(11) Brault, D.; Rougee, M. *Biochem. Biophys. Res. Commun.* **1974,** *57* (3), 654-659.
(12) (a) Rougee, M.; Brault, D. *Biochemistry* **1975,** *14,* 4100-4106. (b) Brault, D.; Rougee, M. *ibid.* **1974,** *13,* 4591-4597.
(13) Unpublished work.
(14) (a) Smith, M. H. *Biochem. J.* **1959,** *73,* 90-101. (b) Geibel, J.; Cannon, J.; Campbell, D.; Traylor, T. G. *J. Am. Chem. Soc.* **1978,** *100,* 3575-3585 and references therein. (c) White, D. K.; Cannon, J. B.; Traylor, T. G. *ibid.*, in press.
(15) Mincey, T.; Traylor, T. G. *J. Am. Chem. Soc.* **1979,** *101,* 765-766.
(16) Use of 18-C-6 instead of DC-18-C-6 reduces k_5 by a factor of two. This relatively small change is not due to competition of 18-C-6 for the sixth coordination site.[13]
(17) Valentine, J. S.; Stanford, M. A.; Hoffman, B. M., unpublished work.

James C. Swartz, Marlene A. Stanford
James N. Moy, Brian M. Hoffman*
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

Joan S. Valentine
Department of Chemistry, Busch Campus
Rutgers, The State University
New Brunswick, New Jersey 08903

Received February 2, 1979

Matrix Isolation of a Triplet Biradical from a Carbene Precursor

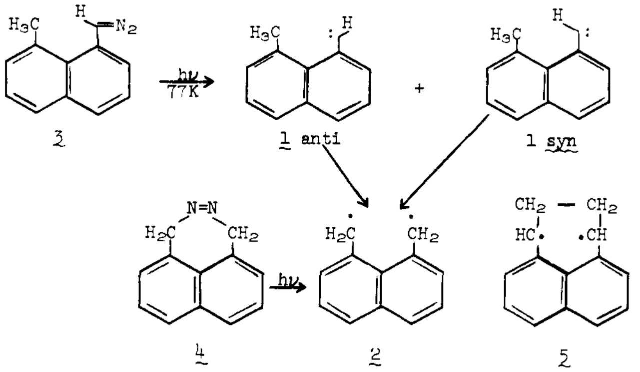
Sir:

Low temperature ESR spectroscopy has been used to determine the geometry,[1] spin distribution,[2] ground-state multiplicity,[3] and dynamical properties[4] of thermally accessible triplet biradicals immobilized in solid solution. The biradical is usually prepared by direct photofragmentation of a cyclic azo or carbonyl compound. The success of the method is dependent upon the synthetic availability of the precursor and a finite quantum yield for formation of the triplet biradical. Even if the triplet is the ground state of the biradical, and it lies in a potential minimum, there may be no pathway for populating and observing it by ESR.

It appeared possible that intramolecular hydrogen abstraction of a carbene might provide an alternate method of biradical matrix isolation. In some cases the acyclic carbene precursor may be more accessible than the requisite cyclic compound. Inter- and intramolecular hydrogen abstractions are well-known reactions of singlet and triplet carbenes.[5,6] The intermolecular process has been detected spectroscopically by NMR (CIDNP)[7] and ESR.[8]

Carbene **1** was chosen to test the feasibility of this method of biradical matrix isolation as α-naphthylcarbene[9] and 1,8-naphthoquinodimethane (**2**)[10] have stable, thermally accessible triplet states at liquid nitrogen temperature.

Mercuric oxide oxidation of the hydrazone[11] of 8-methyl-1-naphthaldehyde[12] yields the diazo compound **3**.[16] Photolysis of **3** (350 < λ < 700 nm) in hexafluorobenzene or 2-methyltetrahydrofuran at 77 K produces the spectrum of a randomly oriented triplet state (Figure 1).[17] This spectrum ($|d/\hbar c|$ = 0.024 = 0.002 cm^{-1}, $|E/\hbar c|$ = 0.001 cm^{-1}) is virtually identical with that reported for 1,8-naphthoquinodimethane obtained from azo compound **4**.[10b] Control experiments with acenaphthene demonstrate that triplet **2** does not arise from a secondary process.[18]



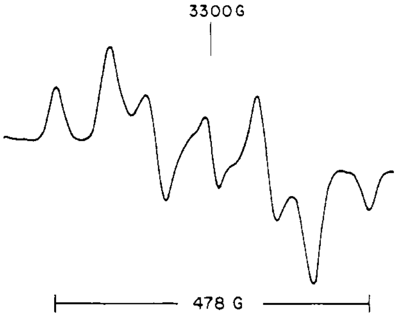


Figure 1. The triplet ESR spectrum of 1,8-naphthoquinodimethane in 2-methyltetrahydrofuran at 77 K.

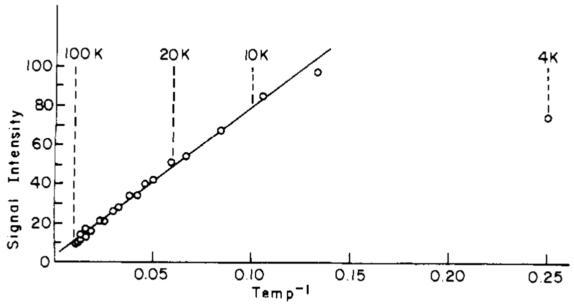
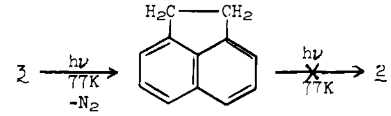


Figure 2. The Curie–Weiss Law analysis of 1,8-naphthoquinodimethane in 2-methyltetrahydrofuran.



Trozzolo, Wasserman, and Yager have shown that triplet α-naphthylcarbene exists in two conformations, syn and anti.[9] The two analogous geometric forms of triplet **1** will show markedly different reactivity toward hydrogen abstraction, provided that their rate of interconversion is slower than the rate of chemical reaction. The photolysis of **3** at 77 or 4 K (λ >350 and >470 nm, respectively) produces no resonances which can be attributed to either form of **1**. However, it remains to be shown whether the free carbene is indeed a direct precursor of the biradical. If this proves to be the case, the carbene must be extremely short lived owing to the proximity of the reactive moieties.

A Curie-Weiss Law[19] analysis of **2** over the temperature range 4-98 K is in agreement with recent work of Wirz on the ethano-bridged biradical **5**.[20] The straight-line plot obtained between 10 and 98 K indicates that 1,8-naphthoquinodimethane is most probably a ground-state triplet biradical (see Figure 2).[21] Although very low microwave power (0.01 mW) is employed in the analysis, the triplet resonance absorptions are still saturated below 10 K, producing apparent nonlinear Curie–Weiss Law behavior in the lower limit of the temperature range.

Further work with carbenes and nitrenes to prepare new heteroatomic biradicals is in progress.

Acknowledgment. Support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

0002-7863/79/1501-3398$01.00/0

References and Notes

(1) P. Dowd, *Acc. Chem. Res.*, **5**, 242 (1972).

(2) (a) G. L. Closs, L. R. Kaplan, and V. I. Bendall, *J. Am. Chem. Soc.*, **89**, 3376 (1967); (b) G. L. Closs and L. R. Kaplan, *J. Am. Chem. Soc.*, **81**, 2168 (1969).

(3) (a) M. S. Platz, J. M. McBride, R. D. Little, J. J. Harrison, A. Shaw, S. E. Potter, and J. A. Berson, *J. Am. Chem. Soc.*, **98**, 5725 (1976); (b) R. J. Baseman, D. W. Pratt, M. Chown, and P. Dowd, *ibid*, **98**, 6726 (1976).

(4) (a) S. L. Buchwalter and G. L. Closs, *J. Am. Chem. Soc.*, **97**, 3857 (1975); (b) M. S. Platz and J. A. Berson, *ibid.*, **98**, 6743 (1976); (c) P. Dowd and M. Chow, *ibid.*, **99**, 6538 (1977).

(5) (a) R. A. Moss, Ed., "Carbenes", Vol. I, Wiley-Interscience, New York, 1975; (b) W. Kirmse, "Carbene Chemistry", Academic Press, New York, 1971.

(6) H. E. Zimmerman and D. H. Paskovich, *J. Am. Chem Soc.*, **85**, 3796 (1963).

(7) G. L. Closs, "Chemically Induced Magnetic Polarization", G. L. Closs and A. R. Lepley, Ed., Wiley, New York, 1972, p 95.

(8) M. Thurnauer, Ph.D. Thesis, University of Chicago, 1974.

(9) A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **87**, 129 (1965).

(10) (a) C. R. Watson, Jr., R. M. Pagni, J. R. Dodd, and J. E. Bloor, *J. Am. Chem. Soc.*, **98**, 2551 (1976). (b) R. M. Pagni, M. N. Burnett, and J. R. Dodd, *J. Am. Chem. Soc.*, **99**, 1972 (1977) ($D/\hbar c$ = 0.0218 cm^{-1}, $E/\hbar c$ = 0.0021 cm^{-1}).

(11) The hydrazone gave satisfactory elemental analysis and spectral data.

(12) 8-Methyl-1-naphthaldehyde[13] was prepared by catalytic hydrogenation of naphthaldehydic acid[14] to 8-methyl-1-naphthoic acid. The acid was reduced to the alcohol with lithium aluminum hydride and then oxidized to the aldehyde with manganese dioxide.[15]

(13) L. P. Zalukaev and V. V. Moiseev, *J. Org. Chem. USSR* (*Engl. Transl.*), **2**, 272 (1966).

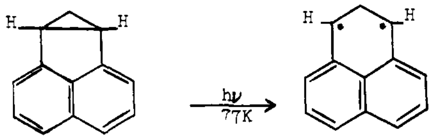
(14) R. C. Fuson and G. Munn, *J. Am. Chem. Soc.*, **71**, 1870 (1949).

(15) I. M. Goldman, *J. Org. Chem.*, **34**, 1979 (1969).

(16) The diazo compound gave satisfactory IR, ultraviolet-visible, and mass spectra.

(17) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964).

(18) J. F. Muller, D. Muller, and H. Dewey and J. Michl have prepared a 1,8-naphthoquinodimethane derivative at 77 K by photolysis of a bicyclic



$|D/\hbar c| = 0026 \pm 0.001\mathrm{cm}^{-1}$, $|E/\hbar c| < .002\mathrm{cm}^{-1}$

acenaphthene: *J. Am. Chem. Soc.*, **100**, 1629 (1978).

(19) R. Breslow, H. W. Chang, R. Hill, and E. Wasserman, *J. Am. Chem. Soc.*, **89**, 1112 (1967).

(20) M. Gisin, E. Rommel, J. Wirz, M. N. Burnett, and R. M. Pagni, *J. Am. Chem. Soc.*, **101**, 2216 (1979).

(21) A linear Curie-Weiss Law plot will also arise when the singlet and triplet states are exactly degenerate.

Matthew S. Platz
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received February 26, 1979

Redox Properties of Small Metallocarborane Clusters: Electrochemistry of Cobalt Triple-Decker Sandwich Compounds

Sir:

Following the reports of Werner and Salzer in 1972[1] on the synthesis of the tris(η^5-cyclopentadienyl)dinickel cation, $Cp_3Ni_2^+$, there has been considerable interest in so-called "triple-decker sandwich" compounds, partly due to the attractive possibility of building extended, electron-delocalized, organometallic chains.[2,3] The oxidation-reduction properties of these molecules, as well as the physical properties of their radical ions, are of obvious interest in attempting to understand the nature of the metal-metal interaction in these compounds and the degree to which delocalization may occur.

We wish to report electrochemical data on the dicobalt species (**1** and **2**)[3-5] which show that the triple-decker compounds are part of a *five-membered* electron-transfer series, at least four of which are stable. For comparison purposes, we include data on the monocobalt species[6] **3** and **4**, $CpCoC_2B_4H_6$.

Table I. Reduction and Oxidation Potentials of Cobalt Carboranes in CH_3CN

compound	$E_{1/2}$[a,b] red$_1$	red$_2$	ox$_1$	ox$_2$
(**1**) 1,7,2,3-$Cp_2Co_2C_2B_3H_5$	−1.44	−2.23	+0.51	+1.72[c]
(**2**) 1,7,2,4-$Cp_2Co_2C_2B_3H_5$	−1.35	−2.30	+0.89	[e]
(**3**) 1,2,3-$CpCoC_2B_4H_6$	−1.62	−2.50	+1.52[d]	
(**4**) 1,2,4-$CpCoC_2B_4H_6$	−1.43	[e]	+1.70[d]	
Cp_2Co^+ [f]	−0.94	−1.88	[e]	

[a] Volts vs. saturated calomel electrode. [b] Each process is a reversible, one-electron step, unless otherwise noted. [c] Irreversible wave in CH_3CN. [d] Reversible in CH_2Cl_2, irreversible in CH_3CN. [e] Not observed within available electrochemical window (+2.0 to −2.8 V). [f] Geiger, W. E. *J. Am. Chem. Soc.*, **1974**, *96*, 2632.

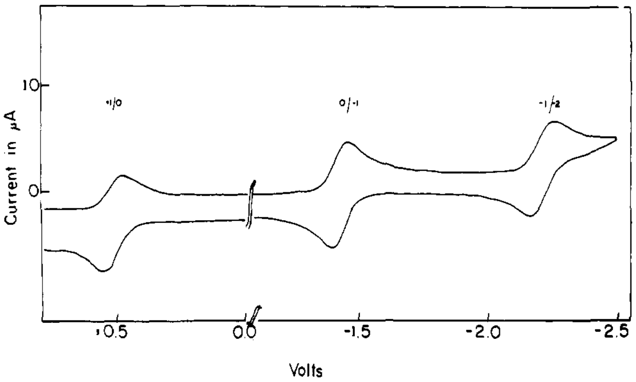
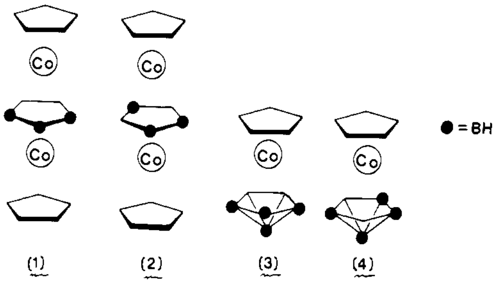


Figure 1. Cyclic voltammogram of an acetonitrile solution containing 2 × 10^{-4} M of **1** and 0.1 M Bu_4NPF_6 at a platinum bead electrode. Scan rate 0.20 V/s.



The triple-deckers **1** and **2** undergo a series of generally reversible one-electron oxidations and reductions in nonaqueous solvents[7] (Table I). A typical cyclic voltammogram (CV) is shown in the figure for 1,7,2,3-$Cp_2Co_2C_2B_3H_5$ (**1**). With the exceptions designated, each redox step is a diffusion-controlled, reversible, one-electron process. These conclusions were reached on the basis of dc polarography[8] (diffusion current constants, compared to Cp_2Co^+, and slope of polarographic wave), cyclic voltammetry[9] (current function dependence on scan rate, anodic-to-cathodic current ratio, anodic-to-cathodic peak potential difference), and thin-layer coulometry, and will be elaborated on in a subsequent forum.

The electron-transfer reactions of the dicobalt triple deckers are typified by a five-membered electron-transfer series in which each process except the second oxidation step is completely reversible in slow (<50 mV/s) cyclic voltammetry scans. This behavior is in marked contrast to that of the neutral

$$? \leftarrow 1^{2+} \rightleftharpoons 1^{+} \rightleftharpoons Cp_2Co_2C_2B_3H_5{}^{0} \rightleftharpoons 1^{-} \rightleftharpoons 1^{2-}$$