such as II–IV are comparable, their relative magnitudes depending on the geometry.

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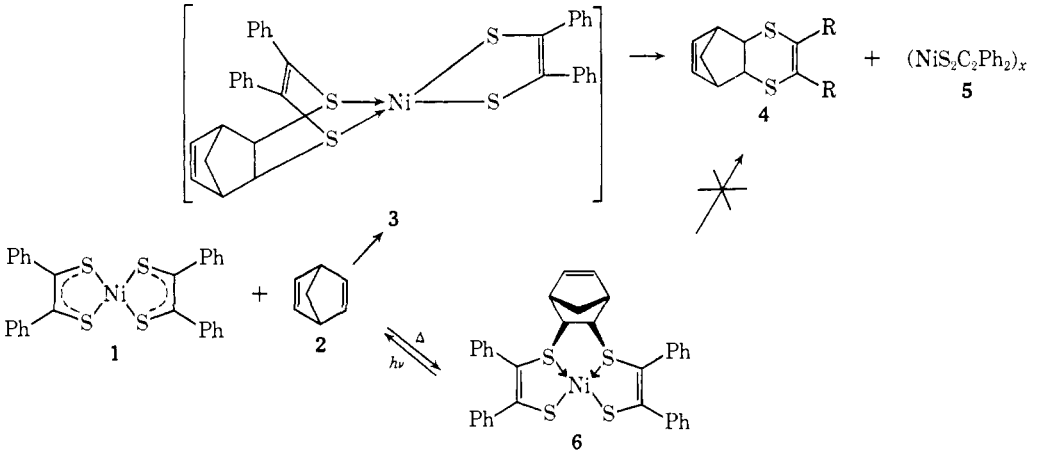
## Structure, Alkylation, and Macrocyclic Derivatives of Bicyclo[2.2.1]hepta-2,5-diene Adducts of Metal Dithienes

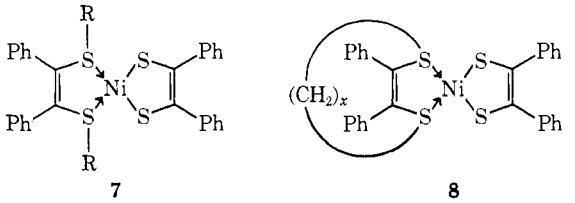
*Sir:*

Light-sensitive 1:1 adducts of group VIII metal bisdithienes such as $NiS_4C_4Ph_4$ (**1**, Ph = phenyl) with norbornadiene (bicyclo[2.2.1]hepta-2,5-diene, **2**) were first reported in 1965,[1] but their intricate nature is only now beginning to be understood. In view of the facile formation of the adduct **4** on reaction of **1** with **2** (eq 1) the complex $NiS_4C_4Ph_4 \cdot C_7H_8$ (mp 165° dec) was considered to be an intermediate in this reaction and was suggested to have structure **3**.[2]



(1)

Wing, *et al.*,[3] recently reported the structure of a norbornadiene adduct of $NiS_4C_4(CF_3)_4$, in which the olefin is linked to two sulfur atoms of the complex, as shown in **6**. Whereas the reaction of **1** with **2** is slow at room temperature, requiring days for the completion, the addition of **2** to the $CF_3$-substituted complex occurs within seconds.[3] The possibility is thus not excluded that both adducts have different structures. A study was therefore undertaken to establish the structure of $NiS_4C_4Ph_4 \cdot C_7H_8$ by chemical means. If the adduct were the intermediate **3** in the formation of **4** (eq 1) the latter should form directly on thermal decomposition. The adduct would in principle behave as the known[2] complexes of type **7** or the new chelates of type **8**, which are obtained for $x$ = 5–12 on reaction of $NiS_4C_4Ph_4^{2-}$ with the corresponding $\alpha,\omega$-dibromoalkanes at high dilution. For example, the complex with $x$ = 10 forms green crystals, mp 150° dec.



*Anal.* Calcd for $C_{38}H_{40}S_4Ni$: C, 66.74; H, 5.91; S, 18.76. Found: C, 66.74; H, 5.94; S, 18.94.

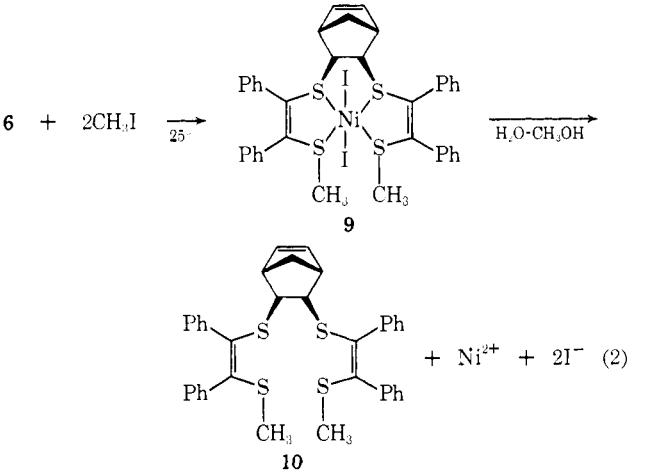
Bisdihaloalkyl derivatives were obtained on reaction of $NiS_4C_4Ph_4^{2-}$ with excess of alkylating agent, or for $x < 5$. Both **7** and **8** yield the unsaturated thioether on thermolysis. However, this is not the case for the norbornadiene adduct. On thermal decomposition, norbornadiene, $NiS_4C_4Ph_4$, NiS, and 2-phenylthianaphthene are formed, but no trace of **4**. Furthermore, no reaction is observed with phosphine ligands under conditions where complexes of type **7** undergo rapid ligand displacement. Chemical proof of structure **6** was obtained by alkylating $NiS_4C_4Ph_4 \cdot C_7H_8$ with excess methyl iodide in $CH_2Cl_2$ at room temperature. A yellow adduct **9**, mp 250° dec, was obtained (eq 2).

*Anal.* Calcd for $C_{37}H_{34}S_4I_2Ni$: C, 48.99; H, 3.68; S, 13.77; I, 27.24, Ni, 6.28. Found: C, 48.65; H, 3.45; S, 13.48; I, 29.8; Ni, 6.67.

Complex **9** hydrolyzes in $H_2O$–$CH_3OH$ or dilute aqueous alkali to produce the free ligand **10** (mp 139°).

*Anal.* Calcd for $C_{37}H_{34}S_4$: C, 74.45; H, 5.38; S, 20.09; mol wt, 637.0. Found: C, 74.49; H, 5.39; S, 20.10; mol wt, 645 (osmometric in $ClCH_2CH_2Cl$).

The structure of **10** was confirmed through nmr measurements. An alkylation reaction similar to eq 2



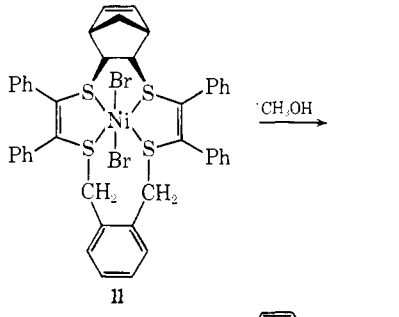
was used to synthesize the first nickel chelate **11** of an unsaturated macrocyclic sulfur chelate by refluxing **6**

(1) G. N. Schrauzer and V. P. Mayweg, *J. Amer. Chem. Soc.*, **87**, 1483 (1965).
(2) G. N. Schrauzer and H. N. Rabinowitz, *ibid.*, **90**, 4297 (1968).
(3) R. M. Wing, G. C. Tustin, and W. H. Okamura, *ibid.*, **92**, 1935 (1970).

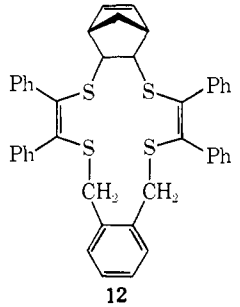
with the calculated amount of $\alpha,\alpha'$-dibromo-*o*-xylene in toluene. The green paramagnetic ($\mu_{eff}$ = 3.5 BM) crystals of **11** (mp 290° dec) decompose immediately on dissolution in methanol to yield the free macrocyclic ligand **12**, mp 258°.

*Anal.* Calcd for $C_{43}H_{36}S_4Br_2Ni$: C, 56.78; H, 3.99. Found: C, 56.64; H, 4.12. Calcd for $C_{43}H_{36}S_4$: C, 75.84; H, 5.33. Found: C, 75.92; H, 5.44.

The structure of **12** was confirmed through nmr measurements.




**11**




**12**

$$+ Ni^{2+} + 2Br^- \quad (3)$$

We conclude that **4** is not formed *via* **6** but rather by an independent pathway involving the labile intermediate **3**. Complex **6** is formed preferentially in the presence of a large excess of norbornadiene, *e.g.*, on refluxing **1** in norbornadiene. Only traces of **6** are produced if **1** is treated with norbornadiene at room temperature in $CH_2Cl_2$ solution. The reaction of $PdS_4C_4Ph_4$ with **2** at 85° yields 35% of **4** in addition to the red adduct $PdS_4C_4Ph_4 \cdot C_7H_8$ (**13**), mp 250° dec. The platinum dithiene reacts very slowly under comparable conditions and only produces the yellow $PtS_4C_4Ph_4 \cdot C_7H_8$ (**14**, mp 350° dec). Structures analogous to **6** are proposed for **13** and **14**.

The olefin adduct formation appears to be limited to the dithienes of Ni, Pd, and Pt. The formation of **4** occurs on refluxing $MoS_6C_6Ph_6$, $CrS_6C_6Ph_6$, and $VS_6C_6Ph_6$ in norbornadiene, but not with $WS_6C_6Ph_6$, $ReS_6C_6Ph_6$, $OsS_6C_6Ph_6$, or with various neutral and anionic iron and cobalt dithienes under comparable conditions. The $CF_3^-$ substituted derivative of **4**, finally, is also produced as a by-product in the reaction of $NiS_4C_4(CF_3)_4$ with **2**. The Diels–Alder adduct formation (an orbitally allowed process) thus is observed rather generally, whereas adducts of type **6** are produced less commonly because they could originate *via* an "orbitally forbidden" reaction.

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## Acetate Synthesis from Carbon Dioxide and Methylcorrinoids. Simulation of the Microbial Carbon Dioxide Fixation Reaction in a Model System

*Sir:*

Cell extracts of *Clostridium thermoaceticum* catalyze the formation of acetic acid from methylcorrinoids (methylcobinamide or methylcobalamin) and carbon dioxide.[1-3] For this microbial $CO_2$ fixation process two mechanisms are presently being discussed.[4] In the first, the acetate is assumed to be formed by a carboxylation reaction analogous to the known reaction of Grignard reagents. In the second, the methylcorrinoid is considered to react with $CO_2$ to produce an enzyme-bound carboxymethylcobalt derivative. The corrin would therefore have to undergo a proton abstraction at the cobalt-bound methyl group, followed by the carboxylation of the resulting methylene–corrinoid carbanion. This hypothetical reaction would give rise to a carboxymethylcobalt derivative, whose reductive Co–C bond cleavage is known to yield acetic acid.[5,6] However, both mechanisms are in serious conflict with known properties of Co-methylcorrinoids and of related model compounds. Thus, methylcobalamin or methylcobaloximes[7] have few, if any, reactions directly in common with Grignard reagents and are inert to carbon dioxide under a variety of conditions. The hydrogen atoms in Co-methyl compounds furthermore are essentially covalent and do not undergo H–D exchange in alkaline, neutral, or acidic solution.[8] Hence, both mechanisms of acetate formation are unacceptable on chemical grounds.

To develop a plausible mechanism of acetate formation we took cognizance of the facile reductive cleavage of the Co–C bond in methylcobalamin by thiols. In this reaction methyl carbanions or related species with the reactivity of methyl carbanions are generated which react with water solvent to form methane.[8] A logical extension of this mechanism of methane formation would be to generate the $CH_3^-$ ions in a locally anhydrous environment in the presence of $CO_2$. Under these conditions the formation of acetate from a methylcobalt derivative should proceed according to eq 1 [(Co) denotes the cobaloxime, B denotes a Lewis base,

(1) J. M. Poston, K. Kuratomi, and E. R. Stadtman, *Ann. N. Y. Acad. Sci.*, 112, 804 (1964).

(2) J. M. Poston, K. Kuratomi, and E. R. Stadtman, *J. Biol. Chem.*, 241, 4209 (1966).

(3) E. Irion and L. Ljungdahl, *Biochemistry*, 4, 2780 (1965).

(4) H. P. C. Hogenkamp, *Annu. Rev. Biochem.*, 37, 225 (1968), and references cited therein.

(5) L. Ljungdahl, D. Glatzle, J. Goodyear, and H. G. Wood, *Abstr. Amer. Soc. Microbiol.*, 128 (1967).

(6) G. N. Schrauzer and R. J. Windgassen, *J. Amer. Chem. Soc.*, 89, 1999 (1967).

(7) Cobaloximes are derivatives of bisdimethylglyoximatocobalt; see G. N. Schrauzer, *Accounts Chem. Res.*, 1, 97 (1968), for detailed discussion.

(8) G. N. Schrauzer and R. J. Windgassen, *J. Amer. Chem. Soc.*, 88, 3738 (1966).