

To confirm that the spectroscopic and electrochemical experiments involve the same species, cyclic voltammetry was performed on a Cs–CsAu solution. The same waves described above were observed, but quantitative results were not possible owing to the large uncompensated resistance.

These experiments prove the existence of a solvated gold anionic species,  $\text{Au}_y^{x-}$ . An alkali metal species is probably not part of this anion because the various alkali cations have so little effect on its spectroscopic properties.  $\text{Au}^-$  seems the most likely species because the electron configuration would be  $5d^{10}6s^2$ , the extinction coefficient is approximately the same as the solvated electron's, and the Zintl potentiometric titration indicates a stoichiometry of  $\text{Au}_x^{x-}$ .<sup>4</sup>

More detailed electrochemical experiments on the gold species in liquid ammonia are currently in progress, as is work to extend these ideas to other metals and solvents. For example, ethylenediamine stabilizes alkali metal anions better than ammonia and, indeed, a cesium–ethylenediamine solution has been observed to dissolve gold.

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#### $^{13}\text{C}$ – $^{13}\text{C}$ and $^{13}\text{C}$ –H Coupling Constants in 2,2,4,4-Tetramethylbicyclo[1.1.0]butane

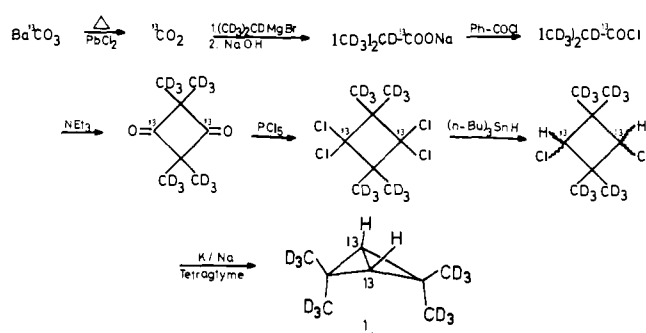
Sir:

The orbitals forming the central bond of bicyclo[1.1.0]butane are characterized by an extremely small s character,<sup>1</sup> which is related to the  $^{13}\text{C}$ – $^{13}\text{C}$  coupling constant  $^1J_{\text{CC}}$  by eq 1:<sup>2</sup>

$$^1J_{\text{CC}} = 621s_{\text{AB}} - 10.2 \quad (1)$$

The extraordinarily low s character and the theoretical prediction of  $^1J_{\text{C}(1)\text{--C}(3)}$  in bicyclobutane being negative<sup>2,3</sup> have given rise to several investigations on  $^{13}\text{C}$ – $^{13}\text{C}$  coupling constants in bicyclobutane derivatives.<sup>2–7</sup>

#### Scheme I



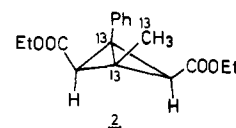
We intended to determine  $^1J_{\text{C}(1)\text{--C}(3)}$  in an alkyl-substituted bicyclobutane to exclude possible influences of polar substituents. For this purpose the readily accessible 2,2,4,4-tetramethylbicyclobutane<sup>8</sup> seemed to be the most suitable compound, since  $^{13}\text{C}$  labeling of the two bridgehead carbons and deuteration of the methyl groups would lead to a hydrocarbon, the proton spectrum of which would allow a precise determination of  $^1J_{\text{C}(1)\text{--C}(3)}$  in absolute value and sign.

Starting with 90%  $^{13}\text{C}$ -labeled barium carbonate, we synthesized 2,2,4,4-tetra(trideuteriomethyl)bicyclo[1.1.0]butane-1,3- $^{13}\text{C}_2$  (**1**) as shown in Scheme I. The proton part of the AA'XX' spectrum of **1** showed the following four coupling constants:  $^1J_{\text{C}(1)\text{--C}(3)} = -17.49 \pm 0.02$  Hz,  $^1J_{\text{C}(1)\text{--H}} = +184.33 \pm 0.02$  Hz,  $^2J_{\text{C}(1)\text{--H}} = -2.02 \pm 0.02$  Hz,  $^3J_{\text{HH}} = +12.22 \pm 0.02$  Hz. The sign of  $^1J_{\text{C}(1)\text{--C}(3)}$  was determined by heteronuclear double resonance.

We also synthesized compound **1** without deuterium in the methyl groups, to obtain all other coupling constants concerning the bridgehead carbons. The  $^{13}\text{C}$  NMR spectrum exhibited  $23.06 \pm 0.12$  Hz for  $^1J_{\text{C}(1)\text{--C}(2)}$ ,  $0.51 \pm 0.12$  Hz for  $^2J_{\text{C}(1)\text{--C}(\text{exo})}$ , and  $2.88 \pm 0.12$  Hz for  $^2J_{\text{C}(1)\text{--C}(\text{endo})}$ .  $^3J_{\text{C}(1)\text{--H}(\text{exo})}$  ( $= 4.60 \pm 0.10$  Hz) and  $^3J_{\text{C}(1)\text{--H}(\text{endo})}$  ( $= 5.20 \pm 0.10$  Hz) were also determined. Moreover  $^1J_{\text{C}(2)\text{--C}(\text{exo})}$  ( $= 40.3 \pm 0.2$  Hz) and  $^1J_{\text{C}(2)\text{--C}(\text{endo})}$  ( $= 46.9 \pm 0.2$  Hz) were measured in natural  $^{13}\text{C}$  abundance.

The value of  $-17.49$  Hz for  $^1J_{\text{C}(1)\text{--C}(3)}$  raises some remarkable aspects.

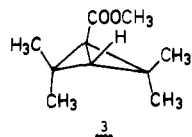
Considering the closely related carbon skeletons of **1** and **2**, the difference between  $^1J_{\text{C}(1)\text{--C}(3)}$  in **1** and  $^1J_{\text{C}(1)\text{--C}(3)}$  in **2** ( $-5.4$  Hz) is extraordinarily large. This leads to the conclusion



that obviously substituents and/or steric influences exert a very strong effect of  $^1J_{\text{C}(1)\text{--C}(3)}$  in bicyclobutane derivatives. On the other hand the value of  $-17.49$  Hz is an absolute value rather close to  $^1J_{\text{C}(1)\text{--C}(3)}$  in 1-cyanobicyclobutane (16 Hz, the sign being undeterminable).<sup>6</sup> This coupling constant was measured in natural  $^{13}\text{C}$  abundance and the absolute value of 16 Hz was regarded as rather uncertain.<sup>7</sup> Our result, however, indicates that an absolute value of 16 Hz for the C(1)–C(3) bond in 1-cyanobicyclobutane would be quite a reasonable result. Recent investigations on other bicyclobutanes<sup>9</sup> support this presumption. If 16 Hz is indeed the correct coupling constant, the sign will certainly have to be negative.

It should also be mentioned that the value of 184.33 Hz for  $^1J_{\text{C}(1)\text{--H}}$  in **1** is  $\sim 20$  Hz smaller than the corresponding value in the unsubstituted bicyclobutane.<sup>10</sup> Using the Muller–Pritchard relationship between  $^1J_{\text{CH}}$  and s character,<sup>11</sup> we obtain 36.9% s character in the C(1)–H bond of **1**, compared with 41.0% s character in the C(1)–H bond of bicyclobutane itself. This reduced s character, however, is nearly compensated for by an increase of the s character in the C(1)–C(2) and C(1)–

C(4) bonds of **1**, corresponding to a coupling constant of 23.06 Hz (compared with 21.0 Hz in bicyclobutane).<sup>12</sup> A rather small  $^1J_{CH}$  (191 Hz) was also found for the C(3)-H bond in



compound **3**.<sup>13</sup> The remarkably small value of  $^1J_{CH}$  in **1** and **3** can be explained with an increase of the angle between the two three-membered rings, caused by the repulsion of the two *endo*-methyl groups,<sup>14</sup> since it is known that a decrease of this angle increases  $^1J_{CH}$ .<sup>15,16</sup> Presumably such a geometry change influences  $^1J_{C(1)-C(3)}$  as well.

To exclude this undesired effect, investigations on other bicyclobutanes, in which there can be no *endo-endo* repulsions, are in progress.<sup>9</sup> The results will shortly be reported.

The most striking result, however, is the fact that a  $^{13}C$ - $^{13}C$  coupling constant of -17.49 Hz (using any of the coupling constant-hybridization relationships, published until now<sup>2,17-19</sup>) leads to a negative  $s^2$  and consequently to an imaginary result for the  $s$  character of the orbitals forming the C(1)-C(3) bond. As there is no physical sense in this result, it is obvious that none of the known quantitative correlations between  $^1J_{CC}$  and  $s$  character can be applied to the central bond in **1**. A similar situation has been predicted for benzvalene.<sup>3</sup> Most likely the noncontact contributions to  $^1J_{CC}$ , which cannot linearly be related to the product of the  $s$  characters, are of even greater importance in this bond than predicted for the corresponding bond of bicyclobutane.<sup>3</sup>

Considering this, it must be doubted that an equation of the simple form

$$^1J_{CC} = x s_A s_B - y \quad (2)$$

will be able to give satisfactory results for all types of C-C bonds even within the saturated hydrocarbons. For strained rings  $y$  in eq 2 would at least have to be  $>17.49$ .

The calculations by Schulman et al.,<sup>2-4</sup> predicting negative coupling constants of an absolute value  $<12.2$  Hz for the central bond in bicyclobutanes, have proved to be correct in tendency and very useful to encourage experimental work on these exceptional coupling constants. The experimental values of -17.49 Hz in **1** (and possibly -16 Hz in 1-cyanobicyclobutane), however, differ from the calculated ones more than expected. We hope that this communication will encourage further theoretical investigations on this subject.

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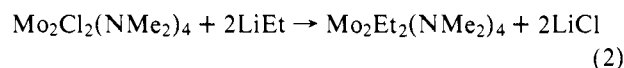
## New $\sigma$ -Ethyl Compounds of Dimolybdenum ( $M \equiv M$ ) and Evidence for Dinuclear Reductive Elimination with a Concomitant Metal-Metal Triple to Quadruple Bond Transformation: $Et-M \equiv M-Et \rightarrow M \equiv M + C_2H_4 + C_2H_6$

Sir:

Transition metal complexes containing  $\sigma$ -ethyl ligands are prone to thermal decomposition by an initial step involving  $\beta$ -hydrogen elimination:<sup>1</sup>  $MC_2H_5 \rightleftharpoons MH + C_2H_4$ . This reaction is suppressed when the metal is coordinatively saturated and attains an 18-valence-shell electronic configuration.<sup>2</sup> We report here (i) the preparation of the thermally stable  $\sigma$ -ethyldimolybdenum compounds  $Mo_2Et_2(NMe_2)_4$  and  $Mo_2Et(OBu^t)_5$ , in which the ethyl ligands are coordinated to unsaturated metal centers<sup>3</sup> and (ii) the reaction between  $Mo_2Et_2(NMe_2)_4$  and  $CO_2$  which proceeds according to eq 1 and provides a model reaction for studies of dinuclear reductive elimination.<sup>4</sup>

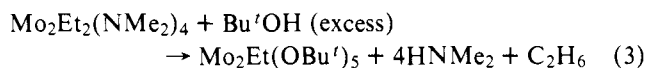


$Mo_2Cl_2(NMe_2)_4$ <sup>5</sup> reacts smoothly at -78 °C with EtLi (2 equiv) in hydrocarbon solvents to give the yellow, crystalline compound  $Mo_2Et_2(NMe_2)_4$  which may be obtained analytically pure<sup>6</sup> by sublimation (60-70 °C,  $10^{-4}$  mmHg) in  $>70\%$  yield based upon eq 2.



The  $^1H$  NMR spectrum of  $Mo_2Et_2(NMe_2)_4$  obtained in toluene- $d_8$  at -61 °C at 270 MHz is shown in Figure 1. This corresponds to the low temperature limiting spectrum of a mixture of anti and gauche rotamers of an ethane-like molecule  $(Me_2N)_2EtMo \equiv MoEt(NMe_2)_2$ .<sup>7</sup> Note the methylene protons of the gauche rotamer (but not the anti rotamer) are diastereotopic and form part of an ABX<sub>3</sub> spectrum. At 90 °C rotation about the M-N bonds is rapid on the NMR time scale leading to the coalescence of proximal and distal  $N$ -Me signals but rotation about the  $M \equiv M$  bond (anti  $\rightleftharpoons$  gauche isomerization) is still slow. In the mass spectrometer there is a strong molecular ion  $Mo_2(NMe_2)_4Et_2^+$  ( $m/e$  430) and an ion  $Mo_2(NMe_2)_4^+$  ( $m/e$  372) corresponding to the loss of 2Et.

$Mo_2Et_2(NMe_2)_4$  reacts rapidly at room temperature with *tert*-butyl alcohol in benzene according to eq 3.



$Mo_2Et(OBu^t)_5$  is a burgundy-red solid which sublimates with some decomposition at 60-70 °C ( $10^{-4}$  mmHg). The  $^1H$  NMR spectrum at low temperature (-76 °C) at 270 MHz in toluene- $d_8$  consists of a simple triplet and quartet for the Et