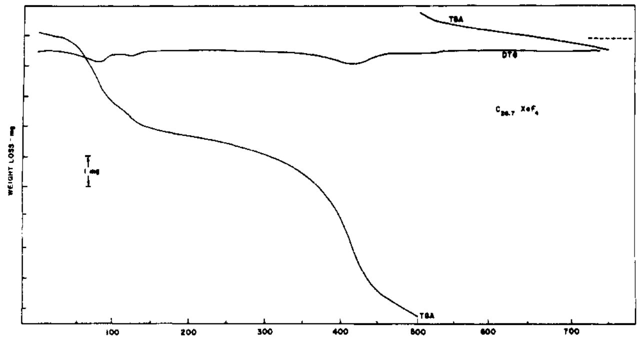

Figure 1. Thermogravimetric analysis of $C_{26.7}XeF_4$: sample weight, 25.7 mg; heating rate, 4°/min; atmosphere argon. Dashed line corresponds to calculated final weight after complete decomposition.

Table I. Analysis of C_nXeF_4

Material	mmol taken	mequiv of I titrated	mequiv of I per mmol of intercalate	% F found	% F calcd
$C_{40}XeF_4$	0.182	0.355	1.95		
$C_{24.3}XeF_4$	0.264	0.525	1.98	16.6	15.2
$C_{26.7}XeF_4$	0.241	0.534	2.21	16.6	14.5
$C_{32.5}XeF_4$	0.249	0.500	2.00	11.9	12.7

increases. Analyses of oxidizing power of the intercalates showed only 2 equiv of iodine liberated per mole of intercalate (Table I). This indicates that the XeF_4 is intercalated in the form of several species, some bound more tenaciously to the graphite than others. Indeed, preliminary wide line ^{19}F nuclear magnetic resonance spectra reveal the presence of both XeF_4 species (a doublet-singlet centered at +29 ppm with respect to $CFCl_3$ with doublet separation (3600 ± 320 Hz) and XeF_2 species (a singlet centered at +148 ppm) possessing derivative extremum line widths of 0.1 to 0.15 G).[4] Consideration of integrated absorption mode peak heights leads to a ratio of $F(XeF_2)/F(XeF_4)$ of 2.3 to 3.0. No proton resonance could be observed.

X-ray patterns of the intercalates obtained with copper radiation showed the complete absence of the original strong graphite line at $d = 3.35$ Å and the appearance of a new pattern containing very broad, diffuse lines at approximately 3.80 and 3.24 Å for $C_{28}XeF_4$ and at 3.65 and 3.28 Å for $C_{40}XeF_4$. If one were to assume the 3.8 Å diffraction line to be [003] reflection of a second stage compound of $I_c = 11.4$ Å and the 3.65 Å line to be the [004] reflection of a third stage compound of $I_c = 14.6$ Å, as is the case in a number of graphite acid salts,[5] one would predict the ratio of carbon atoms to xenon atoms in a single layer to be 13-14/1, a result consistent with the passage of second stage $C_{28}XeF_4$ to third stage $C_{40}XeF_4$.

Thermogravimetric analyses were run on a Mettler thermoanalyzer (Figure 1). The sample begins to lose weight immediately, because $C_{26}XeF_4$ is unstable at room temperature. The first weight loss step is complete at around 150 °C and corresponds to conversion to a higher stage compound of stoichiometry $C_{40}XeF_4$, thus confirming the preparative results with Grafoil. The third stage compound decomposes rapidly above 300 °C, and decomposition is complete above 600 °C. No xenon fluorides were liberated upon heating, xenon gas and carbon tetrafluoride being the only gases detected. After decomposition, the residue again shows the characteristic graphite line at 3.35 Å.

The graphite-xenon tetrafluoride intercalate is easily handled outside the vacuum line, although part of the intercalated fluoride is slowly hydrolyzed, releasing HF. The residue is neither shock-sensitive nor exhibits appreciable oxidizing power.

Preliminary investigations show that the intercalate may also be useful as a moderate fluorinating agent in organic chemistry. Experiments with aromatic systems gave the following results: With benzene, the products were monofluorobenzene (26%), *p*-difluorobenzene (11%), and starting material (63%). Phenanthrene[6] yielded mainly 9-fluorophenanthrene (22%) and 9,9,10-trifluoro-9,10-dihydrophenanthrene (19%). As in the case of XeF_2[7] fluorination of benzene proceeds only in the presence of HF catalyst.

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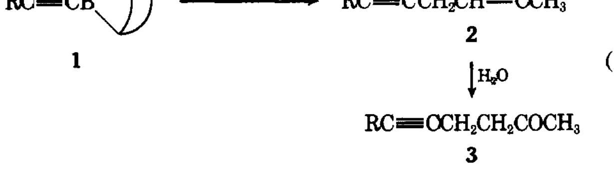
Conjugate Addition of *B*-1-Alkynyl-9-borabicyclo[3.3.1]nonanes to *α,β*-Unsaturated Ketones. A Convenient Synthesis of *γ,δ*-Acetylenic Ketones

Sir:

B-1-Alkynyl-9-borabicyclo[3.3.1]nonanes (*B*-1-alkynyl-9-BBN) (**1**), readily prepared by the reaction of boron trifluoride diethyl etherate with the corresponding lithium methyl alkynyldialkylborinate,[1] undergo a smooth 1,4-addition in pentane at room temperature to methyl vinyl ketone (MVK) and related ketones capable of adopting a cisoid conformation. Hydrolysis of the initially formed enol borinate intermediates (**2**) provide the corresponding 4-alkynyl-2-butanones (**3**) in high yields (eq 1).



(1)

The use of alkynyl copper reagents to effect the 1,4-addition of an alkynyl group to an *α,β*-unsaturated ketone is precluded by the tenacity with which copper binds alkynyl ligands.[2] One possible solution to this difficulty is the temporary transformation of the acetylene to a vinylstannane derivative. Thus, Corey has reported that the cuprate derived from *trans*-1,2-bis(tri-*n*-butylstannyl)ethylene reacts as a nucleophilic ethynyl group equivalent in the conjugate addition to *α,β*-unsaturated ketones.[3] Unfortunately, the generality of this reaction has not

Table I. Conversion of Alkynes into 4-Alkynyl-2-Butanones by the Reaction of the Corresponding *B*-1-Alkynyl-9-BBN Derivatives with Methyl Vinyl Ketone[a]

Alkyne	Product[b]	Yield,[c] %	Bp, °C (mmHg)	n^{20}_D	Mol Wt[d] Calcd	Mol Wt[d] Found
3,3-Dimethyl-1-butyne	7,7-Dimethyl-5-octyn-2-one	100 (83)	85 (15)	1.4384	152.120	152.120
1-Hexyne	5-Decyn-2-one	96	108–109 (15)	1.4501	152.120	152.120
Phenylethyne	6-Phenyl-5-hexyn-2-one	80	102–103 (1)	1.5502	172.088	172.091
Cyclohexylethyne	6-Cyclohexyl-5-hexyn-2-one	97	*e*	1.4805	178.136	178.136
2-Methyl-1-buten-3-yne	7-Methyl-7-octen-5-yn-2-one	81	*e*	1.4767	136.088	136.088
5-Chloro-1-pentyne	9-Chloro-5-nonyn-2-one	87	73 (0.1)	1.4776	172.065	172.067

[a] A 20% excess of methyl vinyl ketone was employed in all reactions. [b] Satisfactory IR and ^{1}H NMR was obtained for all compounds. [c] Yield by GLC analysis. Yield in parentheses by isolation. [d] Exact mass measured on a CEC-21-110 mass spectrometer. [e] Isolated by preparative GLC.

yet been established, and the extension of this synthesis to the higher acetylenes would appear to offer major difficulties.

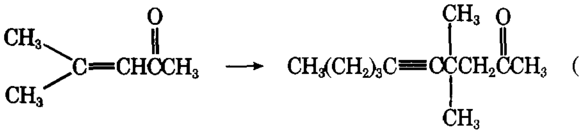
Hooz has achieved the conjugate addition of alkynylalanes to α,β-unsaturated ketones.[4] This reaction proceeds quite well in some cases, but is complicated in others by the concurrent formation of large amounts of the 1,2-addition product. Moreover, the reaction was observed to be highly sensitive to solvent effects, requiring frequent changes in individual reactions. Pappo and Collins reported that, although copper acetylides were too unreactive, they observed that tri-1-octynylboron and tri-1-octynylaluminum, in spite of their high instability, can add 1,4- to pregnenolone acetate.[5a] A trialkynylboron derivative has also been successfully added to methyl vinyl ketone. Unfortunately, the reaction utilizes only one of the three acetylene groups with a yield of only 48% (based on one group) realized.[5b] This constitutes a serious disadvantage in cases where the acetylenic moiety is a valuable intermediate.

Recently we have described the conjugate addition of *B*-1-alkenyl-9-borabicyclo[3.3.1]nonanes to α,β-unsaturated ketones.[6] The extension of this reaction to the recently synthesized *B*-1-alkynyl-9-BBN would provide a simple solution to this synthetic problem. Therefore, we decided to explore the reaction of this reagent with representative α,β-unsaturated ketones. Indeed, we discovered that the reaction proceeds with remarkable ease in pentane at 25 °C, far faster than the previously described reaction of the *B*-1-alkenyl-9-BBN derivatives.

The conjugate addition reaction of *B*-1-alkynyl-9-BBN appears to be one of wide generality (Table I). A variety of structural modifications on the acetylenic unit can be accommodated, including the presence of a heteroatom.

We utilized *B*-1-hexynyl-9-BBN in a brief exploration of the applicability of this reaction to other α,β-enones. Our results are summarized in Table II.

The cisoid ketones (**4–7**) reacted satisfactorily to give the 1,4-addition products in the indicated yields. Especially noteworthy is the successful conjugate addition of the reagent to mesityl oxide (**6**), giving a derivative with a quaternary center (eq 2).

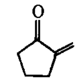
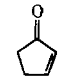
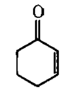


$$(\mathrm{CH_3})_2\mathrm{C{=}CHC(O)CH_3} \longrightarrow \mathrm{CH_3(CH_2)_3C{\equiv}CC(CH_3)_2CH_2C(O)CH_3} \quad (2)$$

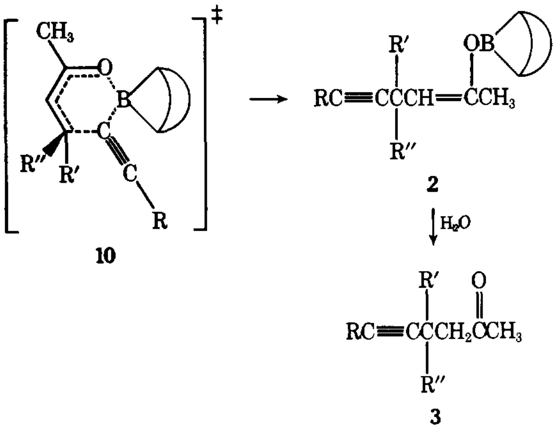
On the other hand, the transoid ketones, **8** and **9** gave no indication of reaction in the desired manner.

These results and the observation that steric bulk at the β-position retarded the reaction are consistent with a process that proceeds through a cyclic transition state (**10**), giving the intermediate (**2**), which is hydrolyzed to the desired product (**3**) (eq 3). Analogous mechanisms have been proposed for the 1,4-addition reactions of Grignard reagents,[7] vinylboranes,[6] and alkynylalanes.[4]

Table II. Synthesis of γ,δ-Acetylenic Ketones by the Conjugate Addition of *B*-1-Hexynyl-9-BBN to α,β-Unsaturated Ketones

Enone[a]	Structure	Reaction time	% yield of 1,4-addition product[c]
Methyl vinyl ketone	$CH_2{=}CHCOCH_3$ (**4**)	10 min	96
trans-3-Penten-2-one	$CH_3CH{=}CHCOCH_3$ (**5**)	1 h	100
Mesityl oxide	$(CH_3)_2CH{=}CHCOCH_3$ (**6**)	5 days	70
α-Methylenecyclopentanone	 (7)	10 min	70
2-Cyclopentenone	 (8)	3 days	0[d]
2-Cyclohexenone	 (9)	3 days	0[d]

[a] A 20% excess of the enones was used. [b] Reaction carried out in pentane at 25 °C. [c] Yield by GLC analysis based on *B*-1-alkynyl-9-BBN. [d] No 1,2- or 1,4-addition products observed by GLC analysis.



(3)

The following procedure for the preparation of 7,7-dimethyl-5-octyn-2-one is representative. An oven-dried, nitrogen-flushed, 250-mL flask equipped with a magnetic stirring bar, a septum inlet, and a gas inlet tube with stopcock was charged with 75 mL of dry THF and 4.12 g (50 mmol) of 3,3-dimethyl-1-butyne. The flask was cooled to −78 °C and 20.2 mL (50 mmol of a 2.47 M solution in hexane) of *n*-butyllithium was added. The clear solution was stirred 15 min at −78 °C, and 7.6 g (50 mmol) of *B*-methoxy-9-BBN was then added. After stirring at −78 °C for 1.5 h, 9.4 g (66 mmol) of boron trifluoride diethyl etherate was introduced and the reaction mixture was stirred at −78 °C for 30 min. The reaction flask was removed from the cold bath and connected to an aspirator, and the volatiles were distilled off to yield a white solid. To the solid was added 50 mL of dry, olefin-free pentane. The resulting suspension was stirred for a few minutes and allowed to settle, and the supernatant liquid carefully decanted via a double-ended needle to another 250-mL flask fitted as before. The remaining solid was washed with pentane (3 × 10 mL), and the pentane solutions were combined. The flask containing the alkynylborane–pentane solution was immersed in a cool water bath, and 4.2 g (60 mmol) of methyl vinyl ketone was added over 5 min. Meanwhile, 3.17 g (52 mmol) of ethanolamine was placed in a centrifuge tube. The reaction mixture was then needled into the centrifuge tube, which was cooled in an ice bath. After centrifugation to settle the precipitate, the supernatant pentane solution was transferred to a distillation setup with a 6 in. Vigreux column. The 9-BBN-ethanolamine adduct in the centrifuge tube was washed with pentane (2 × 20 mL), and the pentane solutions were combined. The pentane was evaporated and the product was distilled to provide 6.34 g (83%) of 7,7-dimethyl-5-octyn-2-one: bp 84–87 °C (20 mm); n^{20}_D 1.4408; IR (neat) 1720; ^{1}H NMR (CCl_4, Me_4Si) δ 1.08 (s, 9 H), 2.10 (s, 3 H), 2.20–2.75 (m, 4 H).

It is evident that this procedure makes it practical to achieve the conjugate addition of alkynyl groups to methyl vinyl ketone and related derivatives. This new 1,4-addition reaction should provide a new route to many complex molecules difficult to prepare by other means, and, moreover, marks the beginning of our studies on reactions of alkynylboranes in typical organoborane reactions.[8]

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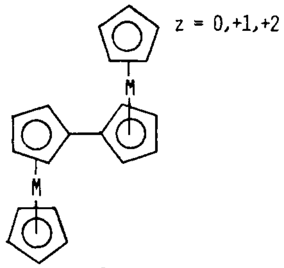
The Synthesis and Characterization of Bis(fulvalene)dinickel, in Three Oxidation Levels

Sir:

Recent interest and controversy regarding the bonding and electronic structure of iron complexes of structural type I and II[1] have led us to explore synthetic routes to other metal derivatives. We wish to report the synthesis and initial physical studies of the bis(fulvalene)dinickel system, II-Ni (z = 0, +1, +2).



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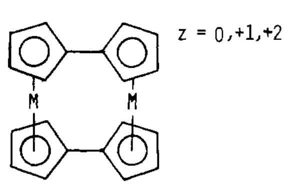

II

M = Fe, Co, Ni

The synthesis of II-Ni (z = 0) utilized an in situ preparation of the fulvalene dianion,[2] similar to that developed independently by Mueller-Westerhoff and Eilbracht for the preparation of II-Fe (z = 0),[1d,3a] and Davison and Smart for II-Co (z = +2).[3b,c] Sodium cyclopentadienide (as the crystalline mono-1,2-dimethoxyethane adduct,[3c] 9.03 g, 50.7 mmol) in THF (250 ml) at −78 °C was treated with iodine (6.7 g, 26 mmol, 5% excess) and the mixture was allowed to warm (ca. 20 min) to yield a cherry red solution of 9,10-dihydrofulvalene. This thermally unstable species[4] is formed in an oxidative coupling reaction, presumably via the intermediate formation of 5-iodocyclopentadiene[5] which undergoes nucleophilic substitution by cyclopentadienyl anion. The THF solution was immediately cooled to −78 °C, followed by the addition of *n*-butyllithium (2.4 M in hexane, 24 ml, 57.6 mmol, 14% excess) to yield a light tan solution of the fulvalene, or bicyclopentadienyl, dianion.[6]

Anhydrous nickel acetylacetonate[7] (6.84 g, 26.6 mmol, 5% excess) was added and the mixture stirred at room temperature for ca. 17 h. The resulting air-sensitive brown material was isolated by filtration, washed with deoxygenated water (200 ml) and THF (30 ml), and dried in vacuo. Extensive Soxhlet extraction of this material with mesitylene (discarding first ten extracts) yielded moderately air-sensitive, reddish brown crystalline II-Ni (z = 0) (2.83 g, 60% yield based on starting $Na(DME)C_5H_5$). An analytically pure sample was obtained by high vacuum sublimation at 200 °C.

Oxidation of the slightly soluble II-Ni (z = 0) with a suspension of anhydrous ferric chloride in benzene for ca. 3 days yielded a brown material that was extracted with *oxygen-saturated* dilute hydrochloric acid (pH 5) to yield an unstable orange solution of II-Ni (z = +2), which was immediately precipitated as a hexafluorophosphate salt in good yield. Recrystallization from *oxygen-saturated* acetone/ether (1/1, v/v) gave an analytically pure sample as air-stable, dark reddish brown crystals.

Orange solutions of II-Ni (z = +2) are somewhat unstable towards reduction to the purple mixed-valence derivative II-Ni (z = +1). This derivative was isolated as an analytically pure, air-stable, very dark purple microcrystalline hexafluorophosphate salt by warming pure II-Ni (z = +2) in acetonitrile, followed by crystallization from acetonitrile/ethanol. Alternatively, this compound was prepared from II-Ni (z = 0), by oxidation with 1 equiv of ferrocinium hexafluorophosphate in THF at 25 °C for 2 h. Methathesis reactions have yielded $B(C_6H_5)_4^-$, BF_4^-, and I_3^- salts.

Previous physical studies[1a–c] indicate that biferrocene derivatives, I-Fe (z = 0, +1, +2), can be viewed qualitatively as substituted ferrocenes or ferrocinium ions, with integral oxidation states of iron. The mixed-valence I-Fe (z = +1) exhibits a unique near-infrared absorbance at 1800 nm (ϵ 750) that has been assigned[1a] as an intervalence transfer transition from theory developed by Hush[8] and utilized by Day.[9] The mixed-valence II-Fe (z = +1) also exhibits unique infrared bands centered at 1550 nm (ϵ 2100) that are absent in both the z = 0, +2 oxidation levels, as well as in ferrocene and the ferrocinium ion. However, the applicability of the Hush model in assigning these transitions has been questioned, and controversy has developed as to whether the II-Fe system (z = 0, +1, +2) exhibits rapid intervalence electron transfer via direct metal–metal exchange,[1c] or is a completely delocalized system involving a ligand-propogated exchange.[1d]