.; Gatsonis, C. *J. Am. Chem. Soc.* **1967**, *89*, 5074-5075. (e) Rosenblum, M.; North, B. *J. Am. Chem. Soc.* **1968**, *90*, 1060-1061.

(6) (a) Weidemüller, W.; Hafner, K. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 925. (b) Miyake, A.; Kanai, A. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 801. (c) Katz, T. J.; Acton, N. *J. Am. Chem. Soc.* **1972**, *94*, 3281-3283. (d) Katz, T. J.; Acton, N.; McGinnis, J. *J. Am. Chem. Soc.* **1972**, *94*, 6205-6206.

(7) Grimme, W.; Köser, H. G. *J. Am. Chem. Soc.* **1981**, *103*, 5919-5920.

(8) Nishino, K.; Ishigami, S.; Tamura, Y.; Imagawa, K.; Ikutani, Y.; Murata, I. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1717-1718.

(9) Mock, W. L. *J. Am. Chem. Soc.* **1967**, *89*, 1281-1283.

(10) All new compounds gave appropriate ^1H NMR, ^{13}C NMR, and mass spectra and satisfactory elemental analyses. See the supplementary material.

(11) Chalbley, G. R.; Snodin, D. J.; Stevens, G.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1580-1587.

(12) Still, I. W. J.; Ablenas, F. J. *J. Org. Chem.* **1983**, *48*, 1617-1620.

(13) Shimagaki, M.; Tsuchiya, H.; Ban, Y.; Oishi, T. *Tetrahedron Lett.* **1978**, *37*, 3435-3438.

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