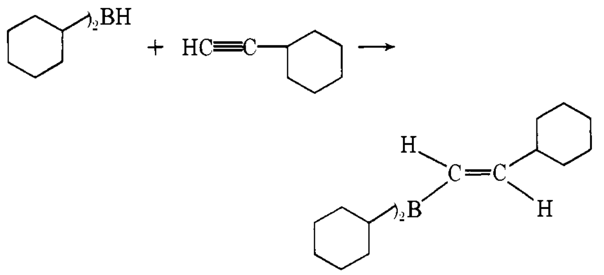
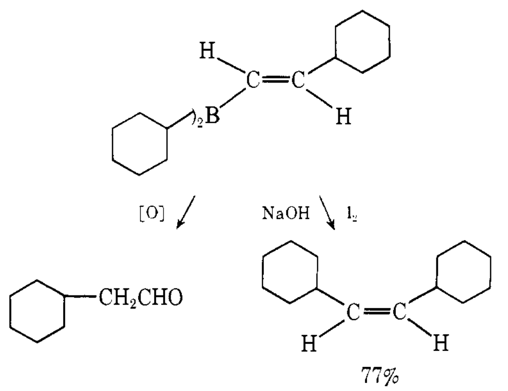
enylboranes are readily oxidized to aldehydes or converted with base and iodine to cis olefins[6] (eq 8).

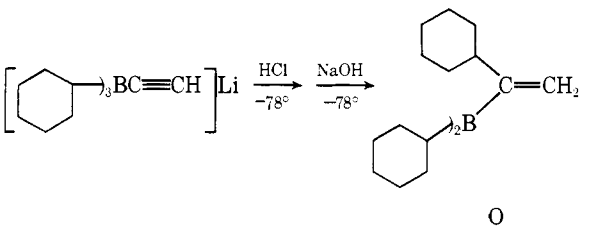


(7)

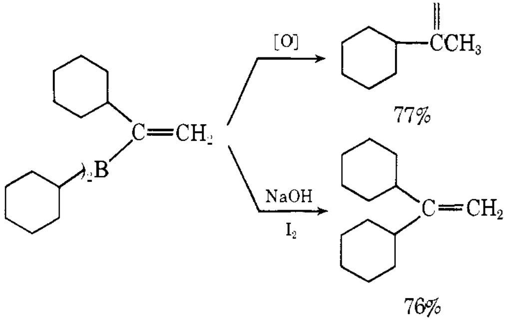


(8)

The corresponding Markovnikov alkenylborane may be prepared from lithium ethynyltricyclohexylborate[7] (eq 9). NMR indicates the absence of the terminal isomer (Vinyl proton NMR (CCl_4, Me_4Si) δ 4.83 (m), 5.23 (m)). This alkenylborane may be oxidized to the methyl ketone or converted with base and iodine to the 1,1-disubstituted ethylene (eq 10).



(9)



(10)

The following procedure for the preparation of 1-(dicyclohexylbora)-1-cyclohexylethylene is representative. A dry 250-ml flask equipped with a septum covered inlet and magnetic stirring bar was flushed with nitrogen. The flask was charged with 82 ml of tetrahydrofuran (THF) and 15 ml (150 mmol) of cyclohexene. Borane·THF (50 mmol, 18 ml of 2.78 *M*) was then added and the solution stirred at 50° for 3 hr. Monolithium acetylide was prepared in the following manner.[8] A dry 500-ml flask similarly equipped was flushed with nitrogen and charged with 100 ml of THF. The flask was cooled to −78° and 125 ml of acetylene (welding grade, passed through a Dry Ice trap, a sulfuric acid bubbler, and a soda lime trap) was added via a 250-ml syringe.[9] Then *n*-butyllithium (23 ml of 2.17 *M*) in hexane was added dropwise. After 10 min the tricyclohexylborane solution was transferred dropwise via a double-ended needle[2c] to the monolithium acetylide. The solution was stirred at −78° for 10 min and then 5 ml of concentrated hydrochloric acid (~60 mmol) was added dropwise. After 10 min, 20 ml of 3 *N* sodium hydroxide was added and the solution warmed to room temperature. Oxidation was achieved by the slow dropwise addition of 18 ml of 30% hydrogen peroxide. The THF solution was salted out with potassium carbonate. GLPC analysis revealed a 77% yield of cyclohexylethone.[10]

The protonation of lithium ethynyl- or vinyltrialkylborates provides for the first time a convenient synthesis of the Markovnikov borane species. This reaction, combined with the wide number of reactions of vinyl- and alkylboranes,[2] should prove to be exceptionally valuable.

References and Notes

(1) G. Zweifel, G. M. Clark, and N. L. Polston, *J. Am. Chem. Soc.*, **93**, 3395 (1971).
(2) (a) H. C. Brown, "Hydroboration", W. A. Benjamin, New York, N.Y., 1962; (b) H. C. Brown, "Boranes in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1972; (c) H. C. Brown, G. W. Kramer, A. B. Levy, and M. M. Midland, "Organic Syntheses via Boranes", Wiley-Interscience, New York, N.Y., 1975.
(3) (a) P. Binger, G. Benedikt, G. W. Rotermund, and R. Köster, *Justus Liebigs Ann. Chem.*, **717**, 21 (1968); (b) M. Naruse, K. Utimoto, and H. Nozaki, *Tetrahedron*, **30**, 3037 (1974); (c) A. Pelter and C. R. Harrison, *J. Chem. Soc., Chem. Commun.*, 828 (1974); (d) M. M. Midland, J. A. Sinclair, and H. C. Brown, *J. Org. Chem.*, **39**, 731 (1974).
(4) (a) A. Pelter, C. R. Harrison, and D. Kirkpatrick, *J. Chem. Soc., Chem. Commun.*, 544 (1973); (b) N. Miyaura, T. Yoshinori, M. Itoh, and A. Suzuki, *Tetrahedron Lett.*, 2961 (1974).
(5) M. M. Midland and H. C. Brown, submitted for publication.
(6) G. Zweifel, H. Arzoumanian, and C. C. Whitney, *J. Am. Chem. Soc.*, **89**, 3652 (1967).
(7) This procedure produces the alkenyldialkylborane either as the free borane or as the hydroxy "ate" complex. In either case, the intermediate readily undergoes representative reactions of alkenylboranes, such as oxidation to ketones by alkaline hydrogen peroxide and conversion to olefins by treatment with iodine.
(8) M. M. Midland, *J. Org. Chem.*, in press.
(9) G. W. Kramer, *J. Chem. Educ.*, **50**, 227 (1973).
(10) Essentially the same procedure was used for the lithium trialkylvinylborates. In this case, the organoborane could be used in situ for subsequent reactions or isolated by distillation. For example, di-*n*-butyl-2-hexylborane was isolated in 73% yield, bp 65–67° (0.5 mm). Vinyl Grignard reagents may be substituted for the lithium reagent in these reactions.
(11) Postdoctorate Research Associate on Grant No. GM10937 from the National Institutes of Health.

Herbert C. Brown,* Alan B. Levy,[11] M. Mark Midland
Richard B. Wetherill Laboratory, Purdue University
West Lafayette, Indiana 47907

Received April 7, 1975

Stabilization of Paramagnetic Metal(I) Complexes of the Nickel Subgroup. Electrochemical and Electron Spin Resonance Studies of Metal Dithiolene Complexes and Their Amino Analogs

Sir:

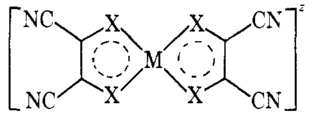
We wish to report electrochemical and ESR evidence for the existence of paramagnetic Pd(I) and Pt(I) complexes of the maleonitriledithiolate ligand, $S_2C_2(CN)_2^{2-}$, mnt. In addition, we give a preliminary report of an electrochemical and ESR study comparing nickel group complexes (**1**) of mnt with those containing the analogous bidente amino chelate, $(NH)_2C_2(CN)_2^{2-}$, derived from diaminomaleonitrile, damn.[1]

An extensive series of square planar anions (z = 1−, 2−) containing the mnt ligand has been known for over a decade,[2,3] and although no neutral bis complexes of this ligand

Table I. Electrochemical Data for Metal Complexes of Maleonitriledithiolate (mnt) and Diaminomaleonitrile (damn)

Complex	$E_{1/2}$[a] (V)				ΔE_{0-1}[b] (V)	ΔE_{1-2}[c] (V)	ΔE_{2-3}[d] (V)
	$1+ \rightleftharpoons 0$[e]	$0 \rightleftharpoons 1-$	$1- \rightleftharpoons 2-$	$2- \rightleftharpoons 3-$			
$Ni(mnt)_2{}^z$	...	+1.09[f,g]	+0.23	−1.67		0.86	1.90
$Pd(mnt)_2{}^z$	...	+1.16[g,h]	+0.44	−1.90		0.72	2.34
$Pt(mnt)_2{}^z$	...	+1.07[h]	+0.22	−2.41, −2.60[i]		0.85	2.63
$Ni(damn)_2{}^z$	+0.55[j]	−0.40	−1.17	...	0.95	0.77	
$Pd(damn)_2{}^z$		−0.42	−1.02	...		0.60	
$Pt(damn)_2{}^z$	+0.97[h]	−0.52	−1.28	...	1.49	0.76	

[a] Half-wave potentials for CH_3CN−0.1 *M* Bu_4NPF_6 with dropping mercury electrode, unless otherwise noted, *vs.* aqueous SCE. [b] $\Delta E_{0-1} = E_{1/2}(z = +1 \rightleftharpoons 0)$ minus $E_{1/2}(z = 0 \rightleftharpoons 1-)$. [c] $\Delta E_{1-2} = E_{1/2}(z = 0 \rightleftharpoons 1-)$ minus $E_{1/2}(z = 1 \rightleftharpoons 2-)$. [d] $\Delta E_{2-3} = E_{1/2}(z = 1 \rightleftharpoons 2-)$ minus $E_{1/2}(z = 2- \rightleftharpoons 3-)$. [e] Redox couple, designated by charge, *z*, on complex. [f] See ref 13 for mechanistic details. [g] In dichloromethane, on platinum electrode. [h] Reversible, platinum electrode. [i] Two successive reductions of *z* = 2−. [j] Irreversible, two-electron process, platinum electrode.



M = Ni, Pd, Pt

1 when X = S, mnt complex
X = NH, damn complex

appear to have been reported,[4] neutral complexes of dithiolenes containing substituents other than -CN are also well known,[5] so that, in general, *z* = 0, 1−, 2− are interrelated by a reversible electron transfer series involving metal-ligand delocalized molecular orbitals. Since the low-lying π orbitals of the ligand are filled when *z* = 2−,[6] the recently reported[7] electrochemical reduction of diamagnetic $Ni(mnt)_2{}^{2-}$ to doublet state $Ni(mnt)_2{}^{3-}$ results in occupation of a metal-based orbital and an example of nickel in the uncommon paramagnetic +1 oxidation state (d^9 electronic configuration). We now report that similar reversible electroreductions of $M^{II}(mnt)_2{}^{2-}$, M = Pd, Pt, occur in nonaqueous solvents to yield the corresponding M(I) containing trianions, and that the Pd complex has been confirmed as being paramagnetic by observation of an ESR spectrum with $g_{iso} = 2.07$, $a_{iso} = 28$ G. These complexes are particularly noteworthy due to the exceptional rarity of these metals in the paramagnetic +1 oxidation state.[8] Indeed, we believe that this is the first example in which it has been demonstrated that the same ligand stabilizes paramagnetic M(I) complexes of Ni, Pd, and Pt. Previous reported efforts to produce Pd(I) or Pt(I) complexes from ligands known to stabilize Ni(I) have led only to M(0) complexes.[9,10] Qualitative confirmation of the metal character of the M(II) → M(I)($z = 2 \rightarrow 3-$) reduction is found by consideration of the $E_{1/2}$ values of Table I, in which the voltage separations (ΔE_{2-1}) between the largely ligand-based first and second reductions of $M(mnt)_2$ are seen to be practically independent of the identity of the metal, but the values of ΔE_{3-2} are highly metal dependent.

Ac polarography and cyclic voltammetry indicate that the M(II) → M(I) reductions are both electrochemically and chemically reversible. The Pd(I) complex is stable in various solvents, including acetonitrile and dimethoxyethane, and no further reductions are observed out to the electrolyte background (−2.8 V vs. SCE for CH_3CN-0.1 *M* Bu_4NPF_6 with a mercury working electrode). However, the platinum(I) complex is subject to another, irreversible, reduction approximately 200 mV more negative than the potential required to form the Pt(I) species. This observation can be compared with that found in a recent investigation of the reduction of M(II) complexes of 1,2-bis(diphenyl)phosphinoethane, which indicated two resolved one-electron transfers for the nickel compound but only single, two-electron, transfers for palladium and platinum.[9] Taken together with our data on the $Pt(mnt)_2{}^{2-}$ complex, these data indicate that a possible reason for the scarcity of Pd(I) and Pt(I) complexes lies in a greater tendency toward disproportionation of the heavier metals.

In an attempt to compare the properties of congeneric thio and amino chelates, we have also investigated the redox properties of the neutral square-planar complexes[11,12] $M(damn)_2$ (**1**), X = NH. Two electrochemically reversible reductions were observed for each complex (Table I). The amino complexes were more difficult to reduce than their thio analogs by approximately 1.4 V and *no* reductions to M(I) species were observed out to the electrolyte background. Cyclic voltammetry and current-reversal coulometry indicated that in the absence of oxygen all three monoanions, as well as the Pd and Pt dianions, were stable, but that the Ni dianion decomposed over several minutes. The monoanions $M(damn)_2{}^-$ have been prepared by vacuum-line electrolysis;[13] as expected, they are paramagnetic, as confirmed by observation of their ESR spectra. Both metal and ligand (nitrogen) hyperfine splittings have been observed for all $M(damn)_2{}^-$ complexes, except for M-Ni, in which the low natural abundance of ^{61}Ni (1.2%) precludes resolution of the metal splitting. In both the Pd and Pt complexes, the isotropic metal splitting is considerably higher than that reported for the analogous $M(mnt)_2{}^-$ complex (e.g., 165 G vs. 82 G for M = Pt). Although one's first impression is to ascribe these differences to more highly metal-localized orbitals for the $M(damn)_2{}^-$ complexes, conclusions on this point must await computer-assisted interpretation of the complex frozen-solution spectra and a detailed analysis of the hyperfine splittings.

The $M(damn)_2$ complexes can also be oxidized electrolytically, and the differences between the potentials of the first oxidation and first reduction for the series M = Ni, Pd, Pt (ΔE_{0-1} in Table I) leave little doubt that in this case the redox process involves an orbital with a high degree of metal character. Preliminary cyclic voltammetry experiments indicate that $Pt(damn)_2$ is oxidized by a one-electron, reversible, process to give a fairly unstable cation; the oxidation of $Ni(damn)_2$ apparently involves two electrons. Details will be forthcoming at a later date.

Finally, electrochemical data not listed in Table I indicate that Co(I), Cu(I), and Au(I) bis(mnt) complexes are also accessible, indicating that the ability of the mnt ligand to stabilize low metal oxidation states is quite general.

Acknowledgments. The authors gratefully acknowledge support from Research Corporation and the National Science Foundation (GP43694X).

References and Notes

(1) Trying to name the complexed, delocalized, amino chelate resurrects the "dithiolate-dithione" controversy which plagued early workers in the "dithiolene" field (see ref 5 for discussion). The authors of ref 12 have chosen to name the ligand as diiminosuccinonitrile on the basis of the bond distances observed for $Pt[(NH_2)C_2(CN)_2]_2$. Since the nature of the ligand presumably changes upon reduction to complex anions, such a

nomenclature system would logically involve changing the ligand name as a function of complex oxidation state. Consequently, we favor using the trivial name diaminomaleonitrile (damn) for the ligand to be consistent with previous literature (ref 11).
(2) H. B. Gray, R. Williams, I. Bernal, and E. Billig, *J. Am. Chem. Soc.*, **84**, 3596 (1962).
(3) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **85**, 2029 (1963).
(4) In this laboratory we have recently been able to electrogenerate stable solutions of $Pt(mnt)_2{}^0$.
(5) J. A. McCleverty, *Prog. Inorg. Chem.*, **10**, 49 (1968).
(6) G. N. Schrauzer, *Acc. Chem. Res.*, **2**, 72 (1969).
(7) T. E. Mines and W. E. Geiger, Jr., *Inorg. Chem.*, **12**, 1189 (1973).
(8) The reader is referred to P. M. Maitlis, "The Organic Chemistry of Palladium", Vol. 1, Academic Press, New York, N.Y., 1971, and to F. R. Hartley, "The Chemistry of Platinum and Palladium", Wiley, New York, N.Y., 1973. γ-Irradiation of Pd(II) or Pt(II) compounds at 77 K have given thermally unstable paramagnetic species assigned as Pd(I) or Pt(I); see M. Nakamura and S. Fujiwara, *J. Phys. Chem.*, **78**, 2136 (1974); T. Krigas and M. T. Rogers, *J. Chem. Phys.*, **55**, 3035 (1971).
(9) M. Martelli, G. Pilloni, G. Zotti, and S. Daoli, *Inorg. Chim. Acta*, **11**, 155 (1974).
(10) D. G. Holah, A. N. Hughes, B. C. Hui, and K. Wright, *Can. J. Chem.*, **52**, 2990 (1974).
(11) M. G. Miles, M. B. Hursthouse, and A. G. Robinson, *J. Inorg. Nucl. Chem.*, **33**, 2015 (1971).
(12) J. W. Lauher and J. A. Ibers, *Inorg. Chem.*, **14**, 640 (1975).
(13) For a full description of the vacuum line procedures see W. Geiger, T. E. Mines, and F. C. Senftleber, *Inorg. Chem.*, in press.
(14) Address correspondence to this author at the University of Vermont.

Fred C. Senftleber, William E. Geiger, Jr.* [14]
Department of Chemistry, University of Vermont
Burlington, Vermont 05401

Department of Chemistry, Southern Illinois University
Carbondale, Illinois 62901

Received March 10, 1975

Synthesis of New β-Lactam Antibiotics[1]

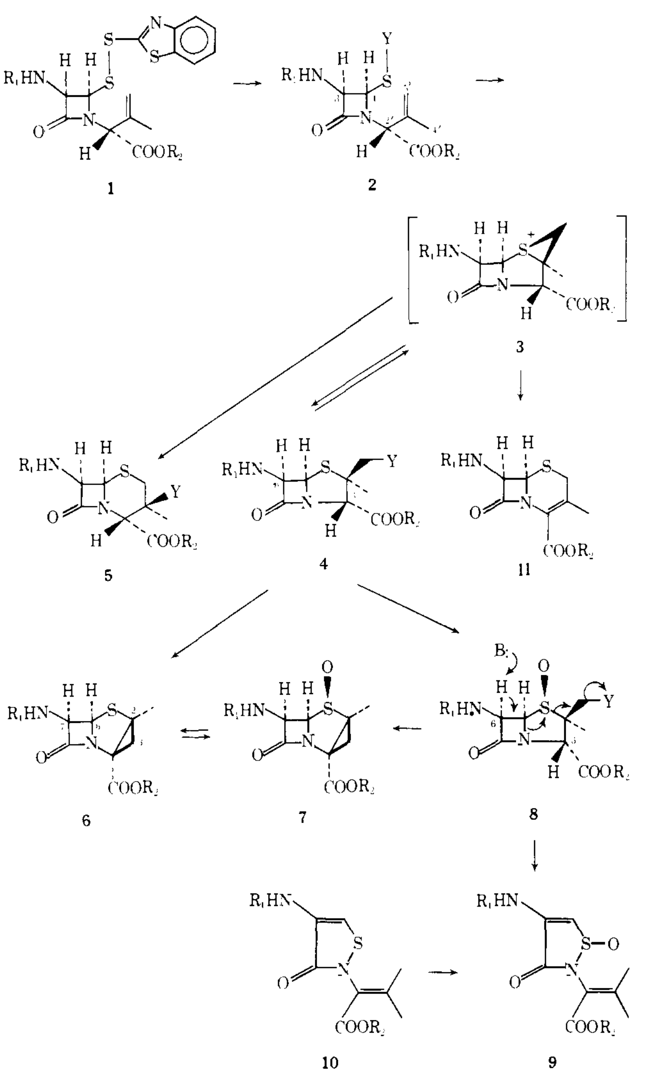
Sir:

In a previous paper[2] we reported the preparations of azetidinone disulfides, **1**, and 2β-halomethylpenicillins, **4** (Y = halogen), which are important precursors for the syntheses of 2β-substituted methylpenicillins **4**, 3β-substituted cephams **5**,[3] and desacetoxycephalosporin **11**.[2] The present communication deals with the isolation of sulfenylanilide **2b** (Y = NHC_6H_5), an intermediate involved in the conversion of **1** into **4** and **5**, and the synthesis of a new tricyclic β-lactam antibiotic **6a** via intramolecular cyclization of **4a** (Y = Br).

We have recently established a method[4] which allows the stereospecific conversion of **1** into **5** as well as **4** (Y = halogen)[2] by treatment with various nucleophiles under the presence of Ag^+. The formation of **4** and **5** presumably proceeds through the sulfenyl derivative **2** which is then transformed into episulfonium ion **3**; we have now secured corroborative evidence for this mechanism by isolation of the sulfenylanilide **2b** (Y = NHC_6H_5). Thus treatment of **1b** with aniline at room temperature in CH_2Cl_2 under the presence of $AgBF_4$ yielded 3β-anilinocepham **5b**[4] (Y = NHC_6H_5), mp 129–130°, $[\alpha]_D$ +58.5° (EtOH), 45% yield. On the other hand, treatment of **1b** with aniline in ethyl acetate under the presence of AgOAc affords **2b** (Y = NHC_6H_5): colorless oil; 90% yield; *m/e* 455; ir 1770 cm^{-1} (β-lactam); NMR ($CDCl_3$), 1.97 (s, 4′-H), 4.78 (s, 2′-H), 5.05 and 5.22 (two br s, 5′-H), 5.08 (d, J = 5 Hz, 4-H), 5.53 (dd, J = 5 and 8 Hz, 3-H). Reaction of **2b** (Y = NHC_6H_5) with BF_3OEt_2 gave **5b** (Y = NHC_6H_5) in 40% yield, thus supporting the intermediacy of **2b** (Y = NHC_6H_5) (Scheme I).

Furthermore, sulfenyl derivative **2b** (Y = NHC_6H_5) may act as an intermediate for introducing other nucleophilic groups. Thus treatment of **2b** (Y = NHC_6H_5) with BF_3OEt_2 in MeOH gave in 80% yield a 1:3 mixture of **4b** (Y = OCH_3) and **5b** (OCH_3).[4] Similarly reaction of **2b** (Y = NHC_6H_5) with HCl yielded **4b** (Y = Cl)[2] in quantitative yield.

Scheme I



a, $R_1 = C_6H_5CH_2CO$; $R_2 = CH_2CCl_3$
b, $R_1 = C_6H_5OCH_2CO$; $R_2 = CH_3$
c, $R_1 = H$; $R_2 = CH_2CCl_3$

We have been able to achieve the conversion of **4a** (Y = Br) into the intramolecularly cyclized product **6a**. Thus base treatment of **4a** (Y = Br) with bases led to the ring-expanded cephem **11a**[2] in high yield, but formation of a minute amount of a by-product was also observed; silica gel chromatography of this gave colorless crystals, mp 140–143°, $[\alpha]_D$ +203.2° ($CHCl_3$). The structure **6a** was assigned on the basis of spectral data: ir, 1795 cm^{-1} (β-lactam); NMR ($CDCl_3$), 1.70 (s, 2-CH_3), 2.06 and 2.27 (ABq, J = 7 Hz, 3-H), 5.47 (dd, J = 4 and 9 Hz, 7-H), 6.19 (d, J = 4 Hz, 6-H). It is reasonable to postulate that in the present case product **6a** is formed directly by an intramolecular nucleophilic displacement in **4a** (Y = Br) and not through an episulfonium ion **3a**, although formation of the latter has been demonstrated in both ring expansion[2,4,5] and nucleophilic substitution[4] reactions of **4**.

Formation of cephem **11a** was avoided by starting from the corresponding sulfoxide **8a** (Y = Br) which would not yield the episulfonium ion **3**. Thus when **8a** (Y = Br) obtained by oxidation of **4a** (Y = Br) with *m*-chloroperbenzoic acid, was treated with Et_3N in acetone at room temperature for 72 hr, a 1:1 mixture of **7a** and **9a** was obtained in ca. 52% yield. The compounds were separated by silica gel