tors, in concert, make the observation of these $^{13}C$ resonances difficult relative to the remaining carbon atoms bearing hydrogens, whose spin-coupling influence is removed by irradiation at the proton frequency.
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(42) A plot showing the percentage of unreacted **1** as a function of time in water at temperatures of 60, 75, and 90 °C has been published by Hirata and coworkers;[8] reliable hydrolysis rate constants could only be extracted from this plot for 75 and 90 °C. Use of the resultant activation parameters ($\Delta H^{\ddagger} = 22.1$ kcal/mol, $\Delta S^{\ddagger} = -13$ eu) leads to a calculated value of $k = 2.0 \times 10^{-6}\ \mathrm{s}^{-1}$ at 37 °C, which is reasonably close to our experimentally determined value of $k = 1.4 \times 10^{-6}\ \mathrm{s}^{-1}$ for **1** in $D_2O$.
(43) Interpretation of the $\Delta S^{\ddagger}$ associated with hydrolysis of **1** is subject to caution which applies to aqueous media wherein entropy changes due to solvation changes may be substantial.[28c]
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# Communications to the Editor

## Synthesis and Reactions of Molybdenum Vinyl Complexes. Evidence for Formation of Carbyne Complexes

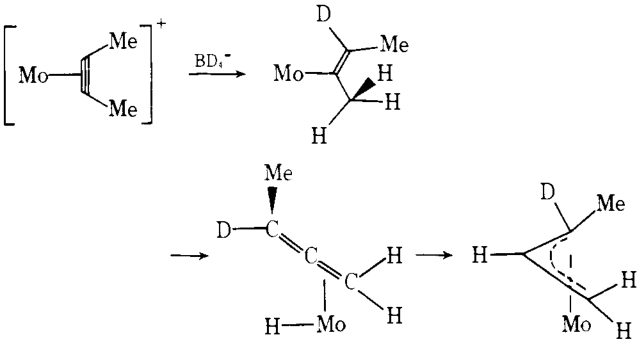
*Sir:*

The chemistry of σ-bonded transition metal vinyl complexes is a relatively unexplored area because of the difficulties associated with their synthesis. Our discovery[1] of a simple route to the formally 16-electron acetylene substituted molybdenum cations (**1** and **2**) provided an opportunity to study their reactions with, for example, the borohydride anion. The resulting vinyl species undergo novel rearrangements to give $\eta^3$-allylic and carbyne complexes.

Reaction (−78 °C, THF) of sodium borohydride with the violet crystalline cation (**1**, R = H, $R^1$ = Bu-*t*) in the presence of an excess of $P(OMe)_3$ affords the yellow crystalline vinyl complex[3] (**3**): $^1H$ NMR resonances ($C_6D_6$) at τ 3.3 (1 H, m, $H^1$, $J_{12} = 17.0$ Hz, $J_{H^1P^a} = 14.0$ Hz, $J_{H^1P^b} = 7.0$ Hz), 4.6 (1 H, dt, $H^2$, $J_{H^2P^a} = 2.0$ Hz), 5.1 (5 H, q, $C_5H_5$, $J_{HP} = 1.0$ Hz), 6.6 (27 H, m, POMe), and 8.8 (9 H, s, Bu); $^{13}C$ NMR resonances ($C_6D_6$) at −151.3 (t, MoC=C, $^2J_{CP} = 4.5$ Hz.), 128.1 (s, MoC=C), −87.4 (s, $C_5H_5$), −51.4 (s, POMe), −37.3 (s, $CMe_3$), −30.6 ppm (s, C**Me**$_3$). Treatment with $NaBD_4$ gives the corresponding deuterio complex of **3**, where $H^2$ is replaced by deuterium, indicating that the formation of **3** involves the intermediacy of a hydride, $MoH[P(OMe)_3]_2(\eta^2\text{-Bu-}t\text{-}C_2H)(\eta^5\text{-}C_5H_5)$, which then undergoes a cis-insertion reaction. This kind of reaction has not been observed previously, although nucleophilic attack by methoxide anion on a cationic platinum(II)-acetylene complex has been shown[4] by Clark and Chisholm to lead to the formation of carbene complexes. However, it is likely in the Pt system initial nucleophilic attack occurs at carbon rather than at the metal center as suggested for the molybdenum cation.

In solution ($C_6D_6$) and also in the solid state (room temperature) the vinyl complex **3** undergoes a very unusual rearrangement (quantitative yield) to form the crystalline *carbyne* complex **4:** $^1H$ NMR resonances ($C_6D_6$) at τ 4.8 (5 H, t, $C_5H_5$, $J_{HP} = 1.0$ Hz), 6.5 (18 H, apparent *t*, POMe, $|J|_{POCH} = 12$ Hz), 7.8 (2 H, t, $CH_2$Bu-*t*, $^4J_{HP} = 4.0$ Hz), and 8.9 (9 H, s, Bu-*t*); $^{13}C$ NMR resonances ($C_6D_6$) at −299.8[5] (t, $MoCCH_2$, $^2J_{CP} = 27.0$ Hz, t in off-resonance spectrum), −89.3 (s, $C_5H_5$), −62.5 (s, $CH_2$, t in off-resonance spectrum), −50.9 (s, POMe), −33.0 (s, $CMe_3$), and −29.9 ppm (s, C**Me**$_3$). The rearrangement reaction is suppressed by the presence of free trimethyl phosphite suggesting the requirement of a vacant coordination site for the H shift to occur. The rearrangement of a vinyl complex to a carbyne complex has not been previously observed, carbyne metal complexes normally being prepared via carbene complexes,[5] and appropriate labeling experiments are in hand, which will, it is hoped, elucidate the mechanistic details of this new reaction.

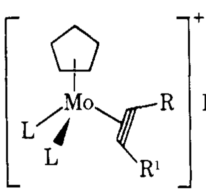
Scheme I$^a$



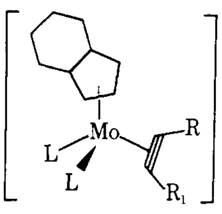
$^a$ Ligands omitted for clarity.

An indication of the potential chemistry of **4** is provided by the observation that protonation ($HBF_4/Ac_2O$, −78 °C) proceeds in high yield to give the cationic hydride species **5:** $\nu_{MoH}$ (Nujol) 1760 $cm^{-1}$ (s); $^1H$ NMR resonances ($CDCl_3$) at τ 4.2 (5 H, t, $C_5H_5$, $J_{HP} = 1.0$ Hz.), 6.2 (18 H, d, POMe, $|J|_{POCH} = 12$ Hz), 7.6 (2 H, t, $CH_2$Bu-*t*, $J_{HP} = 4.0$ Hz), 9.0 (9 H, s, Bu-*t*), and 12.5 (1 H, t, MoH, $^2J_{HP} = 67.0$ Hz.); $^{13}C$ NMR resonances ($CDCl_3$) at −346.7 (t, Mo≡$CCH_2$, $J_{CP} = 24.0$ Hz, t in off-resonance spectrum), −96.2 (s, $C_5H_5$), −64.2 (s, $CH_2$, t in off-resonance spectrum), −53.5 (s, POMe), −33.6 (s, $CMe_3$), and −29.2 ppm (s, C**Me**$_3$). The cation **5** is stable and shows no tendency to rearrange.

It is interesting that the but-2-yne 16-electron cation **2** (R = $R^1$ = Me) undergoes a different type of reaction on treatment with $NaBH_4$ (room temperature, THF) forming selectively the dark red crystalline *anti*-crotyl complex **6**, which at room temperature exists in solution as equilibrating exo and endo isomers.[6] At −40 °C (toluene-$d_8$) the $^1H$ spectrum ($^{31}P$ decoupled) showed resonances corresponding to the two anti conformers. It is suggested that an initially formed vinyl complex undergoes a β-elimination reaction as illustrated in Scheme I giving a molybdenum hydride(allene) complex, which then undergoes an insertion reaction to give the observed $\eta^3$-crotyl species. In agreement with this suggestion reaction with $NaBD_4$ proceeds regioselectively to give **6** with deuterium incorporated in the illustrated position adjacent to the methyl group. A related $\beta$-allylic elimination reaction forming a $\eta^3$-crotyl complex has been observed[7] on heating the *E* isomer of $Ir[C(Me){=}CHMe]COL_2$; however, in contrast to the molybdenum system the *Z* isomer undergoes a *cis*-$\beta$-vinyl H elimination to form the corresponding hydride and but-2-yne.



**1**, L = P(OMe)$_3$



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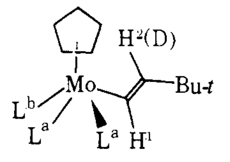
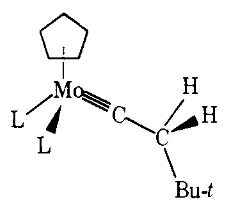
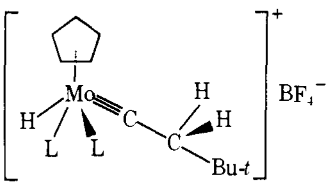


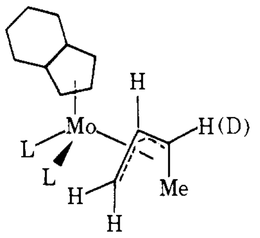
**3**, L = P(OMe)$_3$



**4**, L = P(OMe)$_3$



**5**, L = P(OMe)$_3$



**6**, L = P(OMe)$_3$

**Acknowledgment.** We thank the S.R.C. for support.

## References and Notes

(1) Reaction (room temperature, $CH_2Cl_2$) of $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]_2$ or $[Mo(CO)_3(\eta^5\text{-}C_9H_7)]_2$ with $AgBF_4$ in the presence of an excess of an acetylene affords a silver mirror, and the cations $[Mo(CO)(\eta^2\text{-}RC_2R^1)_2(\eta^5\text{-}C_5H_5$ or $\eta^5\text{-}C_9H_7)]^+BF_4^-$ (R = R$^1$ = H; R = R$^1$ = Me; R = Bu-*t*, R$^1$ = H; R = Me, R$^1$ = H; R = Ph, R$^1$ = H; R = R$^1$ = Ph), which on treatment (room temperature, $CH_2Cl_2$) with $P(OMe)_3$ (excess) gives the highly colored cations **1** and **2** in good yield. The $^1H$ NMR spectrum (20 °C, $CD_3NO_2$) of, for example, $[Mo(\eta^2\text{-}MeC_2Me)[P(OMe)_3]_2(\eta^5\text{-}C_9H_7)]^+BF_4^-$ shows a sharp triplet ($^4J_{HP}$ = 1.0 Hz.) at $\tau$ 7.7 (MeC≡C) collapsing reversibly (coalescence temperature, in $(CD_3)_2CO$ at −40 °C) to two resonances ($\tau$ 7.3 (3 H, brs), 8.4 (3 H, br s)) on cooling, which suggests that acetylene propellor rotation occurs; the observation of $^{31}P$ coupling excludes acetylene dissociation. The coalescence temperature of the corresponding $\eta^5\text{-}C_5H_5$ substituted cation is even lower (>−90 °C), which is interesting in view of the report[2] that the $^1H$ NMR spectrum ($(CD_3)_2CO$) of $[Mo(\eta^2\text{-}MeC_2Me)(diphos)(\eta^5\text{-}C_5H_5)]^+PF_6^-$ collapses to a single MeC≡C signal only at 110 °C.

(2) One example of this type of cation has been recently reported (J. A. Segal, M. L. H. Green, J. C. Daren, and K. Prout, *J. Chem. Soc. Chem. Commun.*, 766 (1976)) the synthesis following a less accessible route via bis(arene)molybdenum chemistry.

(3) Satisfactory elemental analyses, NMR spectra, and mass spectra have been obtained for all the complexes described.

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(5) E. O. Fischer and U. Schubert, *J. Organomet. Chem.*, **100**, 59 (1975).

(6) J. W. Faller, and A. M. Rosan, *J. Am. Chem. Soc.*, **98**, 3388 (1976).

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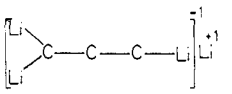
**Martin Bottrill, Michael Green***
*Department of Inorganic Chemistry*
*University of Bristol, Bristol BS8 1TS, England*

*Received April 6, 1977*

## The Curious Structure of the Lithiocarbon[1] $C_3Li_4$

*Sir:*

$C_3Li_4$, prepared by lithiation of propyne by *n*-butyllithium,[2d,3] is a readily available lithiocarbon.[1] Only the most general information is available concerning the structure of this species. $C_3Li_4$ reacts to give either allene- or propyne-type products depending on the reagents and the conditions.[2d] This suggests an open rather than a cyclic arrangement of the carbon atoms. The IR absorption band of $C_3Li_4$ in the 1700-cm$^{-1}$ region has been interpreted in terms of formulation I or II.[2d,3]



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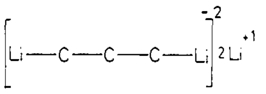

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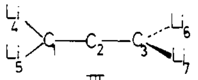

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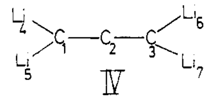

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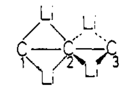

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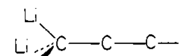

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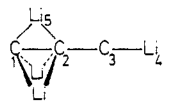
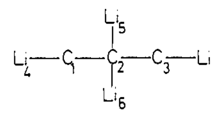
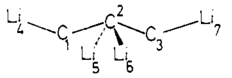


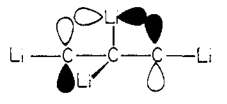
VII



VIII



IX



X

We have used ab initio molecular orbital calculations[4] to investigate possible $C_3Li_4$ structures. Complete geometry optimizations within each assumed symmetry were carried out using the minimal STO-3G basis set.[4b] Single point calculations using these optimized geometries followed, employing the split valence 4-31G (for carbon)[4c] and 5-21G (for lithium)[4d] bases. Our earlier work has shown that polylithio derivatives adopt highly unconventional geometries;[5] the same trend was expected in the present search. Nevertheless, we began with the lithiated analogue of allene, III. Although III proved to be a local minimum when optimized within the constraint of $D_{2d}$ symmetry, the energy compared unfavorably with that of other structures. The *planar* $D_{2h}$ allene (IV) (with four $\pi$ electrons), which had nearly the same bond lengths and angles, was more stable by 0.5 kcal/mol at the 4-31G/5-21G level (Table I). The theoretical estimates for the rotational barrier in allene are between 27 and 92 kcal/mol;[6] experimental values of ~46 kcal/mol have been reported for 1,3-dialkylallenes.[7] Lithiation is thus able not only to reduce the $D_{2d}$-$D_{2h}$ energy differences dramatically, but also to reverse the normal order of stability. Similarly, 1,1-dilithioethylene has been found to prefer the perpendicular, rather than the normal planar conformation.[5a]

Encouraged by the tendency of lithium to bridge,[5c] we examined the *tetrabridged* $D_{2d}$-constrained structure, V, which proved to be more stable than III by 19.5 kcal/mol at STO-3G but 13.3 kcal/mol less stable at 4-31G/5-21G. Since both III and V are $D_{2d}$ it is evident that a barrier (within this symmetry) exists between them. On the other hand, the conventional acetylenic structure, VI, is not a local minimum, but collapses to a triply bridged form, VII, upon optimization under $C_{3v}$ symmetry. VII is more stable than III-V at both basis set levels. The effect of the three bridging lithiums is seen in the