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(21) The calculated charge distributions on carbon and mercury are also consistent with the above results. With the ions derived from Hg^{2+}, $HgCH_3^+$, and $HgCl^+$, conversion from the π complex to the allylic cation resulted in a significant increase in charge at C_1 and C_2 and a concomitant decrease in charge on mercury. The opposite trend was noted with Hg^+ ions thus rendering the cation **2** more stable since mercury can more readily accommodate a positive charge than carbon.

Trimeric Structure and Mixed Cycloaddition from the Nickel-Catalyzed Reaction of Norbornadiene

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Since Cookson[2] reported on the cycloaddition of norbornadiene using $Fe(CO)_5$ as a promotor, several investigators have studied the reaction which yields a myriad of norbornyl dimers, ketones, and trimers.[3] Efforts to catalyze a mixed [2 + 2] cyloaddition of norbornadiene and other olefins have been few.[4] In fact, to the best of our knowledge, no one has been successful in coupling norbornadiene and norbornene. In this paper, we wish to present a structure proof for one of the trimeric compounds of norbornadiene
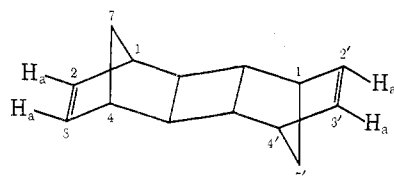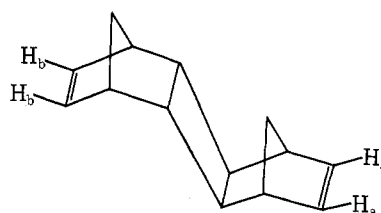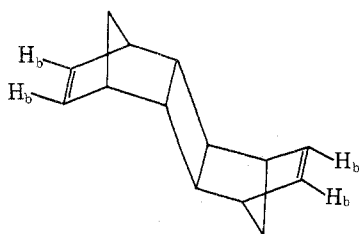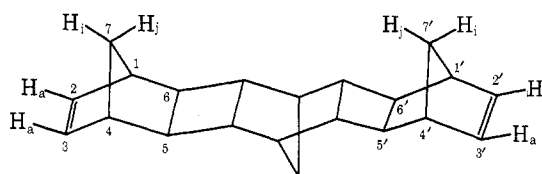
Table I

Position (see Figure I)	Trimer, δ, ppm	exo, trans, exo Dimer	
2,2',3,3'-Olefinic protons	5.93	6.01	
1,1',4,4'-Bridgehead protons	2.61	2.61	
7,7'-Bridge methylenes	1.90 and 1.82 AX	1.88	1.79
	1.20 and 1.12 quartet	1.32	1.23

and to present evidence that $(Ph_3P)_2Ni(CO)_2$ catalyzes the mixed cycloaddition of norbornadiene to the dimer which is a pseudo norbornene.

Chemical shift data garnered from the nmr spectrum of trimer IV are listed in Table I.

By comparing the nmr spectra of IV with well-characterized spectra of analogous dimers, several conclusions could be made. A single olefinic resonance at 5.77[3a,5] accounting for four protons indicated that compound IV had two carbon–carbon double bonds and the protons on them were in identical environments. Mass spectral analysis of IV confirmed the molecular weight as 276 and a m/e of 280 for the hydrogenated product of IV confirmed the presence of two carbon–carbon double bonds. Dimers which have an *exo*-cyclobutane ring across the norbornyl unit from the olefin moiety, as in I, have single olefin resonances between 5.65 and 5.97.[3a] In structures having both endo- and exo-bonded cyclobutane rings, as in II, two olefinic resonances are found. Finally, in compounds such as III where both rings have endo-bonded cyclobutanes, a single olefin resonance is observed around 6.15 to 6.25.[3] Thus, from the close agreement between dimer I and trimer IV nmr spectra (Table I),[9] it was reasonable to conclude that each outer norbornyl unit of IV had an exo-bonded cyclobutane ring across from the olefin.

The bridge proton resonances provided additional proof for the identical character of the two exterior norbornyl units. Again, based on the nmr spectra of dimer structures, the two bridge protons (at 7 or 7') will appear in the spectra as a 4-line AB or AX quartet. Their resonance positions are also a function of the position of the cyclobutane ring. In the spectrum of IV, there appears to be only one AX quartet which indicates again that the outer norbornyl units are identical.

I

exo,trans,exo

II

endo,trans,exo

III

endo,trans,endo

IV

exo,trans,exo,trans,exo

Table II
Relative Concentrations of Products as Obtained from Gc

	Dimer	Trimer
Standard	87 ± 5	0.57 ± 0.04
Fortified expt	200 ± 10	2.50 ± 0.34
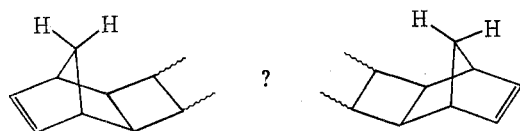
The final question as to how these two units are bonded to the central norbornyl fragment was solved by assuming that trimer originates from dimer plus monomer. Since this catalyst makes only exo,trans,exo dimer (I), it was logical to suspect that this dimer was the timer precursor. Thus if I leads to IV and the two olefin moieties are identical, then exo,trans,exo,trans,exo must describe the stereochemistry of the trimeric compound. In order to test this hypothesis, two parallel experiments were run. Two sets of reaction tubes were charged with identical amounts of catalyst and norbornadiene. Then, to each of the second set of reaction tubes, 0.50 g of exo,trans,exo dimer was added. All the tubes were treated identically in degassing, irradiation, and analysis. The results are shown in Table II. The results of these experiments show a fourfold increase of trimer in the fortified case confirming that dimer I was converted to IV and thereby proving the stereochemistry of the trimer.

These results also prove that nickel catalyzed a mixed coupling between norbornadiene and a norbornene-type molecule.[6] The obvious difference between norbornene and the pseudo norbornene (dimer I) is the cyclobutane ring which must be activating the transannular olefin. This effect is being investigated further.

Experimental Section

Glc analyses were performed on a Varian Model 1740 chromatograph using a 6 ft, 20% carbowax 20 M on 80–100 mesh Chromosorb W column. Nmr data were collected on Varian A-60 and HA-100[7] spectrometers.

Correlation of Trimer Preparation and Fortified Experiment. Standard. To three, 10 × 100 mm Pyrex test tubes containing 0.35 g (0.056 mmol) of bis(triphenylphosphine)dicarbonylnickel(0), 5.00 ml of freshly prepared norbornadiene was added using a vacuum line. These samples were degassed through three freeze-thaw cycles, sealed, and irradiated for 30 hr with Pyrex-filtered[8] light from a Hanovia 450-W mercury arc. The yields for Table II were garnered from glc data.

Fortified. To each of three test tubes prepared identically as above, 0.50 g (2.72 mmol) of exo,trans,exo dimer was added. These samples were analyzed and run simultaneously with the three standard samples.

Preparation of Trimer. In a typical experiment to prepare trimer IV a 450-W Hanovia mercury lamp equipped with a Pyrex filter, cooling jacket, and a "merry-go-round" sample holder was used to irradiate a sealed-degassed sample containing 6.5 ml of neat norbornadiene and 0.0465 g (7.28 × 10⁻² mmol) of (Ph₃P)₂Ni(CO)₂. A total yield of 31% was obtained after 3 days of irradiation in which 93% was dimer I and 5% was trimer IV. There was a trace of another dimer which was not identified. Purification was effected through fractional sublimation giving white solid, mp 205–206°, *m/e* 276.

Anal. Calcd for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 91.43; H, 8.84.

Registry No.—I, 53166-41-9; IV, 53187-83-0; (Ph₃P)₂Ni(CO)₂, 13007-90-4; norbornadiene, 121-46-0.

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(5) All values for nmr resonance positions are reported in δ (ppm).
(6) Attempts on our part to effect the same reaction with norbornene were unsuccessful.
(7) Special thanks to the National Science Foundation for providing partial support for a HA-100 for the latter part of this work.
(8) Appropriate filters were used to ensure that only the metal complex absorbed the light.
(9) Spectra of dimers I, II, and III were obtained from compounds prepared in some of our previous studies.[3h]


Tetrachlorocyclopentadienoneiron Tricarbonyl

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Few transition metal complexes of chlorocarbons are known and those with iron as the transition metal have been obtained indirectly by a series of metallation–halogenation reactions.[1] It has now been found that diiron nonacarbonyl reacts readily with dichloroacetylene to form tetrachlorocyclopentadienoneiron tricarbonyl (1) in moderate yield. The yellow-orange complex 1, isolated by chromatography on alumina, is sufficiently stable at its melting point of 101–102° to be melted and remelted without change, and crystalline samples were unchanged on handling in air. The compound is, however, photodegraded in solution, slowly by incidental light and rapidly by irradiation with a low-pressure ultraviolet lamp.
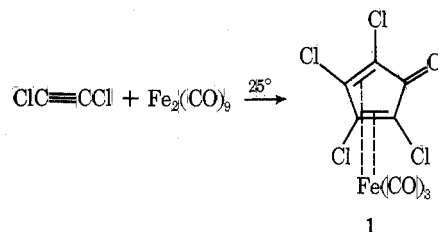
Dichloroacetylene, prepared by the solution method of Siegel, *et al.*,[2] was used as an approximately 20% solution in ether. No explosions were encountered during several such preparations, but suitable precautions against the possibility of violent detonation and toxic vapors should nevertheless be taken. Preparations of dichloroacetylene in ether were routinely monitored by gas chromatography. Although dichloroacetylene is not a reactive dienophile, it could be derivatized easily at atmospheric pressure by Diels–Alder addition to diphenylisobenzofuran to form adduct 2.