The benzene-sensitized photolysis of 2 proceeds six times more efficiently than direct photolysis at 254 nm, but the major product appears to be derived by a singlet pathway. In fact, under our conditions excited singlet benzene should collide with 2 with $k = 2.6 \times$ 10^{7} /sec and the known rate of decay of benzene singlets is 1.2×10^{7} /sec,¹² so there is opportunity for singlet sensitization of 2, especially considering the high collision cross sections for such sensitization when the fluorescence spectrum of the sensitizer overlaps the absorption spectrum of the acceptor.¹³ Of importance in this connection is the fact that intersystem crossing of singlet benzene $(k_{\rm isc} = 1.1 \times 10^7 \text{ sec})^{12}$ is about half as fast as collisions of singlet excited benzene with 2 under conditions of our experiment, so the fact that a mixture of 3 and 4 is produced with more of the former in these reactions is not unreasonable if 4 is formed from triplet 1 or triplet 2. The suggestion that 4 is a triplet-derived product is a conclusion reached by Skell in attempting to explain the presence of 4 (and p-xylene) and the absence of 3 in the reaction of 2-iodomethylallyl iodide with potassium vapor.¹⁴ Similarly, Berson found only dimeric products upon attempted generation of 5-isopropylidenebicyclo[2.1.0]pentane¹⁵ and these products exhibited strong nmr emission signals when initially produced, consistent with their formation via at least one triplet species according to Closs.¹⁶ It is unclear why Andrews and Day did not obtain dimeric products in the triplet ketone sensitized photolyses of 4-chloromethylene-3,3,5,5-tetramethyl-1-pyrazoline although steric effects may be important.¹⁷

The oxygen-quenched, sensitized photolyses of 2 suggest that both singlet and triplet reactions are being quenched. Oxygen quenches singlet benzene with k = $1.2 \times 10^{11} \text{ l./(mol sec)}^{18}$ so under our conditions each benzene singlet is quenched with $k = 8 \times 10^{7}$ /sec. Since oxygen apparently quenched only 28% of the reaction (34% of 3 vs. 48% of 3), singlet energy transfer from benzene to pyrazoline would have to be approximately ten times faster than collisions, a possibility in light of ref 13. However, oxygen quenching of benzene singlets appears to give benzene triplets¹⁸ which should be quenched by oxygen with a frequency of 7×10^6 /sec under our conditions.¹⁸ Under these conditions benzene triplets can collide with 2 with $k = 2.6 \times 10^{7}/\text{sec}$ giving triplet 2 which could give triplet 1. Apparently oxygen also quenches these species before they can give dimeric material, 4, and, quenching of triplet 1 could give 3 directly in which case the suggestion that singlet sensitization is faster than collision rates and that the 34% of 3 in the oxygen-quenched sensitized photolyses comes from singlet sensitization may not be valid.

We put forward these mechanistic hypotheses recognizing that more complicated alternatives exist and that important questions remain unanswered. Do the states of 1 produced here resemble the singlet

and triplet ground states of 1? What are the geometries of these species? Wherein lies the inefficiency of the direct photolyses of 2, and how are the dimeric products formed? These are being investigated with effort being focused on direct spectroscopic observation of the trimethylenemethane species.

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Trialkylcyclopropenium Metal Compounds¹

Sir:

Several triphenylcyclopropenium compounds with transition metals have been prepared²⁻⁵ since the initial report by Gowling and Kettle⁶ of a substance formulated as $[h^3-C_3(C_6H_5)_3Ni(CO)Br]_2$ (1). Trihapto-alkylsubstituted cyclopropenium compounds of transition metals have not as yet been observed; the only reported reaction involving a trialkylcyclopropenium compound results in carbonyl ring insertion to produce h^3 -trimethylcyclobutenone-cobalt tricarbonyl from C₃- $(CH_3)_3^+$ and $Co(CO)_4^{-.7}$

The chemical properties of the cyclopropenium group acting as a trihapto ligand are not as yet clear, because the phenyl derivatives prepared thus far have generally low solubility. It is of particular interest to compare the cyclopropenium and allyl groups, which are closely related electronically. We report here syntheses of the first alkylcyclopropenium metal compounds and several observations which clarify the nature of the cyclopropenium-metal bonding.



Addition of excess nickel carbonyl to a methanolic solution of tri-tert-butylcyclopropenium fluoroborate8 and sodium bromide under nitrogen and recrystallization of the product from toluene yields crystals of 2 [Anal. Calcd for NiC₁₆H₂₇OBr: Ni, 15.70; C, 51.38; H, 7.28; Br, 21.36; mol wt, 373. Found: Ni, 16.00; C, 50.66; H, 7.41; Br, 21.69; mol wt, 332, 337

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Similarly using dibutylmethylcyclopropenium fluoroborate⁸ yellow crystals of **3** are isolated: ir (Nujol) ν_{CO} 2038 cm⁻¹; pmr (CH₂Cl₂) τ 7.89 (s, 3 H), 8.78 (s, 18 H).

Stirring 2 with a stoichiometric amount of sodium cyclopentadienide in ethanol under nitrogen for 1 hr followed by addition of degassed water and sublimation of the product at 40° and 0.1 mm yields (h^5 -C₅H₅)- $(h^3-C_3(t-C_4H_9)_3)Ni$ (4) as a yellow powder: mp 295° dec (Anal. Calcd for $NiC_{20}H_{32}$: Ni, 17.73; C, 72.63; H, 9.73. Found: Ni, 16.97; C, 72.98; H, 9.91); pmr (CS₂) τ 4.97 (s, 5 H), 8.97 (s, 27 H).

All three complexes are air stable as solids for a short period only and decompose rapidly in polar solvents when in contact with air.

These results strongly indicate that 2 and 3, and probably Gowling and Kettle's compound, are monomeric. The mass spectrum of 2 at 100° (10 or 70 eV) shows no ions derived from CO-containing species but exhibits strong peaks corresponding to $[h^3-C_3(t C_4H_9$)₃NiBr]₂.

Addition of carbon monoxide to a methylcyclohexane solution of 2 (ν_{CO} 2052 cm⁻¹) results in the rapid equilibria shown in eq 1 and 2. Carbonyl bands appear

$$C_{3}(t-C_{4}H_{9})_{3}Ni(CO)Br + CO \rightleftharpoons C_{3}(t-C_{4}H_{9})_{3}Ni(CO)_{2}Br \quad (1)$$

 $C_3(t-C_4H_9)_3Ni(CO)_2Br + 2CO \swarrow$

$$Ni(CO)_4 + C_3(t-C_4H_9)_3^+Br^-$$
 (2)

at 2089 (s), 2060 (s), 2055 (s), and 2044 cm⁻¹ (m). The two highest energy bands, which appear together, are assigned to tri-tert-butylcyclopropenium nickel dicarbonyl bromide (5). Nickel carbonyl is isolated from this solution by prolonged addition of carbon monoxide and trapping of the volatile components with a Dry Ice-acetone bath. The 2044-cm⁻¹ band is due to Ni(CO)₄. The band at 2055 cm⁻¹, shifted slightly by overlap with adjacent bands, is assigned to 2.

In nonhydrocarbon solvents 5 is formed from 2 through a slight amount of disproportionation. In chloroform ir CO bands are observed at 2054 (s) and 2096 cm^{-1} (w). Designation of the high energy band as arising from the dicarbonyl species, 5, is based on the following observations. Addition of CO to a yellow chloroform solution of 2 in a closed vessel produces a colorless solution with an intense ir band at 2044 cm⁻¹ due to nickel carbonyl, considerable enhancement of the band at 2096 cm^{-1} , and a shoulder of comparable intensity at approximately 2063 cm^{-1} . Removal of the CO atmosphere causes the nickel carbonyl spectrum to be displaced by the original band at 2054 cm⁻¹ and instantaneous color change back to yellow. The band at 2096 cm⁻¹ remains about three times more intense than before addition of CO; the lower energy band of the dicarbonyl is obscured by the intense band at 2054 cm⁻¹. The pmr spectrum of a CO saturated chloroform solution of 2 exhibits a new resonance at τ 8.31, inexplicably shifted from the τ 8.41 for $[C_3(t-C_4H_9)_3]Br$ alone in chloroform.

Heating of 2 under vacuum at 80° for 20 hr results in loss of CO and formation of a very air-sensitive red-brown solid which we assume to be $[h^3-C_3(t-C_4H_9)_3-$ NiBr]2, analog of the well-known allylnickel halide compounds. The solid dissolves in methylcyclohexane to yield a red solution which shows no ir CO band. Addition of CO to this solution results in ir spectra identical with those obtained on addition of CO to methylcyclohexane solutions of 2.

These observations suggest that 2 behaves similarly to the analogous allyl-nickel complex⁹ in those properties which allow it to remain trihapto. In contrast to the facile coupling reaction of methallylnickel bromide in the presence of carbon monoxide,9 however, no cyclopropenium coupling products have been detected. The steric requirements of the tert-butyl groups in 2 could be accountable for the inability of the C₃ system to assume a monohapto configuration and thus to undergo coupling. On the other hand 3seems equally stable in this respect.

Addition of $[C_3(C_6H_5)_3]BF_4$ to a methanolic solution of 2 yields analytically pure triphenylcyclopropenium nickel carbonyl bromide as a precipitate after 1 hr at room temperature.

Reaction of $[C_3(t-C_4H_9)_3]BF_4$ with NaMn(CO)₅ in THF at -15° results in the formation of air-sensitive orange crystals of $[C_3(t-C_4H_9)_3]Mn(CO)_5$ (6). The ir spectrum in the 2000-cm⁻¹ region closely resembles that of $Mn(CO)_5^-$ and the pmr spectrum, (CD_3COCD_3) τ 8.38 (s), makes reasonable the assignment of **6** as ionic. At room temperature in THF solution the carbonyl ir spectrum is more complex, indicating formation of contact ion pairs or perhaps a monohapto interaction of the C₃ system with $Mn(CO)_5^-$. 6 decomposes rapidly in polar solvents to yield Mn₂(CO)₁₀ and $[C_3(t-C_4H_9)_3]_2$ and lesser amounts of $C_3(t-C_4H_9)_3H$. The same reaction with $[C_3(C_6H_5)_3]BF_4$ and $NaMn(CO)_5$ yields $Mn_2(CO)_{10}$ and $[C_3(C_6H_5)_3]_2$. Attempts to prepare the analogous trimethylcyclopropenium compounds have so far been unsuccessful, nor have the products of reductive coupling been clearly identified as yet.

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Antarafacial Allylic Participation in a Thermal **1,3-Sigmatropic Carbon Migration**

Sir:

Orbital symmetry theory recognizes two thermally allowed 1,3-sigmatropic pathways for migration of an allylic moiety: inversion at the migrating carbon with suprafacial allylic utilization, and retention at the migrating carbon with antarafacial allylic participation.¹⁻⁴ This second allowed stereochemical combination has not been reported; it has been explicitly judged a difficult or perhaps impossible mode of reaction.^{2,5}

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