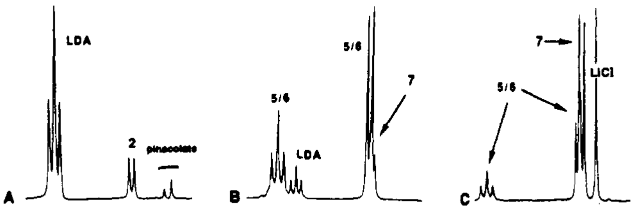


Figure 1. ^{6}Li NMR spectra of 0.1 M [^{6}Li,^{15}N]LDA in 3:1 THF/pentane at −115 °C: (A) with 0.5 equiv of [^{6}Li]pinacolate; (B) with 0.4 equiv of [^{6}Li]LiCl; (C) with 1.5 equiv of [^{6}Li]LiCl. The spins of ^{6}Li and ^{15}N are 1 and $^1/_2$, respectively.

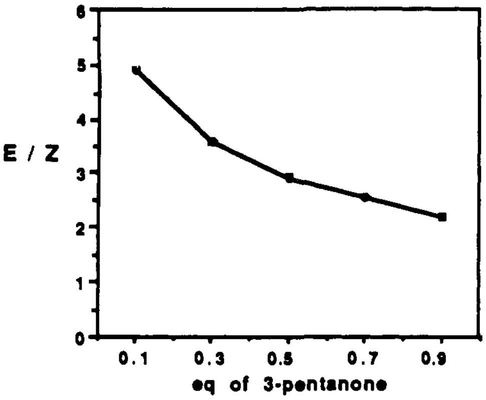


Figure 2.

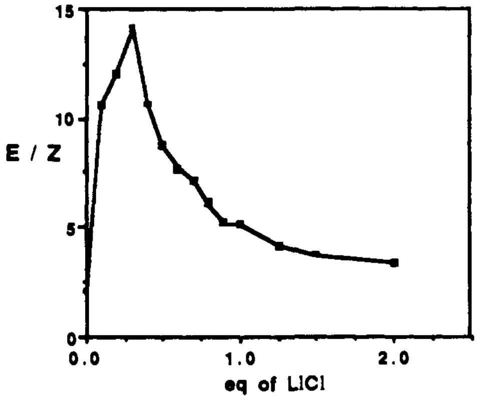


Figure 3.

with ketone enolates is both limited and structure dependent, but still may be of some practical consequence. The corresponding LDA/LiCl mixed aggregates are also observable and may have a substantial impact on the selectivity and reactivity of LDA. However, the approximate correlation of optimal concentrations of mixed aggregate **5** with maximal selectivities *must* be illusory; the continuously changing proportions of LDA, lithium enolate, and LiCl throughout the course of the enolization would result in a continuously changing structure distribution. Furthermore, studies of lithium 2,2,6,6-tetramethylpiperidide reveal that added lithium salts can have a substantially greater (and more complex) influence on the structures and reactivities of highly hindered lithium amides.[20]

Acknowledgment. We acknowledge the National Science Foundation Instrumentation Program (CHE 7904825 and PCM 8018643), the National Institutes of Health (RR02002), and IBM for support of the Cornell Nuclear Magnetic Resonance Facility. We also thank the National Institutes of Health for direct support of this work.

---

(20) Hall, P.; Gilchrist, J. H.; Fuller, D. J.; Harrison, A. T.; Collum, D. B. *J. Am. Chem. Soc.* In press.

Support for a Dimer of Di-μ-oxo Dimers Model for the Photosystem II Manganese Aggregate. Synthesis and Properties of $[(Mn_2O_2)_2(tphpn)_2](ClO_4)_4$[1]

Michael K. Chan and William H. Armstrong*

Department of Chemistry, University of California
Berkeley, California 94720

Received July 12, 1990

The task of elucidating the structure of the manganese aggregate in the oxygen-evolving complex of photosystem II (MnOEC), generally assumed to be the catalytic site of photosynthetic water oxidation, provides an interesting challenge for bioinorganic and biophysical chemists.[2-6] Characteristics of this active-site complex include (i) a nuclearity of three or four manganese atoms, (ii) a broad low-field parallel polarization mode EPR absorption ($g_{eff} = 4.8$) at the S_1 oxidation level,[4] (iii) multiline (19–21 lines, $g_{eff} = 2$) and $g_{eff} = 4.1$ EPR signals at the S_2 oxidation level,[2,3] and (iv) at least two relatively short range Mn···Mn contacts (2.7 Å) as indicated by X-ray absorption spectroscopy.[3,5,7] Furthermore, a peak in the Fourier transformed EXAFS data for MnOEC has been assigned to a 3.3-Å Mn···Mn interaction.[5,7]

Complexes that contain the $\{Mn_2O_2\}^{3+}$ core[6] may be viewed as preliminary or "first-generation" models for the MnOEC because they possess Mn···Mn distances of 2.7 Å and 16-line EPR spectra. However, the aforementioned binuclear complexes are not fully

---

(1) Abbreviations used: tphpn = *N,N,N′,N′*-tetrakis(2-pyridylmethyl)-2-hydroxypropane-1,3-diamine, MnOEC = manganese aggregate in the oxygen-evolving complex of Photosystem II, EXAFS = extended X-ray absorption fine structure, EPR = electron paramagnetic resonance.

(2) (a) Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1153–1172. (b) Pecoraro, V. L. *Photochem. Photobiol.* **1988**, *48*, 249–264. (c) Christou, G. *Acc. Chem. Res.* **1989**, *22*, 328–335. (d) Brudvig, G. W.; Crabtree, R. H. *Prog. Inorg. Chem.* **1989**, *37*, 99–142. (e) Armstrong, W. H. In *Manganese Redox Enzymes*; Pecoraro, V. L., Ed.; VCH, to be submitted.

(3) (a) Renger, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 643–660. (b) Babcock, G. T. In *New Comprehensive Biochemistry*: *Photosynthesis*: Amesz, J., Ed.; Elsevier: Amsterdam, 1987; pp 125–158. (c) Govindjee; Kambara, T.; Coleman, W. *Photochem. Photobiol.* **1985**, *42*, 187–210. (d) Dismukes, G. *Photochem. Photobiol.* **1986**, *43*, 99–115. (e) Brudvig, G. W. In *Metal Clusters in Proteins*: Que, L., Jr., Ed.; ACS Symposium Series 372; American Chemical Society: Washington, DC, 1988; pp 221–237. (f) Babcock, G. T.; Barry, B. A.; Debus, R. J.; Hoganson, C. W.; Atamian, M.; McIntosh, L.; Sithole, I.; Yocum, C. F. *Biochemistry* **1989**, *28*, 9557–9565.

(4) (a) Dexheimer, S. L.; Sauer, K.; Klein, M. P. In *Current Research in Photosynthesis*; Battscheffsky, M., Ed.; Kluwer, Academic Publishers: Netherlands, 1990; Vol. 1, pp 761–764. (b) Dexheimer, S. L. Ph.D. Dissertation, University of California, Berkeley, CA, 1990.

(5) (a) George, G. N.; Prince, R. C.; Cramer, S. P. *Science* **1989**, *243*, 789–791. (b) Penner-Hahn, J. E.; Fronko, R. M.; Pecoraro, V. L.; Yocum, C. F.; Betts, S. D.; Bowlby, N. R. *J. Am. Chem. Soc.* **1990**, *112*, 2549–2557. (c) Kirby, J. A.; Robertson, A. S.; Smith, J. P.; Thompson, A. C.; Cooper, S. R.; Klein, M. P. *J. Am. Chem. Soc.* **1981**, *103*, 5529–5537. (d) McDermott, A. E.; Yachandra, V. K.; Guiles, R. D.; Cole, J. L.; Dexheimer, S. L.; Britt, R. D.; Sauer, K.; Klein, M. P. *Biochemistry* **1988**, *27*, 4021–4031.

(6) (a) Hagen, K. S.; Armstrong, W. H.; Hope, H. *Inorg. Chem.* **1988**, *27*, 967–969. (b) Plaskin, P. M.; Stoufer, R. C.; Mathew, M.; Palenik, G. J. *J. Am. Chem. Soc.* **1972**, *94*, 2121–2122. (c) Stebler, M.; Ludi, A.; Bürgi, H.-B. *Inorg. Chem.* **1986**, *25*, 4743–4750. (d) Collins, M. A.; Hodgson, D. J.; Michelsen, K.; Towle, D. K. *J. Chem. Soc., Chem. Commun.* **1987**, 1659–1660. (e) Towle, D. K.; Botsford, C. A.; Hodgson, D. J. *Inorg. Chim. Acta* **1988**, *141*, 167–168. (f) Suzuki, M.; Tokura, S.; Suhara, M.; Uehara, A. *Chem. Lett.* **1988**, 477–480. (g) Hoof, D. L.; Tisley, D. G.; Walton, R. A. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 571–576. (h) Goodson, P. A.; Hodgson, D. J. *Inorg. Chem.* **1989**, *28*, 3606–3608. (i) Libby, E.; Webb, R. J.; Streib, W. E.; Folting, K.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *Inorg. Chem.* **1989**, *28*, 4037–4040. (j) Brewer, K. J.; Liegeois, A.; Otvos, J. W.; Calvin, M.; Spreer, L. O. *J. Chem. Soc., Chem. Commun.* **1988**, 1219–1220. (k) Suzuki, M.; Senda, H.; Kobayashi, Y.; Oshio, H.; Uehara, A. *Chem. Lett.* **1988**, 1763–1766. (l) Goodson, P. A.; Glerup, J.; Hodgson, D. J.; Michelsen, K.; Pedersen, E. *Inorg. Chem.* **1990**, *29*, 503–508. (m) Cooper, S.; Calvin, M. *J. Am. Chem. Soc.* **1977**, *99*, 6623–6630. (n) Brewer, K. J.; Calvin, M.; Lumpkin, R. S.; Otvos, J. W.; Spreer, L. O. *Inorg. Chem.* **1989**, *28*, 4446–4451.

(7) (a) Guiles, R. D.; Zimmermann, J.-L.; McDermott, A. E.; Yachandra, V. K.; Cole, J. L.; Dexheimer, S. L.; Britt, R. D.; Wieghardt, K.; Bossek, U.; Sauer, K.; Klein, M. P. *Biochemistry* **1990**, *29*, 471–485. (b) Guiles, R. D.; Yachandra, V. K.; McDermott, A. E.; DeRose, V. J.; Zimmermann, J.-L.; Sauer, K.; Klein, M. P. In *Current Research in Photosynthesis*; Battscheffsky, M., Ed.; Kluwer Academic Publishers: Netherlands, 1990; Vol. 1, pp 789–792. (c) Guiles R. D. Ph.D. Dissertation, Lawrence Berkeley Laboratory, University of California, Berkeley, CA, 1988.

0002-7863/91/1513-5055$02.50/0

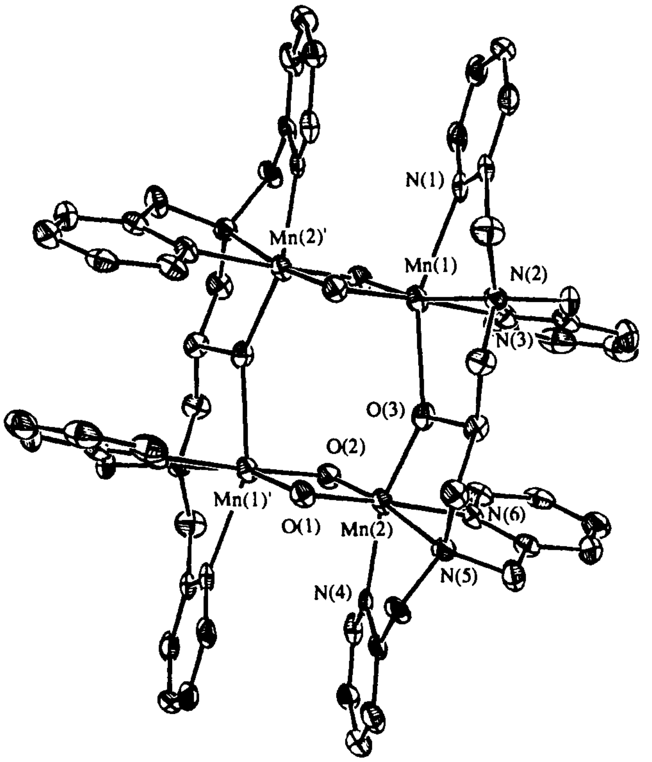


Figure 1. Structure of $[(Mn_2O_2)_2(tphpn)_2]^{4+}$ (**1**), showing the 50% probability thermal ellipsoids and atom-labeling scheme. Hydrogen atoms are omitted for clarity. Primed atoms are related to unprimed ones by an inversion operation. Selected interatomic distances (Å) and angles (deg) are as follows: Mn(1)–O(1′), 1.821 (4); Mn(1)–O(2′), 1.838 (5); Mn(1)–O(3), 2.295 (5); Mn(1)–N(1), 2.297 (6); Mn(1)–N(2), 2.120 (5); Mn(1)–N(3), 2.045 (6), Mn(2)–O(1), 1.799 (4); Mn(2)–O(2), 1.782 (4); Mn(2)–O(3), 1.929 (5); Mn(2)–N(4), 2.030 (6); Mn(2)–N(5), 2.067 (5); Mn(2)–N(6), 2.053 (5); Mn(1)···Mn(2′), 2.654 (1); Mn(1)···Mn(2), 3.971 (2); Mn(1′)–O(1)–Mn(2), 94.3 (2); Mn(1′)–O(2)–Mn(2), 94.3 (2); Mn(1)–O(3)–Mn(2), 140.0 (2).

accurate mimics for the MnOEC, and we conjectured that one possible way to more closely match the properties of the native system would be to couple two such dimers together by use of a spanning polydentate ligand, thereby enforcing an interdimer interaction. Klein, Sauer, and co-workers have suggested that the MnOEC may consist of a dimer of di-oxo-bridged dimers.[7] Here, we report the synthesis and properties of one such "dimer-of-dimers" structural type: $[(Mn_2O_2)_2(tphpn)_2]^{4+}$ (**1**). Complex **1** does indeed represent the first example of the target structural type mentioned above; a linked pair of $\{Mn_2O_2\}^{3+}$ cores. The remarkable similarity between the parallel polarization mode EPR spectrum of **1** and that of the MnOEC S_1 state lends support to the notion that the latter possesses a "dimer-of-dimers"-type electronic structure.

Our initial studies with the heptadentate ligand tphpn, which have been described elsewhere,[8] provided interesting tetranuclear structural types $[\{Mn_2(tphpn)(O_2CCH_3)(H_2O)\}_2O]^{4+}$ (**2**)[8a] and $[Mn_4O_2(tphpn)_2(H_2O)_2(CF_3SO_3)_2]^{3+}$ (**3**),[8b] but only recently have we discovered reaction conditions that yield a complex that contains an intimately bridged pair of $\{Mn_2O_2\}^{3+}$ cores, as shown in Figure 1. Vapor diffusion of acetone into a MeCN solution of **3** under ambient conditions yielded a crystalline material, which, on the basis of spectral analysis (see below), was deduced to be distinct from **3**. Samples of **1** suitable for elemental analysis,[9] EPR spectroscopic characterization, and X-ray studies[10] were obtained by recrystallization (CH_3CN) of material from the CH_3CN/acetone reaction mixture. In the solid-state structure of $\mathbf{1}(ClO_4)_4{\cdot}3H_2O{\cdot}2CH_3COCH_3$, the cation, shown in Figure 1, resides on a crystallographic inversion center, and by inspection of the bond distances to Mn atoms it is apparent that the complex is a trapped mixed-valence species that is reasonably well-ordered in the crystal lattice. Charge considerations indicate that **1** consists of a pair of $\{Mn^{III}Mn^{IV}O_2\}^{3+}$ cores, and $Mn{-}O_{oxo}$ bond distances require that Mn(1) and Mn(2) be assigned as Mn^{III} and Mn^{IV} ions, respectively.[6] In contrast to the binding mode for tphpn in **2** and **3**, in which the tripodal termini of the ligand coordinate in a meridional fashion, in the structure of **1** the ligand binds in a facial manner.

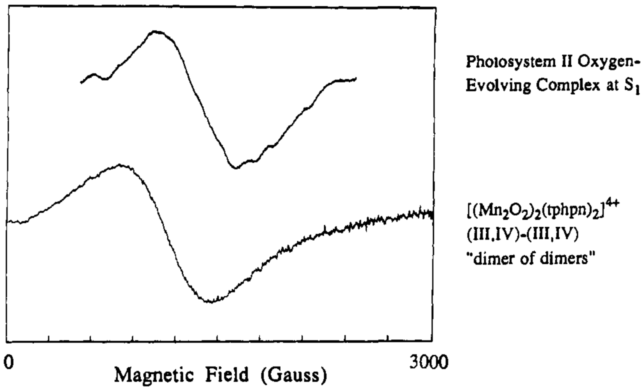


Figure 2. Top: Difference EPR spectrum of the spinach photosystem II S_1 state.[4] Bottom: X-band (ν = 9.25 GHz) EPR spectrum of $[(Mn_2O_2)_2(tphpn)_2]^{4+}$ in CH_3CN at 4.0 K employing parallel polarization geometry[4,12] and the following spectrometer settings: microwave power, 22.5 mW; field modulation, 16 G; modulation frequency, 100 kHz.

Our observations indicate that the spectral properties of **1** are influenced by interactions between the two di-oxo-bridged dimers. For example, whereas compounds that contain a single $\{Mn_2O_2\}^{3+}$ core have distinct visible features at 548–561 and 644–684 nm,[61] complex **1** has a single broad shoulder at ~600 nm. In frozen CH_3CN solution, compound **1** is EPR-silent at X-band frequencies when the conventional (perpendicular polarization) spectrometer configuration is used at 77 K, in contrast to isolated binuclear species that display relatively intense 16-line spectra.[6]

Recently, Dexheimer et al. discovered[4] an EPR signal associated with the Kok S_1 state[11] of photosystem II by using the parallel polarization spectrometer geometry.[4,12] They proposed that this signal may arise from a low-lying $S = 1$ spin state. As we anticipated that compound **1** should have a low-lying $S = 1$ state,[13]

---

(8) (a) Chan, M. K.; Armstrong, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 9121–9122. (b) Chan, M. K.; Armstrong, W. H. *J. Am. Chem. Soc.* **1990**, *112*, 4985–4986. See also: Suzuki, M.; Sugisawa, T.; Senda, H.; Oshio, H.; Uehara, A. *Chem. Lett.* **1989**, 1091–1094.

(9) Elemental analysis of $\mathbf{1}(ClO_4)_4$. Calcd for $C_{54}H_{58}Cl_4Mn_4N_{12}O_{22}$: C, 40.82; H, 3.68; Cl, 8.93; Mn, 13.84; N, 10.58. Found: C, 40.62; H, 3.66; Cl, 8.89; Mn, 13.6; N, 10.53.

(10) X-ray analysis: Compound $\mathbf{1}(ClO_4)_4{\cdot}3H_2O{\cdot}2CH_3COCH_3$ crystallizes in the monoclinic space group $P2_1/c$, with a = 13.605 (4) Å, b = 16.851 (6) Å, c = 15.445 (5) Å, β = 93.89 (2)°, V = 3533 Å^3, ρ_{calcd} = 1.648 g cm^{-3}, and Z = 2. Data collection at 152 K out to 45° in 2θ using Mo Kα radiation provided 3086 reflections with $I > 3\sigma(I)$. The structure was solved by direct methods and refined by using 491 parameters to final R (R_w) values of 5.48% (6.48%).

(11) Kok, B.; Forbush, B.; McGloin, M. *Photochem. Photobiol.* **1970**, *11*, 457.

(12) Dexheimer, S. L.; Gohdes, J. W.; Chan, M. K.; Hagen, K. S.; Armstrong, W. H.; Klein, M. P. *J. Am. Chem. Soc.* **1989**, *111*, 8923–8925 and references therein.

(13) It has been demonstrated that binuclear species containing the $\{Mn_2O_2\}^{3+}$ core have $S = {}^1/_2$ ground states well separated from the first excited state.[6] Thus at low temperature only the ground state is populated. For compound **1**, we speculated that perhaps in the low-temperature regime its magnetic properties could be modelled by an exchange interaction between two $S = {}^1/_2$ dimers. This would yield overall $S = 0$ and $S = 1$ states of the tetranuclear complex, and if the alkoxide bridges provide for only relatively weak magnetic coupling, then the $S = 1$ state would certainly be low-lying. Support for this view of the electronic structure of **1** comes from preliminary magnetic susceptibility measurements. For example, at 60 K with a 5-kG applied magnetic field, compound **1** has a magnetic moment of 2.80 μ_B, in excellent agreement with the predicted value for an $S = 1$ complex (2.83 μ_B). Full details of the magnetic properties of **1** will be reported elsewhere. A related dimer-of-dimers electronic structure for the S_2 state of the MnOEC has been discussed by Brudvig and co-workers.[14]

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

G. M. Jamison, A. E. Bruce, P. S. White, and
J. L. Templeton*

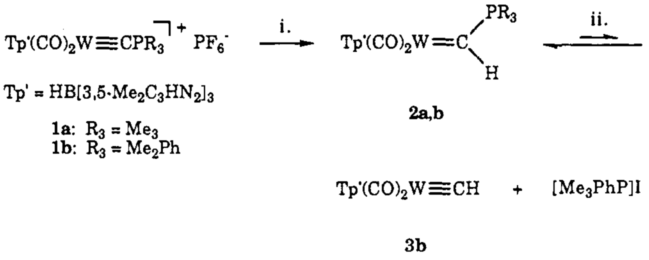
W. R. Kenan, Jr., Laboratories
Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27599-3290

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.

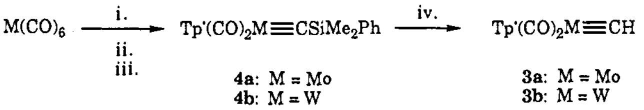
In a previous communication[2a] we reported that the cationic phosphonium carbyne complex **1a**, $[Tp'(CO)_2W{\equiv}CPMe_3][PF_6]$, was susceptible to nucleophilic attack at C_α to generate a neutral carbene complex, $Tp'(CO)_2W{=}C(H)(PMe_3)$ (Scheme I). Addition of MeI to the (dimethylphenyl)phosphonium 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]



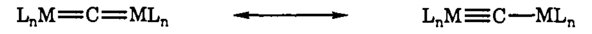
[a] (i) $KHB(O\text{-}i\text{-}Pr)_3$, MeCN, −23 °C; (ii) MeI, MeCN.

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



A B

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-CH_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′ CCH_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.

0002-7863/91/1513-5057$02.50/0